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A unified mechanistic view obtained from the temperature and pressure dependence of the spontaneous, acid-, and base-assisted cyclometallation reactions of dirhodium(II) complexes†

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The reaction of compounds $[Rh_2(O_2CMe)(\mu\text{-}O_2CMe)_2\{\mu\text{-}(XC_6H_3)P(C_6H_4X\text{-}p)_2\}\{P(C_6H_4X'\text{-}p)_3\}]$ (X = H, X' = H or Me; X = Me, X' = H or Me), having a metallated and an equatorial phosphine in a head-to-tail cisoid configuration, to produce the corresponding doubly metallated compounds $[Rh_2(\mu\text{-}O_2CMe)_2\{\mu\text{-}(XC_6H_3)P(C_6H_4X\text{-}p)_2\}_2]$, has been studied in detail. The thermal, acid-, and base-assisted conditions include toluene solution, neat acetic acid, and different bases [PPh_3, $P(C_6H_4Me\text{-}p)_3$ or pyridine] in toluene solution and as a function of temperature, pressure and base concentration (when applicable). The doubly metallated compounds always show retention of the head-to-tail cisoid configuration according to ^{31}P NMR spectroscopy. The reported activation parameters allow a clear differentiation between the spontaneous, acid-assisted and base-assisted processes, some of which had been previously studied ($\Delta H^‡ = 80 \pm 5, 68 \pm 1, 38 \pm 3$ kJ mol^{-1}; $\Delta S^‡ = -105 \pm 15, -85 \pm 3, -150 \pm 30$ J K^{-1} mol^{-1}; $\Delta V^‡ = -22.7 \pm 0.2, -15.3 \pm 0.2, -35.0 \pm 0.5$ cm^3 mol^{-1} respectively, for the compound with X, X' = H). For the reactions under base-assisted conditions, when long reaction times and/or high added Lewis-base concentrations were applied, the non-metallated phosphine was displaced from equatorial to axial co-ordination. Under these conditions a mixture of the bis adducts of the monometallated $[Rh_2(\mu\text{-}O_2CMe)_3\{\mu\text{-}(XC_6H_3)P(C_6H_4X\text{-}p)_2\}]$, and the doubly-metallated compounds was detected by ^{31}P NMR spectroscopy. The activation parameters obtained for this slower process agree with those expected for substitution reactions and are interpreted in terms of the steric demands of the mono and bis adducts formed immediately on mixing the reaction solutions.

Cyclometallation reactions of mononuclear compounds are well known.[1] Nevertheless, such reactions occurring on compounds having two metal centres have been less extensively studied in comparison to substitution reactions on organoplatinum(II) or -nickel(II) square-planar complexes.[2] In fact there is a lack of information concerning the volumes of activation, $\Delta V^‡$, and the nature of the intimate reaction mechanism for these processes. We have recently developed an interest in the cyclometallation mechanism arising from the reactivity of arylphosphines in dirhodium(II) compounds.[3] The isolation and study of some reaction intermediates from the mono- to doubly-metallated compounds, shown in Scheme 1, have been achieved.[3a,4]

In this respect we have already reported synthetic and mechanistic studies of some of the **2** $\longrightarrow$ **3** (X = H, X' = H or Me) cyclometallation reactions shown in Scheme 1 both in aprotic, non-co-ordinating, solvents and in acidic media.[3a] The results showed that a clear acid-assisted reaction was operating when the compounds underwent cyclometallation reactions in the presence of acetic or trifluoromethanesulfonic (triflic) acids in solution. An acceleration of one order of magnitude was observed together with an increase in the $\Delta S^‡$ value on going from the spontaneous to the acid-assisted process in all cases. We also observed that, in the presence of an excess of phosphine, the monometallated compounds **1** undergo a much faster cyclometallation reaction than that mentioned above, and that mixtures of head-to-tail and head-to-head doubly metallated compounds are obtained in a ratio depending on the different $P(C_6H_4X\text{-}p)_3$ and $P(C_6H_4X'\text{-}p)_3$ combinations.[3a,5]

In this paper we report a detailed study of the kinetics and mechanism of the **2** $\longrightarrow$ **3** cyclometallation reaction in the presence of co-ordinating Lewis bases, along with the spontaneous and acid-assisted processes, in order to assess the mechanistic differences between the various paths found for this reaction.[3a] The results for the acid-assisted and spontaneous processes are interpreted in a similar way to that previously.[3a] As for the base-assisted process, the results are interpreted in view of the steric demands of the added bases[6] on the mono and bis adducts of the monometallated compounds **2**, leading to the species **3** and back to **1** respectively. That is, while steric demands on the mono base adduct of compounds **2** assist the metallation process to produce the doubly metallated species **3**, those on the bis(base) adducts favour substitution of the phosphine by a chelating acetate ligand. The complete metallation process from **1** to **3**, or the equivalent head-to-head doubly metallated species,[3a,5] is interpreted in terms of the mono- to bis-phosphine adduct concentration ratio of compounds **1** that should produce the head-to-tail and head-to-head doubly metallated complexes, respectively.

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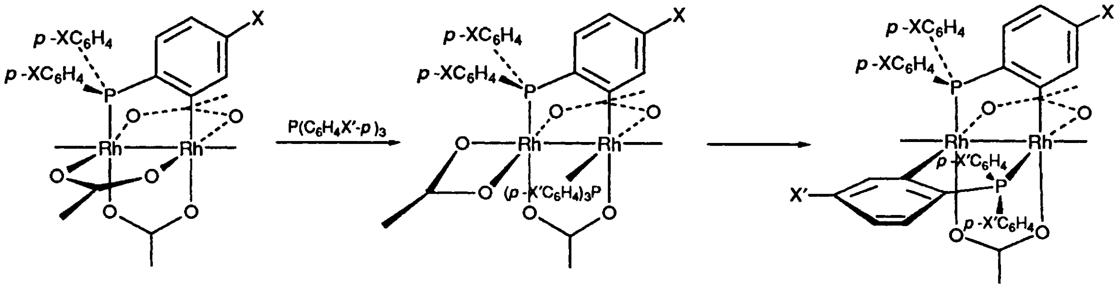
† *Supplementary data available* (No. SUP 57123, 8 pp.): observed rate constants. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.



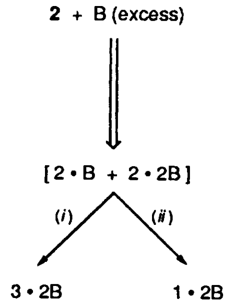
1 2 3

Scheme 1 Axial positions are occupied by any Lewis base present in the solution. X, X′ = H or Me

Results

The stability of some compounds of the type **2** (X = H, X′ = H or Me) in chloroform and toluene solutions previously enabled us to study their cyclometallation reaction under spontaneous and acid-assisted conditions.[3a] The reaction with an excess of $P(C_6H_4X'\text{-}p)_3$ phosphine was found to be rapid and a base-assisted (accelerated by the presence of Lewis bases) reaction was postulated. Nevertheless, the multiple adduct formation equilibria, existing under the selected reaction conditions, create many difficulties in the interpretation of the observed reaction pattern. Except under very precise conditions, a mixture of bis- and mono-adducts, as well as dirhodium(II) species with empty axial co-ordination positions, is present in solution.[7]

When an excess of a Lewis base, B [= $P(C_6H_4X'\text{-}p)_3$, $P(C_6H_4X\text{-}p)_3$ or pyridine (py)], is added at room temperature to a chloroform or toluene solution of compounds **2** most of it disappears immediately after mixing, as shown by the ^{31}P NMR spectrum, and the **3**·2B and **1**·2B adducts are found to be the main species in solution on standing. Based on earlier data,[3a,5b] Scheme 2 seems to operate under these conditions.



Scheme 2 (*i*) Metallation; (*ii*) substitution

The mono- and bis-adducts of compounds **1** are found to metallate very slowly in the absence of UV/VIS irradiation or an acidic medium.[3a] The rate constants (SUP 57123) obtained for the **1**·$PPh_3 \longrightarrow$ **2** process (X, X′ = H) in chloroform solution, and studied under the conditions [**1**]/[PPh_3] $\gg$ 1, are 2.79×10^{-4}, 5.94×10^{-4}, 1.60×10^{-3} and 2.50×10^{-3} s^{-1} (at 25, 35, 45 and 55 °C respectively), indicating that compounds **3** cannot be generated from a direct metallation of **1** on the experimental time-scale used for this study. On the other hand, if the $P(C_6H_4X'\text{-}p)_3$-assisted metallation of compounds **2** proceeds through **1**, the process would produce practically a total lack of metallated $P(C_6H_4X'\text{-}p)_3$ in the final products **3** due to total adduct scrambling on compound **1**, produced by the substitution reaction in Scheme 2. The relative **1**·2B and **3**·2B ratios, monitored by ^{31}P NMR spectroscopy, suggest that the nature of the added base plays a very important role in the process as indicated by the fact that the addition of a 15-fold excess of PPh_3 to a solution of **2** (X, X′ = H) produces 60% of **1**·2PPh_3, whereas the addition of the same excess of py gives only 35% of **1**·2py, the remaining rhodium(II) dimer being in the form of **3**·2PPh_3 or **3**·2py (X, X′ = H) respectively.

In view of these facts, the **2** + B process was studied by means of UV/VIS spectroscopy in order to detect possible kinetic differences between the metallation and substitution processes indicated in Scheme 2. When toluene solutions of compounds **2**, at concentrations of (1–60) × 10^{-4} mol dm^{-3}, are treated with an excess of base, B, two reaction steps are observed. Gross separation of these, yields reaction half-times of approximately 20 and 150 s, for the rapid and slow processes at 35 °C, respectively. When pseudo-first-order conditions [**2**] < 20[B] were applied to the kinetic experiments it was very difficult to quantify the rapid step and only the slow step could be measured, the absorbance *versus* time traces being nearly single exponential. The observed pseudo-first-order rate constants obtained did not depend on the rhodium(II) dimer concentration, but varied with the added base concentration as shown in Fig. 1.

A rate in equation (1) was applied,[8] and the kinetic

$$ {}^{s}k_{obs} = \frac{{}^{s}k\,{}^{s}K[B]}{1 + {}^{s}K[B]} \qquad (1) $$

parameters collected in Table 1 were derived. Standard Eyring plots applied to the first-order rate constants, ${}^{s}k$, allowed the determination of the thermal activation parameters. From the experiments run with compound **2** (X, X′ = H) having $P(C_6D_5)_3$ in the equatorial position it was clear that a deuterium kinetic isotopic effect does not exist for this slow reaction step.

For the faster reaction step, the [**2**] > [B] approach was followed, in order to assure the sole existence of compounds **2**·B and **2** in solution. Under these conditions only the rapid reaction was clearly observed, as demonstrated by the monophasic behaviour of the absorbance *versus* time traces obtained. Small subsequent changes (and biphasic behaviour), especially at higher [B] values, were quantified and assigned to the slow process indicated above. For the rapid process well behaved first-order traces were obtained and the observed first-order rate constants were independent of both the rhodium(II) dimer and the base concentration, as shown in Fig. 2.

These observations are a good indication that the rapid reaction is first order in the concentration of the mono adduct **2**·B, ${}^{r}k_{obs} = {}^{r}k$. Table 2 summarizes all the kinetic, thermal and pressure activation parameters obtained for this process. Experiments run with compound **2** (X, X′ = H) having $P(C_6D_5)_3$ in the equatorial position indicated that no clear deuterium kinetic isotopic effect exists for this step.

Some ^{31}P NMR experiments at low temperature were designed in order to resolve the nature of the products existing in the reaction medium at a low relative concentration ratio of base, B ([B]/[**2**] = 0.1). The results indicate that the two possible mono adducts **2**·B are present in the reaction medium when **2** (X, X′ = H) and PPh_3 [or **2** (X, X′ = Me) and $P(C_6H_4Me\text{-}p)_3$] are mixed at low temperature (−40 °C) in

Table 1 Kinetic and thermal activation parameters for the slow step in the **2** + B reaction of the different systems studied in toluene solution with [**2**] = (1–10) × 10^{-4} mol dm^{-3}

X	X′	B	T/°C	$10^3\,{}^sk$/s^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	${}^sK$(average)/dm^3 mol^{-1}
H	H	PPh$_3$	15	4.20	63 ± 7	−74 ± 9	35
			25	12.1			
			35	23.4			
		py	15	7.32	65 ± 9	−30 ± 7	40
			25	16.0			
			35	48.0			
H	H^a	py	25	16.8			
Me	H	PPh$_3$	15	2.21	87 ± 2	7 ± 1	23
			25	8.00			
			35	24.8			
		py	15	2.80	109 ± 8	83 ± 8	27
			25	11.0			
			35	56.8			
H	Me	P(C$_6$H$_4$Me-p)$_3$	15	2.60	92 ± 3	26 ± 8	15
			25	8.60			
			35	32.0			
		py	15	1.90	96 ± 3	34 ± 12	45
			25	7.50			
			35	25.0			
Me	Me	P(C$_6$H$_4$Me-p)$_3$	15	3.31	61 ± 1	−80 ± 2	36
			25	8.16			
			35	18.4			
		py^b	15	2.01	97 ± 3	40 ± 2	37
			25	8.51			
			35	29.5			

^{a} P(C$_6$D$_5$)$_3$ as equatorial non-metallated phosphine ligand. ^{b} $\Delta V^{\ddagger}$ = 0.2 ± 0.1 cm^3 mol^{-1} at 282.5 K.

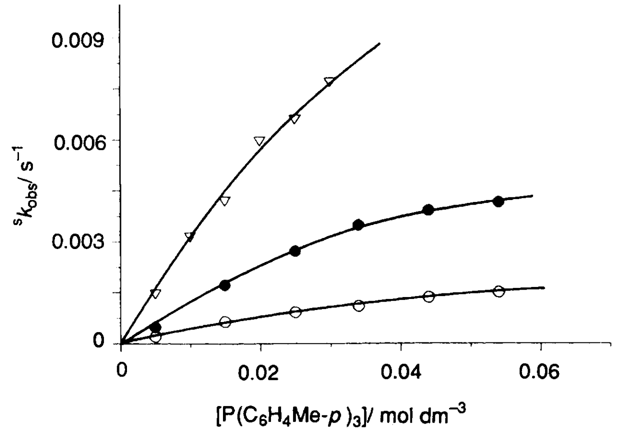


Fig. 1 Plot of the observed rate constants, ${}^sk_{obs}$, as a function of added base concentration, [B], and temperature [15 (○), 25 (●), 35 °C (▽)] for the slow process observed in the **2** + P(C$_6$H$_4$Me-P)$_3$ system in toluene solution and [**2**] = (1–5) × 10^{-4} mol dm^{-3}. X = H, X′ = Me

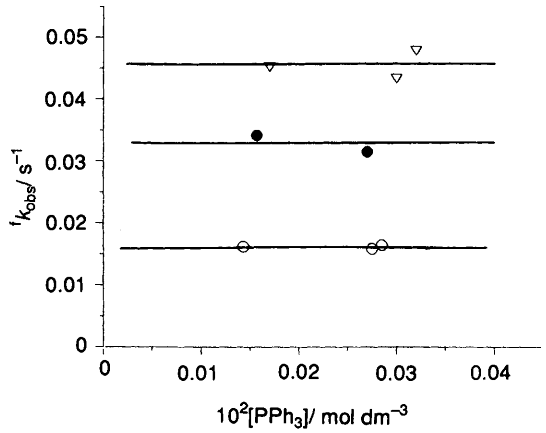


Fig. 2 Plots of the observed rate constants, ${}^fk_{obs}$, as a function of added base concentration, [B], and temperature [15 (○), 25 (●), 35 °C (▽)] for the rapid process observed in the **2** + PPh$_3$ system in toluene solution and [**2**] = (3–4) × 10^{-3} mol dm^{-3}. X, X′ = H

chloroform solution. When the reaction mixture is allowed to reach room temperature the signal corresponding to the adducts disappears. If the temperature is then lowered back to −40 °C the presence of the doubly metallated mono adduct, **3**·B, is also detected. On standing for longer periods at room temperature further metallation occurs at a rate corresponding to the known spontaneous process.[3a]

In this respect the sensitivity of the adduct stability constants to temperature and pressure merits some comment. In all cases, variation in temperature and pressure resulted in changes in the absorbance increase observed during the cyclometallation reactions. Whereas the temperature could be adjusted to a point where absorbance changes were optimal, pressure changes could not be tuned in the same way and the decrease in the changes in absorbance on increasing pressure made some of the systems unsuitable for study at elevated pressures [as in the case of the **2** (X, X′ = Me) + P(C$_6$H$_4$Me-p)$_3$ reaction].

In order to assess the differences between these reactions and the corresponding spontaneous and acid-assisted processes, the cyclometallation reactions of complexes **2** (X = Me, X′ = H or Me) was studied in neat toluene and acetic acid solutions. The reactions of **2** (X = H, X′ = H or Me) were also reinvestigated in neat acetic acid, instead of chloroform or toluene solutions of acetic acid, in order to check the validity of the first-order rate constants obtained previously under different conditions.[3a] The agreement of the data clearly indicates that the earlier treatment was correct, as shown by the values of the activation parameters collected in Table 3. In particular, from the acid-assisted studies, where three different solvents were used, it is clear that electrostriction effects do not seem to play an important role in the values of $\Delta S^{\ddagger}$ and consequently, $\Delta V^{\ddagger}$.

Discussion

Analysis of the data in Tables 1 and 2 clearly indicates that two very different processes are taking place when any amount of base is added to a solution of compounds **2**, as shown in Scheme

2. From a comparison of the thermal and pressure activation parameters, with those for the spontaneous and acid-assisted cyclometallation reactions (Table 3), it seems clear that, while $^{\mathrm{r}}k$ can be assigned to the **2** ⟶ **3** (k_m) metallation, the values of $^{\mathrm{s}}k$ should correspond to the **2** ⟶ **1** (k_s) substitution reaction.

For the rapid reaction step consistently negative $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ and low $\Delta H^{\ddagger}$ values are obtained independently of the metallating phosphine, as observed for other metallation processes than those indicated in Table 3 and other related systems.[3a,9] Furthermore, the thermal and pressure activation parameters for the slow step show consistently larger values of $\Delta H^{\ddagger}$ and much higher (from negative to positive) values of $\Delta S^{\ddagger}$, and $\Delta V^{\ddagger}$, as found for other substitution processes on the same type of complexes, *viz.* acetate exchange on compound **1** (X = H).[10]

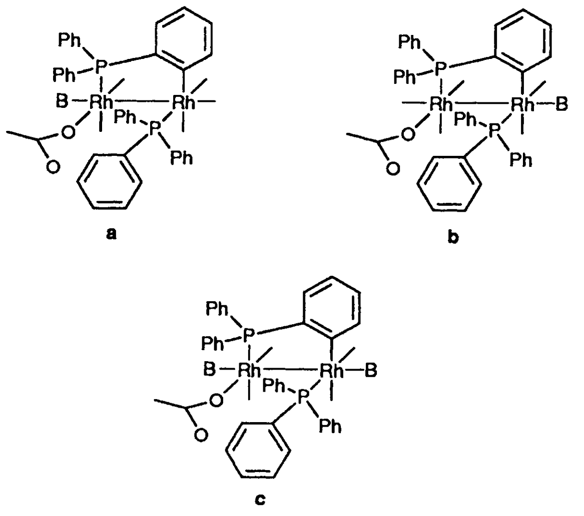
Taking all these observations into account, along with the fact that at low [B]/[**2**] ratios only the rapid step was observed, the reaction depicted in Scheme 2 can be separated into two parallel reaction paths (2) and (3).

$$\mathbf{2} + \mathrm{B} \xrightarrow{\text{rapid}} \mathbf{2}\cdot\mathrm{B} \xrightarrow[\text{slow}]{k_m} \mathbf{3}\cdot\mathrm{B} \qquad (2)$$

$$\mathbf{2} + \mathrm{B} \xrightarrow{\text{rapid}} \mathbf{2}\cdot\mathrm{B} + \mathrm{B} \underset{\text{rapid}}{\overset{^{\mathrm{s}}K}{\rightleftharpoons}} \mathbf{2}\cdot 2\mathrm{B} \xrightarrow[\text{slow}]{k_s} \mathbf{1}\cdot 2\mathrm{B} \qquad (3)$$

While the mono adduct formation is always complete, producing $^{\mathrm{r}}k_{\mathrm{obs}} = k_{\mathrm{m}}$ at low [B]/[**2**] ratios, the bis adduct formation is less complete and even at high [B]/[**2**] ratios a mixture of **2**·B and **2**·2B is present in the reaction medium. The latter species should react to produce **1**·2B *via* the limiting kinetics rate equation (1) as observed, given the existence of the equilibrium constant $^{\mathrm{s}}K$. The values obtained for $^{\mathrm{s}}K$ for the systems studied, shown in Table 1, agree very well with those previously determined for the adduct formation equilibrium constants for **3** (X, X′ = H) ($10^{1.9}$ and $10^{1.0}$ dm^3 mol^{-1} for the mono- and bis-adduct formation, respectively).[7] Although an analysis of the product distribution of these compounds would be informative, the difficulties in running ^{31}P NMR spectra at high concentrations of added bases at room temperature where the exchange is very rapid makes it impossible. Furthermore, as already found in similar thermodynamic equilibrium studies,[7] the adduct distribution of these compounds is very difficult to evaluate.

As for the base-assisted cyclometallation reaction, comparison of the data in Tables 2 and 3 indicates that the values of $\Delta H^{\ddagger}$ are much lower and mainly responsible for the rapidness of the reaction. The $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ values are very negative and have the same order of magnitude as those obtained for the spontaneous reaction, indicating that the compression to go to the transition state is very important. As for the nature of the **2**·B mono adduct responsible for the metallation (k_m), it seems clear that, if the cyclometallating species has the base on the non-carbon-bound rhodium axial position (Scheme 3, **a**), a complete conversion of all the monometallated compound **2** present in the medium would be expected, given the lower stability of the adduct of the **3** species formed and the consequent **3**·B ⟶ **2**·B migration of the axially co-ordinated base on metallation. This is not found, and we can speculate



Scheme 3

Table 2 Kinetic, thermal and pressure activation parameters for the rapid step in the **2** + B reaction of the different systems studied in toluene solution with [**2**] = (2–6) × 10^{-3} mol dm^{-3}

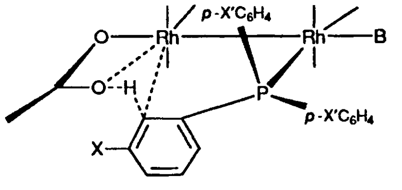
X	X′	B	T/°C	$10^2\,^{\mathrm{r}}k$/s^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	$\Delta V^{\ddagger}$/cm^3 mol^{-1}
H	H	PPh$_3$	25	1.61	38 ± 3	−150 ± 30	−35.0 ± 0.5
			35	3.28			
			45	4.54			
		py	15	4.60	37 ± 2	−72 ± 5	−23.1 ± 1.6
			25	8.15			
			35	13.3			
H	H*	PPh$_3$	45	4.84			
		py	15	4.67	35 ± 2	−75 ± 8	
			25	8.17			
			35	12.8			
Me	H	PPh$_3$	25	2.15	51 ± 1	−105 ± 3	−37.2 ± 1.2
			35	4.29			
			45	8.51			
		py	25	0.84	61 ± 1	−80 ± 2	−25.9 ± 0.5
			35	1.88			
			45	4.20			
Me	Me	P(C$_6$H$_4$Me-*p*)$_3$	15	3.53	42 ± 2	−125 ± 9	
			25	6.87			
			35	11.7			
H	Me	P(C$_6$H$_4$Me-*p*)$_3$	25	0.78	42 ± 1	−144 ± 6	−34.4 ± 1.4
			35	1.43			
			45	2.43			
		py	25	0.36	57 ± 1	−100 ± 1	−27.4 ± 0.4
			35	0.79			
			45	1.66			

* P(C$_6$D$_5$)$_3$ as equatorial non-metallated phosphine ligand.

Table 3 Thermal and pressure activation parameters for the spontaneous and acid-assisted processes of the **2** ⟶ **3** cyclometallation reaction for the different systems studied

		Spontaneous process[a]				Acid-assisted process[b]			
X	X′	10^4k^{353}/s^{-1}	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}	$\Delta V^\ddagger$/cm^3 mol^{-1}	10^3k^{293}/s^{-1}	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}	$\Delta V^\ddagger$/cm^3 mol^{-1}
H	H	1.0[c]	80 ± 5[c]	−105 ± 15[c]	−22.7 ± 0.2	0.20[d]	67 ± 1[d]	−86 ± 5[d]	
						0.34[e]	67 ± 1[e]	−88 ± 3[e]	
						0.25	68 ± 1	−85 ± 3	−15.3 ± 0.2
H	H[f]	0.90[c]	65 ± 7[c]	−140 ± 2[c]		0.097[d]	73 ± 2[d]	−60 ± 8[d]	
H	Me	2.3[c]	91 ± 3[c]	−64 ± 11[c]	−21.5 ± 0.5	0.61[e]	73 ± 8[e]	−60 ± 27[e]	
						0.24	75 ± 1	−59 ± 1	−13.8 ± 0.2
Me	H	1.9	81 ± 4	−88 ± 8	−23.1 ± 1.1	0.25	71 ± 2	−73 ± 4	−14.8 ± 0.2
Me	Me	3.1	78 ± 3	−91 ± 7	−21.4 ± 0.7	0.64	67 ± 2	−77 ± 4	−13.7 ± 0.3

[a] In toluene solution. [b] In neat acetic acid unless stated. [c] Ref. 3(*a*). [d] Derived from the acetic acid dependence of k_{obs} in toluene solution.[3a] [e] Derived from the acetic acid dependence of k_{obs} in chloroform solution.[3a] [f] $P(C_6D_5)_3$ as equatorial non-metallated phosphine ligand.



Scheme 4

about the 'active' cyclometallating species being the **2**·B adduct having the Lewis base attached to the rhodium(II) centre which holds the already metallated phosphine (Scheme 3, **b**). The steric demands of the base on this species would force the phosphine to a position where metallation can take place with lower $\Delta G^\ddagger$ than that obtained for the corresponding spontaneous reactions (Table 3). If this were the case, differences on changing the steric demands of the Lewis base, B, should be found. The $\Delta S^\ddagger$ and $\Delta V^\ddagger$ values in Table 2 also support these assumptions.

In view of these facts a reaction intermediate of the type shown in Scheme 4 is postulated for this process, as for the other cyclometallation reactions studied for these systems.[3a] The absence of a kinetic deuterium isotopic effect shows that the degree of C–H bond breakage in the transition state is fully compensated by O–H bond formation, contrary to that observed for the acid-assisted process. On the other hand, the less negative values of $\Delta S^\ddagger$ and $\Delta V^\ddagger$ when B = py indicate that the smaller steric demands (cone angles of 145° for the triarylphosphines and 120° for pyridine)[6] of this base do not require an intrinsic reorganization as significant as that for B = PPh_3.

In the case where the concentration of base is high enough to have **2**·2B as the main species in solution, the above-mentioned steric effect results in a reaction involving acetate ring closure in preference to cyclometallation; the steric release of the complete process being much more important (Scheme 3, **c**) under these conditions.

In conclusion, the overall metallation process **2** + $P(C_6H_4X'$-*p*$)_3$ ⟶ **3** shown in Scheme 1 has been studied in detail; the steric hindrance on the mono and bis adducts of compounds **2** seems to direct the reaction product distribution. While mono adducts of compound **2** lead to metallation of the equatorial phosphine, the corresponding bis adducts produce substitution of the non-metallated phosphine by the acetate chelating ligand.

Experimental

Procedures and materials

The complexes $[Rh_2(O_2CMe)(\mu\text{-}O_2CMe)_2\{\mu\text{-}(C_6H_4)PPh_2\}\{P(C_6H_4X'\text{-}p)_3\}]\cdot H_2O$ and $[Rh_2(\mu\text{-}O_2CMe)_2\{\mu\text{-}(C_6H_4)PPh_2\}\{\mu\text{-}(p\text{-}X'C_6H_3)P(C_6H_4X'\text{-}p)_2\}]\cdot 2H_2O$, *i.e.* **2**·$H_2O$, and **3**·$2H_2O$ (X = H, X′ = H or Me), were prepared according to literature methods.[3a,4,5b] The preparation of compound **3**·$2H_2O$ (X, X′ = Me), has also already been described.[4] All chemicals were of analytical grade and were used as purchased. The NMR spectra were recorded on AC-200 Bruker spectrometer (^{31}P) and 400 MHz Varian spectrometers (^{13}C and ^1H), UV/ VIS spectra on a HP8452A or Shimadzu UV-160A instrument.

Preparation of compounds

No analytical data are available from the following compounds, the small differences expected for the elemental analyses for compounds **2**·H_2O and **3**·$2H_2O$, together with the reliability of well established ^1H and ^{31}P NMR spectral data, made them unnecessary.

The compounds **2**·H_2O (X = Me, X′ = H or Me) were prepared in a similar manner. The complex $[Rh_2(\mu\text{-}O_2CMe)_3\{\mu\text{-}(p\text{-}MeC_6H_3)P(C_6H_4Me\text{-}p)_2\}]\cdot 2H_2O$, **1**·$2H_2O$ (X = Me) (0.2 mmol) and the corresponding phosphine (0.2 mmol) were dissolved in CH_2Cl_2 (100 cm^3) in a photochemical reactor. After irradiation for *ca.* 30 min with a mercury-vapour lamp the mixture changed from orange-red to green. After vacuum evaporation of the solvent at room temperature, the green solid was dissolved in the minimum volume of CH_2Cl_2 and transferred to a column of silica suspended in hexane (1 × 30 cm). Elution with C_6H_{14}–CH_2Cl_2–Me_2CO (20:20:3) separated a green band which was collected, reduced in volume and hexane added to give a green precipitate which was filtered off and washed with hexane. Compound **2**·H_2O: (X = Me, X′ = H), yield 64%; ^{31}P-{^1H} NMR ($CDCl_3$, reference $SiMe_4$) δ 15.0 [dd, ^1J(Rh–P) = 143.5, ^2J(Rh–P) = 10.1] and 43.9 [dd, ^1J(Rh–P) = 186.5, ^2J(Rh–P) = 4.2 Hz]; (X, X′ = Me), yield 65%; NMR, ^1H, δ 1.14 (3 H, s), 1.18 (3 H, s), 1.74 (3 H, s), 1.91 (3 H, s), 2.24 (3 H, s), 2.32 (3 H, s), 2.38 (9 H, s) and 6.6–6.8 (23 H, aromatics); ^{31}P-{^1H}, δ 13.8 [dd, ^1J(Rh–P) = 137.8, ^2J(Rh–P) = 10.6] and 40.9 [dd, ^1J(Rh–P) = 188.1, ^2J(Rh–P) = 4.8 Hz].

The complex **3**·$2H_2O$ (X = Me, X′ = H) was prepared from the corresponding **1**·H_2O complex. Thus $[Rh_2(\mu\text{-}O_2CMe)_3\{\mu\text{-}(p\text{-}MeC_6H_3)P(C_6H_4Me\text{-}p)_2\}]\cdot 2H_2O$ (0.2 mmol) was dissolved in $CHCl_3$ (10 cm^3) and PPh_3 (0.6 mmol) was added. After stirring the solution at room temperature for 24 h the solvent was evaporated under vacuum and the solid residue dissolved in the minimum volume of CH_2Cl_2. The solution was then transferred to a chromatography column of silica suspended in hexane (1 × 30 cm). Elution with C_6H_{14}–CH_2Cl_2–Me_2CO (10:10:1) separated a violet band and a purple band which was collected. Reduction in volume of the purple eluate and addition of hexane produced a green precipitate which was filtered off and washed with hexane, yield 80%. NMR: ^1H, δ 1.20 (3 H, s), 1.24 (3 H, s), 2.15 (3 H, s), 2.22 (3 H, s), 2.32 (3 H, s) and 6.2–7.8 (25 H, aromatics); ^{31}P-{^1H}, δ 16.5 [dd,

^1J(Rh–P) = 164.6, ^2J(Rh–P) = 7.8] and 19.3 [dd, ^1J(Rh–P) = 173.0, ^2J(Rh–P) = 8.1 Hz].

Kinetic measurements

The reactions were followed by UV/VIS spectroscopy in the full 750–300 nm range on a HP8452A instrument equipped with a multicell transport, thermostated (±0.1 °C) with a circulation bath. Observed rate constants were derived from absorbance *versus* time traces at the wavelengths where a maximum increase and/or decrease in absorbance was observed. No dependence of the values on the selected wavelengths was detected, as expected for reactions where there is a good retention of isosbestic points.[8a] The general kinetic technique was that previously described.[11] Solutions for the kinetic runs were prepared by mixing calculated amounts of solutions of the rhodium compound and the corresponding Lewis base in the spectrophotometric cells.

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 5–10% of the calculated value. All post-run fittings by rate equations were done by standard commercially available fitting programs. Eyring plots were always weighted by (% error)$^{-1}$ for the constants involved.

Atmospheric pressure kinetic runs with $t_{\frac{1}{2}} > 170$ s were recorded on a HP8452A instrument equipped with a thermostatted multicell transport; runs within the 7–170 s margin were recorded on a HP8452A instrument equipped with a High-Tech SFA-11 Rapid Kinetics Accessory. For runs at elevated pressure with $t_{\frac{1}{2}} < 100$ s a laboratory-made high-pressure stopped-flow spectrophotometer was used as described previously;[12] for $t_{\frac{1}{2}} > 800$ s a previously described pressurizing system and high-pressure cell were used.[13]

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