Exchange Reaction of Bridging Acetate Ligands and Reversible Electrophilic Rhodium–Carbon Activation in Ortho-Metalated Rhodium(II) Compounds with Acetic Acid. Kinetic Study of the Exchange Reaction of Acetates with CD_3CO_2D in the Compound $Rh_2(O_2CCH_3)_3[(C_6H_4)P(C_6H_5)_2]\cdot 2HO_2CCH_3$

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Stepwise exchange reactions of $CH_3CO_2^-$ groups by $CD_3CO_2^-$ groups are observed for $Rh_2(O_2CCH_3)_3[(C_6H_4)P(C_6H_5)_2]\cdot 2HO_2CCH_3$ in $CHCl_3/CD_3CO_2D$ mixtures. The first reaction step involves a fast exchange of the acetate group trans to the metalated phosphine as well as exchange of the two axial molecules of acetic acid. In a second and slower step the exchange of the acetate groups cis to the metalated phosphine occurs. The kinetics of the second process has been studied by ^1H NMR spectroscopy using different $CHCl_3/CD_3CO_2D$ mixtures as reaction solvents. The kinetic data follow a two-term rate law, $v = [k_1 + k_2[CD_3CO_2D]^{1/2}][Rh_2]$. The first-order constant k_1 at 298 K is $(2.08 \pm 0.02) \times 10^{-6}$ s^{-1} ($\Delta H^\ddagger = 98 \pm 5$ kJ mol^{-1}; $\Delta S^\ddagger = 45 \pm 20$ J K^{-1} mol^{-1}), and the second-order rate constant at the same temperature is $k_2 = (3.83 \pm 0.01) \times 10^{-6}$ s^{-1} M$^{-1/2}$ ($\Delta H^\ddagger = 103 \pm 5$ kJ mol^{-1}; $\Delta S^\ddagger = -15 \pm 15$ J K^{-1} mol^{-1}). Electrophilic attack at one oxygen atom of the bridging acetate group by a proton of acetic acid is concluded to be the first and rate-determining step of the exchange process. The axially coordinated acetic acid is likely responsible for the intramolecular attack. Very fast exchange of all the $CH_3CO_2^-$ groups by $CD_3CO_2^-$ is observed for the compound $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2\cdot 2HO_2CCH_3$ in the presence of CD_3CO_2D. The partially deuterated compound $Rh_2(O_2CCH_3)_3[(C_6D_4)P(C_6D_5)_2]\cdot 2HO_2CCH_3$ undergoes 90% D–H exchange at the ortho position of the phenyl rings of the phosphine after 3 h of reflux in acetic acid. Much slower exchange is observed for $Rh_2(O_2CCH_3)_2[(C_6D_4)P(C_6D_5)_2]_2\cdot 2HO_2CCH_3$ in the same conditions. The observed D–H exchange is explained by an electrophilic attack at the rhodium–carbon bond by acetic acid, which produces the protonation of the ortho aromatic carbon atom, followed by a cyclometalation at one of the ortho C–H bonds.

Introduction

Cyclometalation reactions are well-known in mononuclear compounds,[1] but few studies have been reported for this type of reaction in dinuclear compounds containing a metal–metal bond.[2] Several singly and doubly metalated dirhodium(II) compounds have been structurally characterized[3] and contain one or two arylphosphine anions acting as bridging P,C donor ligands.

These compounds are obtained by thermal reaction of dirhodium tetraacetate and the arylphosphine in different molar ratios. In all these reactions intramolecular activation of aromatic C–H bonds has been observed even when alkylarylphosphines are used.[3b] In the course of our investigation of orthometalation reactions of triphenylphosphine in dirhodium(II) compounds, we have studied the reaction of $Rh_2(O_2CCH_3)_3[(C_6H_4)P(C_6H_5)_2]\cdot 2HO_2CCH_3$ with $P(C_6H_5)_3$ yielding $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2\cdot 2HO_2CCH_3$.[3c] We have observed that this reaction is considerably faster if acetic acid is present in the reaction medium. Although the same observation was made for other related metalation reactions,[3h] this point has not been investigated at all. The same activation has been reported for the cyclopalladation of *N,N*-dimethylbenzylamines when acetic acid[4] is present. However, in this case different starting palladium species have been proposed to be present in solution depending on the reaction medium, chloroform or acetic acid, used. In the latter medium the cleavage of acetate bridges in $Pd_3(O_2CCH_3)_6$ has been described as the rate-determining step of the process.[4]

In order to gain some insight into the role of the acid in the metalation reactions of rhodium compounds, we have investigated the effect of acetic acid on the compounds $Rh_2(O_2CCH_3)_3[(C_6H_4)P(C_6H_5)_2]\cdot 2HO_2CCH_3$ (**1**) and $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2\cdot 2HO_2CCH_3$ (**2**). The results obtained indicate that when **1** is in acetic acid-d_4 medium, two processes occur simultaneously with different reaction rates: the stepwise exchange of acetate ligands and a reversible electrophilic rhodium–carbon activation. The same two processes are observed for compound **2**, although with different relative rates.

Results

The monometalated compound $Rh_2(O_2CCH_3)_3[(C_6H_4)P(C_6H_5)_2]\cdot 2HO_2CCH_3$ (**1**) has a molecular structure with one

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triphenylphosphine anion $(C_6H_4)P(C_6H_5)_2^-$ (PC^-) and three acetate groups bridging the Rh_2^{4+} unit.[3c] Two molecules of acetic acid are located in axial coordination sites, lying along the Rh–Rh axis.

The ^1H NMR spectrum of this compound shows three signals in the methyl region at 2.32 (3 H, $CH_3CO_2^-$ trans to PC^-), 2.18 (6 H, axial CH_3CO_2H), and 1.29 ppm (6 H, $CH_3CO_2^-$ cis to PC^-).

When **1** is dissolved in a mixture of $CDCl_3/CD_3CO_2D$ (CD_3CO_2D/Rh_2 molar ratio of 130/1), the ^1H NMR signal due to the trans $CH_3CO_2^-$ group disappears, while the signal due to the cis acetate groups remains unchanged. The spectrum of a freshly prepared sample shows only two ^1H NMR methyl signals due to cis acetate groups (1.29 ppm) and to free acetic acid (2.14 ppm). The ^1H NMR of the solid isolated from the solution after 5 min of stirring shows that the exchange of the trans acetate and the axial acetic acid by the deuterated groups has occurred to a very high extent (ca. 94%). According to the CD_3CO_2D/Rh_2 molar ratio utilized, the maximum level of exchange should be 97.7%.

Slow exchange of the cis acetate groups is observed when **1** is maintained in $CDCl_3/CD_3CO_2D$ mixture at room temperature for several hours. The kinetics of this slow exchange is described later in this paper. In contrast to this behavior the doubly metalated compound **2** rapidly exchanges both bridging acetate groups in the presence of CD_3CO_2D.

No H–D exchange occurs in the aromatic rings of the metalated phosphine under the experimental conditions that produce complete exchange of the acetate groups. However, if **1** is boiled in pure acetic acid-d_1 for 3 h, some changes can be observed in the aromatic part of the ^1H NMR spectrum of the resulting compound. A clearer result can be obtained by reacting the partially deuterated compound $Rh_2(O_2CCH_3)_3[(C_6D_4)P(C_6D_5)_2]\cdot 2HO_2CCH_3$ (**1**-d_{14}) in boiling acetic acid.

The compound **1**-d_{14} is easily prepared by reacting rhodium acetate and $P(C_6D_5)_3$ according to the method described for the nondeuterated compound.[3c] In the ^1H NMR spectrum of this compound only two doublets of low intensity are detected in the aromatic region at δ_H = 6.89 ppm, $^3J_{P-H}$ = 10.2 Hz, and δ_H = 7.49 ppm, $^3J_{P-H}$ = 11.1 Hz, of relative intensity 4:1, due to partial protonation at the ortho carbon of the phenyl rings. Such protonation can be minimized (≤2%) by making the reaction time shorter or by using acetic acid-d_1 as reaction solvent.

These two signals increase in intensity when **1**-d_{14} is refluxed in acetic acid for several hours. From the calculated integral values in the ^1H NMR spectrum, we have observed up to 90% exchange in 3 h of reaction. Longer refluxing times produce compound rearrangement giving dirhodium tetraacetate and the doubly metalated compound $Rh_2(O_2CCH_3)_2[(C_6HD_3)P(C_6H_2D_3)_2]_2\cdot 2HO_2CCH_3$. If a sample of the deuterated compound **1**-d_{14} is reacted with *p*-toluenesulfonic acid (HPTS) in the presence of acetic acid, in addition to the exchange of carboxylate groups, the slow D–H exchange in the ortho position of the phenyl rings is observed even at room temperature (36% after 48 h of reaction).

The doubly metalated compound $Rh_2(O_2CCH_3)_2[(C_6D_4)P(C_6D_5)_2]_2\cdot 2HO_2CCH_3$ experiences very low D–H exchange even in refluxing pure acetic acid. In the latter case, we did not reach 60% of protonation after 48 h of reaction.

Kinetic Study. The slow carboxylate exchange process has been studied kinetically by ^1H NMR spectroscopy, monitoring the disappearance of the signal at 1.26 ppm corresponding to the cis acetate groups, in solutions of constant concentration of **1** in $CDCl_3$ with variable concentrations of CD_3CO_2D.

$$Rh_2(O_2CCH_3)_3[PC]\cdot 2HO_2CCH_3 \xrightarrow{CD_3CO_2D} Rh_2(O_2CCH_3)_{2cis}(O_2CCD_3)_{trans}[PC]\cdot 2DO_2CCD_3 \xrightarrow[k_{obs}]{CD_3CO_2D} Rh_2(O_2CCD_3)_3[PC]\cdot 2DO_2CCD_3$$

$$[PC] = (C_6H_4)PPh_2$$

According to the procedure described in the Experimental Section, we obtained k_{obs} values from the slopes of the plots of ln R vs time, in which $R = {}^5/_2[i(CH_3CO_2^-{}_{cis})/[\sum_i(CH_3)]$. As the modification of the concentration of compound **1** does not lead to any significant change in the observed rate constant (k_{obs}), we assume that the reaction is first order in **1** (Table I).

The plot of k_{obs} against acetic acid-d_4 concentration (Figure 1) was best fitted to eq 1 with a correlation coefficient of 0.999. These results clearly show that the exchange of cis acetate groups by CD_3CO_2D occurs by two independent processes.

$$k_{obs} = k_1 + k_2[CD_3CO_2D]^{1/2} \quad (1)$$

The second-order rate constant k_2 is associated with an *intermolecular* process, while k_1 relates to an *intramolecular* process. This first-order rate constant can also be experimentally determined by monitoring the rearrangement produced in the partially deuterated monometalated compound $Rh_2(O_2CCH_3)_{2cis}(O_2CCD_3)_{trans}[(C_6H_4)P(C_6H_5)_2]\cdot 2DO_2CCD_3)_2$ (**1**-d_{11}). This compound in chloroform solution shows evolution to a random distribution of the $CH_3CO_2^-$ groups in the cis, trans, and axial coordination sites. The observed rate constant for this process (2.04×10^{-6} s^{-1}) is in good agreement with the value calculated from the k_{obs} vs $[CD_3CO_2D]^{1/2}$ plot (2.08×10^{-6} s^{-1}). The rate constants for the exchange in acetic acid/toluene show no difference from those obtained in acetic acid/chloroform. This result indicates that there is not an important contribution of ionic strength in the reaction rate.

In the presence of the poorly coordinating and stronger acid *p*-toluene-4-sulfonic acid (HPTS), k_{obs} increases considerably as shown in Table II. No change in k_{obs} was observed when the concentration of CD_3CO_2D was changed, keeping [HPTS] constant.

Experiments oriented to determine isotopic effects in this exchange reaction can only be performed at zero concentration of acetic acid-d_4, monitoring the equilibrium reactions 2a,b. From these two reactions $k_{1(H)}$ and $k_{1(D)}$ were respectively measured. We find that reaction 2b is considerably faster with $k_{1(H)}/k_{1(D)}$ = 2.14.

$$\underset{\textbf{1}\text{-}d_{11}}{Rh_2(O_2CCH_3)_{2cis}(O_2CCD_3)_{trans}[PC]\cdot 2DO_2CCD_3} \xrightarrow{k_{1(D)}} \underset{X = 60\%\ D,\ 40\%\ H}{Rh_2(O_2CCX_3)_3[PC]\cdot 2DO_2CCX_3} \quad (2a)$$

$$\underset{\textbf{1}\text{-}d_6}{Rh_2(O_2CCD_3)_{2cis}(O_2CCH_3)_{trans}[PC]\cdot 2HO_2CCH_3} \xrightarrow{k_{1(H)}} \underset{X = 40\%\ D,\ 60\%\ H}{Rh_2(O_2CCX_3)_3[PC]\cdot 2HO_2CCX_3} \quad (2b)$$

The reaction rate constants (k_1 and k_2) were determined at several temperatures. From the Eyring plots shown in Figure 2 the activation parameters were calculated (Table III).

Discussion

The observed dependence of the reaction rate on the square root of the total acetic acid concentration arises from the weak

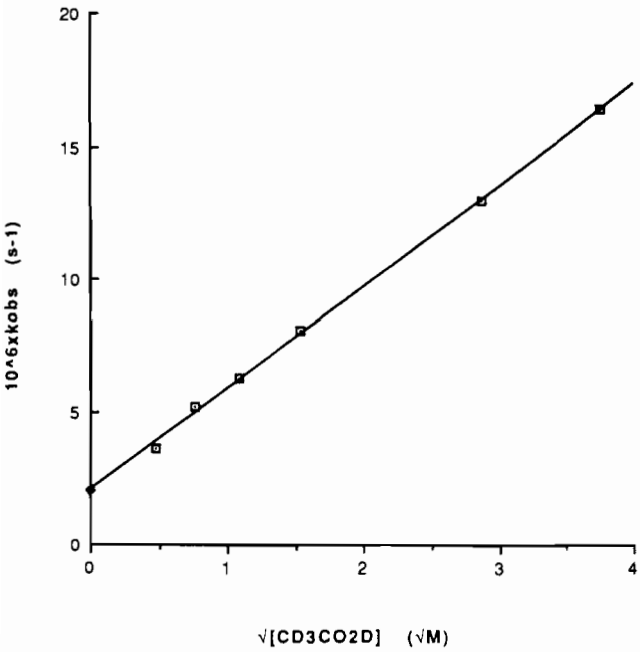

Figure 1. Plot of k_{obs} vs $[CD_3CO_2D]^{1/2}$ for the exchange of acetate groups between **1** and $CD_3CO_2^-$.

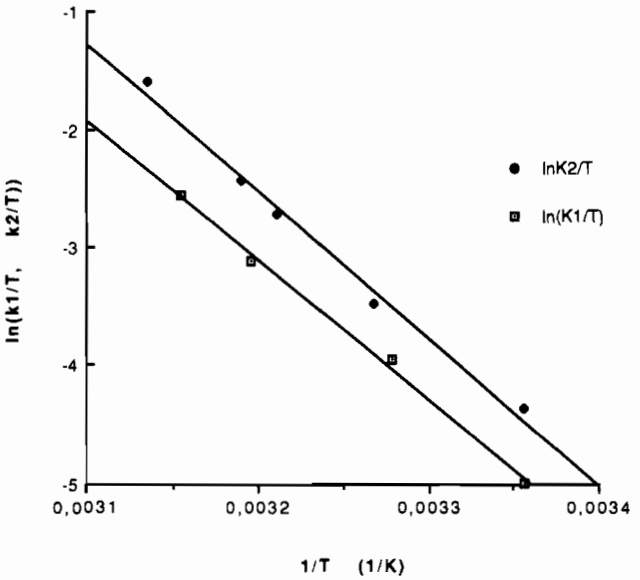

Figure 2. Eyring plots for the intra- and intermolecular mechanisms of exchange of acetate bridges by $CD_3CO_2^-$ in **1**.

Table I. Observed Values of k_{obs} at Different Concentrations of CD_3CO_2D at 25 °C

$[CD_3CO_2D]$ (M)	14.08	8.18	2.34	1.17	0.59	0.23
10^6k_{obs} (s^{-1})	16.42	12.98	8.05	6.29	5.22	3.63

Table II. Observed Values of k_{obs} at Different Concentrations of HPTS ($[CD_3CO_2D]$ = 8.18 M; 25 °C)

[HPTS] (M)	0	0.075	0.173	0.315
10^6k_{obs} (s^{-1})	12.98	159.67	380.97	747.29

dissociation of CD_3CO_2D in chloroform-*d* solution according to $2CD_3CO_2D \leftrightarrow CD_3CO_2D_2^+ + CD_3CO_2^-$. When we use *p*-toluenesulfonic acid in the reaction medium, $[CD_3CO_2D_2^+]$ is increased, so increasing the observed rate constant. Preliminary results[5] from an independent study of the exchange reaction of the monometalated compound **1** with CF_3CO_2H gave values for

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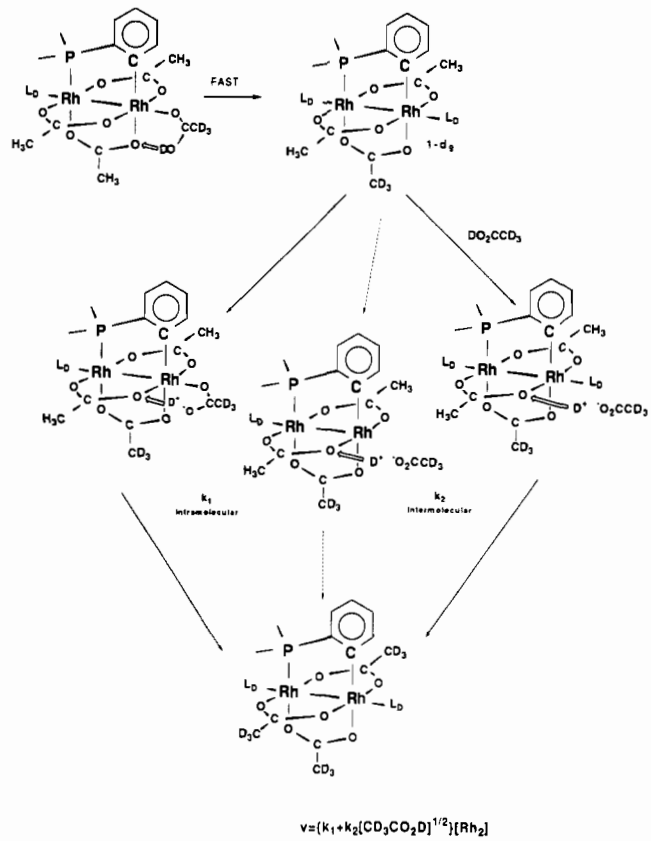
Table III. Activation Parameters for Intra- (1) and Intermolecular (2) Mechanisms

mechanism	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})
1_D[a]	98 ± 5	−45 ± 20
2_D[a,b]	103 ± 5	−15 ± 15
1_H[c]	105 ± 3	−13 ± 10

[a] D = mechanism involving deuterium transfer. [b] Data obtained from k_2 values in s^{-1} $M^{-1/2}$. [c] H = mechanism involving proton transfer.

Scheme I. Mechanism Proposed for the Exchange of Acetate Groups by $CD_3CO_2^-$ in Compound **1**



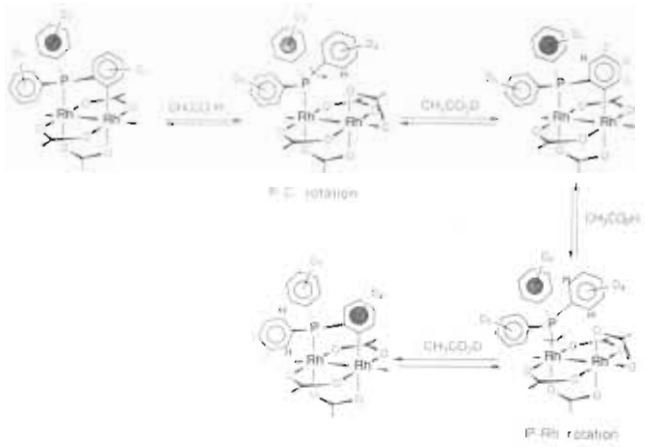
the observed rate constants 1–2 orders of magnitude higher consistent with the stronger acid character of the trifluoroacetic acid.

The suggested reaction mechanism is presented in Scheme I. The intermolecular process is described as (i) concerted transfer of one D^+ from one protonated acetic acid to one oxygen of the bridging group followed by (ii) cleavage of the Rh–O bond of the protonated acetate with coordination of one acetate group.

The observed isotopic effect, $k_{1(H)}/k_{1(D)} = 2.14$, can be due to changes in the dissociation constant of the acetic acid and also to differences in the lability of the Rh–O bond of the protonated acetate group.

The lability of the acetate group trans to the metalated phosphine, which exchanges as fast as the axial ligands, requires some comments. Compound **1**, as well as other related compounds, shows in the crystal structure hydrogen bonding between the OH group of the axial acetic acid and one oxygen atom of one carboxylate bridge.[3c] In this particular case both molecules of acetic acid interact with the same acetate group, the one trans to the PC ligand. In addition to that, the Rh–O distances trans to the P and C atoms are considerably longer than the other four. These two factors must be responsible for the observed lability in these exchange reactions. The very fast exchange of this trans acetate group prevents us from getting detailed kinetic results. However, it is reasonable to assume that a mechanism similar to the one proposed for the exchange of the cis acetate groups is also operating in this case.

Scheme II. Rh–C Electrophilic Activation of Compound **1** in the Presence of Acetic Acid



In connection with this point, the doubly metalated compound $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2{\cdot}2HO_2CCH_3$ exchanges very rapidly both acetate groups with acetic acid in similar reaction conditions. The crystal structure[3a] shows that each axial ligand has a hydrogen bonding interaction with a different acetate group.

There are two possible interpretations of the data obtained for the intramolecular process. The first one is to assume that the axial carboxylic acid can rotate around the Rh–O bond interacting with the cis acetate group. An alternative view is to assume that the axial acetic acid undergoes Rh–O bond cleavage prior to the attack. Even though the dissociative path seems more attractive, as it is a particular case of the intermolecular mechanism at zero acid concentration, the "pure" intramolecular path cannot be discarded with the available data. The fact that $\Delta S^{\ddagger}$ is more negative for the intramolecular process supports the pure intramolecular path, which requires a highly ordered intermediate.

When we use stronger reaction conditions (refluxing acetic acid, addition of *p*-toluenesulfonic acid), the proton of the carboxylic acid also produces the electrophilic cleavage of the Rh–C bond as shown in Scheme II; the carbon atom becomes protonated and the carboxylate coordinated to the rhodium atom adopts a chelating coordination mode. This structural arrangement suggested for the intermediate II, with one equatorial phosphine and one chelating carboxylate group, is already known[3h] for dirhodium(II) compounds. There is also an opposite reaction, the proton transfer from the phenyl to the acetate group, that regenerates the metalated compound from the nonmetalated intermediate. In order to account for all the observations, we have to accept that a rapid rotation around the P–C and Rh–P bonds occurs in the intermediate with equatorial phosphine and that this rotation process is fast compared to the C–H activation reaction. At the end of the process, we observe the equal amount of protonation at all the ortho positions of the aromatic rings.

These results indicate that two simultaneous processes, exchange of acetate ligands and electrophilic Rh–C bond activation, are also occurring while the ortho-metalation takes place. In particular, the observation of an electrophilic rhodium–carbon bond activation in compound **1** confirms the reversible character of the metalation reaction, and it is relevant to understand this particular reactivity of dirhodium(II) compounds. It is noteworthy that, besides the observed lability of the acetate trans to the metalated phosphine, all the reported doubly metalated compounds exhibit a cisoid configuration. Further investigation of this particular reaction is in progress.

Experimental Section

Procedures and Materials. $Rh_2(O_2CCH_3)_3[(C_6H_4)P(C_6H_5)_2]{\cdot}2HO_2CCH_3$ (**1**) and $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2{\cdot}2HO_2CCH_3$ (**2**) were prepared according to literature methods.[3g] $Rh_2(O_2CCH_3)_3[(C_6D_4)P(C_6D_5)_2]{\cdot}2HO_2CCH_3$ (**1**-d_{14}) and $Rh_2(O_2CCH_3)_3[(C_6D_4)P(C_6D_5)_2]{\cdot}2HO_2CCH_3$ (**2**-d_{28}) were prepared using $P(C_6D_5)_3$ according to the general way of obtention of monometalated compounds.[3g] Commercially available $P(C_6D_5)_3$ (Aldrich) and $CDCl_3$ and CD_3CO_2D (acetic acid-d_4) were used as purchased. ^1H NMR measurements were recorded on a Bruker AC-200 spectrometer. All solvents were of analytical grade. Chloroform and toluene were dried and degassed before using; acetic acid was only degassed.

Reaction of $Rh_2(O_2CCH_3)_3[(C_6D_4)P(C_6D_5)_2]{\cdot}2HO_2CCH_3$ with Acetic Acid. A 5-mL volume of CH_3CO_2H was added to 50 mg of $Rh_2(O_2CCH_3)_3[(C_6D_4)P(C_6D_5)_2]{\cdot}2HO_2CCH_3$ (0.064 mmol). The resulting suspension was taken to reflux during 1 h giving a deep violet solution. CH_3CO_2H was removed under vacuum, and the resulting solid was precipitated in 5 mL of 1/1 CH_2Cl_2/hexane. Partial protonation of the ortho position of the metalated phosphine was observed by ^1H NMR spectroscopy. This operation was repeated until 95% of H–D exchange was obtained for the ortho position.

Data for $Rh_2(O_2CCH_3)_3[(C_6HD_3)P(C_6HD_4)_2]{\cdot}2HO_2CCH_3$: ^1H NMR ($CDCl_3$) (in ppm) 1.30 (6 H, CH_3, s), 2.23 (6 H, CH_3, s), 2.32 (3 H, CH_3, s), 6.88 (0.95 H, aromatic, d, $^3J_{P-H}$ = 10.1 Hz), 7.49 (3.9 H, aromatics, d, $^3J_{P-H}$ = 10.1 Hz).

Reaction of $Rh_2(O_2CCH_3)_3[(C_6D_4)P(C_6D_5)_2]{\cdot}2HO_2CCH_3$ with Acetic Acid and *p*-Toluenesulfonic Acid. A 25-mg amount (0.13 mmol) of *p*-toluenesulfonic acid was added to a 5-mL solution of compound **1** in 1/1 $CHCl_3/CH_3CO_2H$. The solution was stirred at room temperature during 48 h, and the solvent was removed under vacuum. The resulting solid was crystallized in a 1/1 CH_2Cl_2/hexane mixture, yielding a monometalated compound with a 36% level of protonation at the ortho positions of the aromatic rings.

Reaction of $Rh_2(O_2CCH_3)_2[(C_6D_4)P(C_6D_5)_2]_2{\cdot}2HO_2CCH_3$ with Acetic Acid. A 5-mL volume of CH_3CO_2H was added to 50 mg of $Rh_2(O_2CCH_3)_2[(C_6D_4)P(C_6D_5)_2]_2{\cdot}2HO_2CCH_3$ (0.052 mmol). The resulting suspension was taken to reflux during 48 h giving a deep purple solution. CH_3CO_2H was removed under vacuum, and the resulting solid was precipitated in 5 mL of 1/1 CH_2Cl_2/hexane. Partial protonation of the orto position of the metalated phosphine was observed by ^1H NMR spectroscopy.

Data for $Rh_2(O_2CCH_3)_2[(C_6HD_3)P(C_6HD_4)_2]_2{\cdot}2HO_2CCH_3$: ^1H NMR ($CDCl_3$) (in ppm) 1.23 (6 H, CH_3, s), 2.18 (6 H, CH_3, s), 6.54 (0.36 H, aromatic, d, $^3J_{P-H}$ = 10.1 Hz), 6.82 (0.72 H, aromatics, d, $^3J_{P-H}$ = 10.1 Hz), 7.74 (0.72 H, aromatics, d, $^3J_{P-H}$ = 10.1 Hz).

Synthesis of Compounds. Preparation of 1-d_6. A 100-mg amount (0.13 mmol) of **1** is dissolved in 1 mL of $CHCl_3$. A 0.5-mL volume of acetic acid-d_4 is added to the deep violet solution, and the whole solvent is removed under vacuum. The crude solid is crystallized in a mixture of CH_2Cl_2/hexane (5 mL/5 mL). The $^{31}P\{^1H\}$ NMR spectrum of the product obtained is identical with that of **1**. The ^1H NMR spectrum shows one signal on the methyl region (1.29 ppm, 2 CH_3) due to the two acetate groups cis to the metalated phosphine.

Preparation of 1-d_{11}. A 100-mg amount (0.13 mmol) of **1** is dissolved in 1 mL of $CHCl_3$ and 1 mL of acetic acid-d_4. The solution is stirred at room temperature for 48 h. The deep violet solution is evaporated to dryness under vacuum. The crude solid is crystallized in a mixture of CH_2Cl_2/CH_3CO_2H (2 mL/2 mL). The $^{31}P\{^1H\}$ NMR spectrum of the product obtained is identical to that of **1**. The ^1H NMR spectrum shows two signals on the methyl region (2.18 ppm, 2 CH_3; 2.32 ppm, 1 CH_3) due to the two axial molecules of acetic acid and to the acetate group trans to the metalated phosphine.

Kinetical Measurements. Kinetics of Exchange of 1 with Acetic Acid-d_4. A 35-mg amount (0.045 mmol) of **1** was added to an NMR tube. The solid was dissolved in 0.7 mL of a mixture of $CDCl_3/CD_3CO_2D$ of variable composition. The probe of the NMR spectrometer was equilibrated at 298, 306, 311.5, 313.5, and 319 K. The reaction progress was monitored by recording ^1H NMR spectra of the sample every 5–30 min depending on the reaction rates by measuring the decrease of the signal at 1.29 ppm corresponding to the cis $CH_3CO_2^-$ groups. The total intensity of all the methyl resonances, $\sum_i(CH_3)$, was taken as an internal reference. This value corresponds to 5 methyl groups/mol of rhodium dimer. The percentage of protonated cis methyl groups is given by $100R$, with $R = {}^5/_2[i(CH_3CO_2^-{}_{cis})/\sum_i(CH_3)]$. The plotting of ln R vs time gave linearity with correlation coefficients within the range 0.992–0.999. Activation parameters were calculated from the corresponding Eyring plots according to the data obtained from variable-temperature measurements.

Kinetics of Exchange of 1 with Acetic Acid-d_4 in the Presence of *p*-Toluenesulfonic Acid (HPTS). A 35-mg amount (0.045 mmol) of **1**

and a variable amount of HPTS (0.075–0.315 M) were added to an NMR tube. The solid was dissolved in 0.7 mL of a mixture of 1/1 $CDCl_3/CD_3CO_2D$. The probe of the NMR spectrometer was equilibrated at 298 K. The reaction progress and the treatment of the data were similar to that described for **1** in acetic acid. The same reaction was performed by modifying the concentration of acetic acid in the range 1.17–8.14 M maintaining [HPTS] = 0.315 M. The plotting of ln R vs time gave linearity with correlation coefficients within the range 0.992–0.999.

Kinetics of the Evolution of 1-d_6. A 35-mg amount (0.045 mmol) of **1**-d_6 was dissolved in a sealed NMR tube with 0.7 mL of $CDCl_3$. The temperature was graduated at 298, 305, 313, and 317 K. The reaction progress was monitored by measuring the decrease of the signal at 1.29 ppm and the increase of the two signals at 2.18 and 2.32 ppm. The total intensity of all the methyl resonances, $\sum_i(CH_3)$, was taken as an internal reference assuming this value to correspond to 2 methyl groups/mol of rhodium dimer. The percentage of protonated cis methyl groups is given by $100R'$, being $R' = [i(CH_3CO_2^-{}_{cis})/\sum_i(CH_3)]$. The treatment of the observed data was similar to that described above. At the equilibrium state these three signals showed a 2/2/1 ratio. Activation parameters shown in Table I were calculated according to the data obtained from the variable-temperature measurements.

Kinetics of the Evolution of 1-d_{11}. This reaction was performed in a similar manner to that described above for **1**-d_6. The temperature was graduated at 298, 307, 314, 316, and 321 K. The reaction progress was monitored by measuring the increase of the signal at 1.29 ppm and the decrease of the two signals at 2.18 and 2.32 ppm. The total intensity of all the methyl resonances, $\sum_i(CH_3)$, was taken as internal reference assuming this value to correspond to 3 methyl groups/mol of rhodium dimer. The percentage of protonated cis methyl groups is given by $100R''$ with $R'' = {}^3/_2[i(CH_3CO_2^-{}_{cis})/\sum_i(CH_3)]$. At the equilibrium state the integral ratio of these three signals was 2/2/1. Activation parameters were calculated as indicated above.

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