

Determination of Equilibrium Constants and Computational Interaction Energies for Adducts of $[\text{Rh}_2(\text{RCO}_2)_{4-n}(\text{PC})_n]$ ($n = 0-2$) with Lewis Bases

Pipsa Hirva,^{*†} Julio Esteban,[‡] Julio Lloret,[‡] Pascual Lahuerta,^{*‡} and Julia Pérez-Prieto^{*§}

Department of Chemistry, University of Joensuu, P.O. Box 111, FI-80101 Joensuu, Finland, and Departamentos de Química Inorgánica and de Química Orgánica/ICMOL, Universidad de Valencia, Burjassot, E-46100 Valencia, Spain

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Properties of dirhodium catalysts with cyclometalated aryl phosphine ligands have been studied. We report here the study of the acid–base reaction of $\text{Rh}_2(\text{RCO}_2)_2(\text{PC})_2(\text{H}_2\text{O})_2$ catalysts (PC = cyclometalated aryl phosphine) with different Lewis bases. The determination of the equilibrium constants of these reactions can be used to study to which extent the properties of the axial coordination site of the catalyst, considered the active site, are affected by modification of the metalated phosphines, the carboxylate ligands, or the incoming axial ligand. The trends in the computational density functional theory interaction energies show good agreement with the major trends in the equilibrium constants, thus enabling a further study of the influence of the modification of the ligand core.

1. Introduction

There is a large selection of catalytic results^{1–5} for decomposition of α -diazocarbonyl compounds mediated by bis-cyclometalated dirhodium compounds of formula $\text{Rh}_2(\text{RCO}_2)_2(\text{PC})_2$ (PC = cyclometalated aryl phosphine). It is generally accepted that in dirhodium (II,II) complexes the catalytic center is the axial coordination site, which stabilizes the transient carbene prior to the nucleophilic attack that will create the C–C bond. This initiation step appears to govern the reactivity of these catalysts in carbene-transfer reactions.^{6–8} The structure of the ligand core has been found

to have a significant effect on the initial carbene formation, and therefore on the overall reaction pathway.⁹ However, it has been difficult to establish detailed information about the effect of ligand modifications in the complex on its catalytic behavior. Locating full reaction pathways is always a difficult and time-consuming task, both experimentally and computationally, although examples of such studies exist for reactions catalyzed by dirhodium complexes.^{10–12}

A suitable selection of a simplified model system can help in acquiring information on the most important properties of the catalysts. A model system can be consistently altered, and it will be easier to correlate experimental and computational results. In a previous publication, we have described computational structural and electronic trends involved in the modification of the catalyst ligand core of cyclometalated dirhodium(II,II) complexes including two axial water ligands.¹³ Exchange reactions of the axial pyrazole and imidazole

* To whom correspondence should be addressed. E-mail: pipsa.hirva@joensuu.fi (P.H.), pascual.lahuerta@uv.es (P.L.), (J.P.-P.).

† University of Joensuu.

‡ Departamento de Química Inorgánica, Universidad de Valencia.

§ Departamento de Química Orgánica/ICMOL, Universidad de Valencia.

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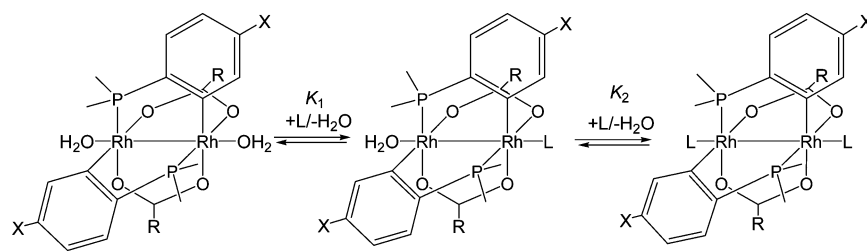
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Scheme 1



ligands in dirhodium(II,II) complexes with metalated phosphines have also been studied earlier.¹⁴

We report here the evaluation of the electronic properties of ortho-metalated dirhodium(II,II) complexes by experimental determination of equilibrium constants for the adduct formation between the dirhodium compounds and a Lewis base that could be used to model the rhodium–carbene coordination. Calculations at the density functional theory (DFT) level have been performed to detect trends between experimental and related calculated parameters. The results obtained for compounds of the general type $\text{Rh}_2(\text{RCO}_2)_{4-n}(\text{PC})_n$, ($n = 0-2$) and a pyridine Lewis base are presented. The effect of other related bases has also been studied. The work represents a systematic search of the factors affecting the properties of the catalysts upon modification of the environment of the active site.

2. Methods and Models

2.1. Experimental Details. All of the bis-cyclometalated compounds $\text{Rh}_2(\text{RCO}_2)_2(\text{PC})_2 \cdot 2\text{RCO}_2\text{H}$ were prepared by literature methods,^{15–18} using dirhodium tetraacetate and the corresponding phosphines as starting materials. The trifluoroacetate and pivalate derivatives were prepared by an exchange reaction between the corresponding acid and the $\text{Rh}_2(\text{RCO}_2)_2(\text{PC})_2 \cdot 2\text{RCO}_2\text{H}$ compound.¹⁹ The replacement of axial carboxylic acid by water molecules was achieved by stirring an acetone solution of the acid adduct in the presence of sodium carbonate for 2 h.

The replacement of water molecules by N-donor ligands (Scheme 1) was easily followed by UV–visible spectroscopy.

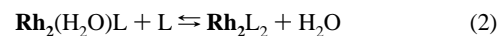
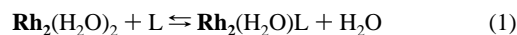
A number of solutions with the same concentration of the water adduct of the dirhodium compound ($5 \times 10^{-4} \text{ mol dm}^{-3}$) were prepared in each case. Increasing amounts of ligand were added to each of these solutions, producing ligand concentrations from 0 to $1 \times 10^{-1} \text{ mol dm}^{-3}$. In these conditions, the absorbance spectra of all of the solutions were recorded (Figure 1).

Equilibrium constants, at room temperature, for the two reactions were calculated from a best fit of the absorbance data in the range of 400–800 nm using Hyperquad 2000. All of the obtained equilibrium constants are presented in Figures 2–9. The second equilibrium constant, K_2 , was obtained by the expression $\beta_2 = K_2 K_1$, where $K_2 = \beta_2 / K_1$, and the imprecision related to this constant was

obtained by the expression $\epsilon(\log K_2) = [\epsilon(\log \beta_1)^2 + \epsilon(\log \beta_2)^2]^{1/2}$. Similarly, the change in the visible spectra of rhodium(II) tetracarboxylates, resulting from the addition of a Lewis base, has been previously used for determination of the equilibrium constants.²⁰

2.2. Computational Methods. All calculations were carried out with the *Gaussian03* program package.²¹ The DFT level with the nonlocal hybrid density functional B3PW91^{22,23} was selected for the quantum chemical studies. The basis set was comprised of a Stuttgart–Dresden effective small core potential²⁴ augmented with an extra p-polarization function for rhodium [SDD(p)] and a standard all-electron basis set 6-31G* for other atoms. The system had been found to be reliable in the previous preliminary study on the structural and electronic trends in dirhodium(II,II) compounds.¹³ Frequency analysis with no scaling was performed to ensure that the optimized stationary points located were minima.

We studied the effect of modifying the ligand core on the properties of the active site by calculating the interaction energies for a set of reactions with model bases (eqs 1 and 2) where $\text{Rh}_2 =$



$\text{Rh}_2(\text{RCO}_2)_2(\text{PC})_2$. In the calculated compounds, various R groups in the carboxylates as well as different X groups in the phosphine rings were utilized (see Scheme 1). Also the effect of changing the axial ligand L was considered. The modifications were chosen to represent different electronic environments of the active rhodium sites.

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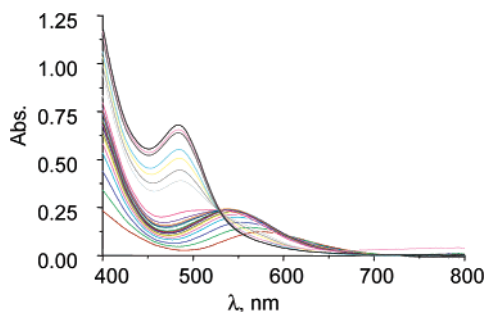


Figure 1. Absorbance spectra for different solutions of $Rh_2(CH_3CO_2)_2-(PC)_2 \cdot 2H_2O$ (5×10^{-4} mol dm^{-3}) with different quantities of 3-COMepy. All of the solutions were prepared in $CHCl_3$ at room temperature.

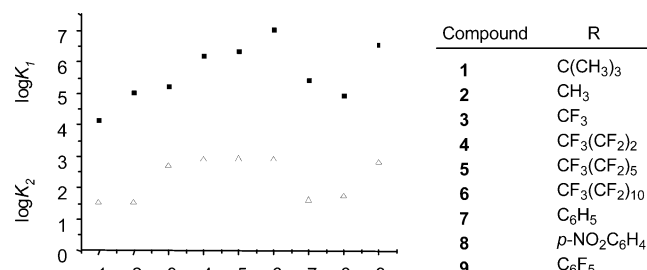


Figure 2. $\log K_1$ and $\log K_2$ values for the $Rh_2(RCO_2)_2[(C_6H_4)PPh_2]_2-(H_2O)_2$ complexes with different R groups.

3. Results and Discussion

Two different equilibrium constants, K_1 and K_2 , have been determined (Scheme 1). For synthetic convenience, symmetric phosphines, $P(p\text{-XC}_6\text{H}_4)_3$ ($X = H, CH_3, OCH_3, F, CF_3$), were mainly used. A few compounds with $P(m\text{-XC}_6\text{H}_4)_3$ ($X = CH_3, CF_3$) were also studied. In the latter cases, the phosphines are known to react with activation of the C–H bond *para* to the substituent.²⁵

The relative difference between the stability of the compounds was examined by measuring the equilibrium constants (Figures 2–9) for the model reactions presented in eqs 1 and 2. In order to compare the influence of the metalated phosphine as a ligand, selected tetracarboxylates were also studied.

3.1. Bis-cyclometalated Dirhodium Compounds. 3.1.1. Modification of the Carboxylate. It has been observed that a change in the carboxylate group (R in Scheme 1) in compounds of the formula $Rh_2(RCO_2)_2(PC)_2$ has an important influence on their catalytic properties.¹ Therefore, at the first stage, we studied the effect of different carboxylate groups on the formation of pyridine adducts (Figure 2 and Table 1).

Figure 2 represents the logarithm of the equilibrium constants K_1 and K_2 for the different $Rh_2(RCO_2)_2[(C_6H_4)PPh_2]_2$ compounds (for complete tables, see the Supporting Information).

The first observation from the data included in Figure 2 is that K_1 is always 2–4 orders of magnitude larger than K_2 . In these compounds, both axial positions are equivalent. For this reason, the difference in the K_1 and K_2 values cannot be explained attending to steric effects. Instead, this fact

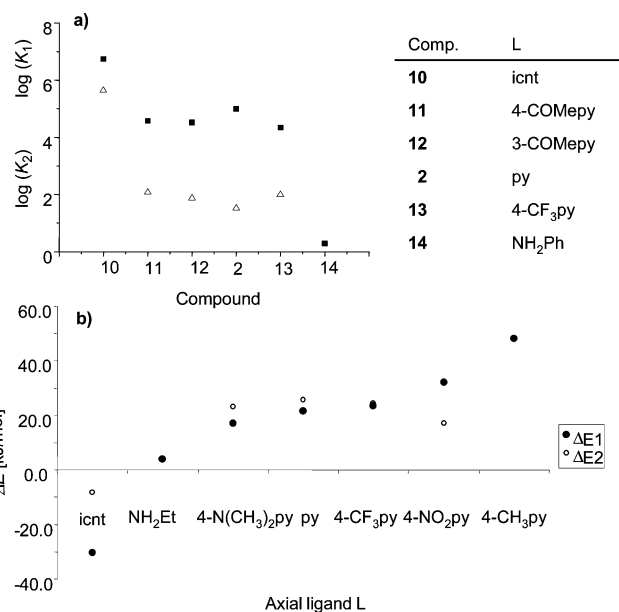


Figure 3. (a) $\log K_1$ and $\log K_2$ for different axial ligand adducts with the complex $Rh_2(CH_3CO_2)_2[(C_6H_4)PPh_2]_2-(H_2O)_2$. (b) Computational reaction energies for the $Rh_2(CH_3CO_2)_2[(C_6H_4)P(CH_3)_2]_2-(H_2O)_2$ complex.

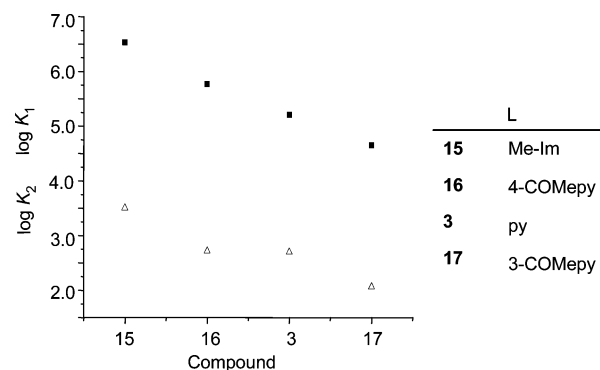


Figure 4. $\log K_1$ and $\log K_2$ for different axial ligand adducts with $Rh_2(CF_3CO_2)_2[(C_6H_4)PPh_2]_2-(H_2O)_2$ complexes. py = pyridine; Me-Im = *N*-methylimidazole, 3-MeCOPy = 3-acetylpyridine; 4-MeCOPy = 4-acetylpyridine, 4-CF₃py = 4-(trifluoromethyl)pyridine.

indicates that the electronic effects are transmitted via the Rh–Rh metal bond and the coordination of one pyridine at one metal center considerably decreases the coordinating ability of the second pyridine. Similar weakening of the second coordination via an axial *trans* effect has been suggested for the rhodium tetracarboxylate compounds.²⁶

We have separated the data for aliphatic (1–6) and aromatic (7–9) carboxylate groups. In the first block, we observe roughly increasing K_1 and K_2 values when electron-withdrawing substituents are attached to the carboxylate groups. However, the K_2 values follow two separate trends: electron donor by one side and withdrawing groups by the other. The same tendency could not be observed for the compounds with aromatic carboxylates; introducing a withdrawing substituent in the aromatic ring produced a slight decrease in the K_1 value ($8 < 7$). On the other hand, in agreement with the above-mentioned *trans* effect, the trend in the K_2 value is the opposite ($8 > 7$). The K_1 and K_2 values

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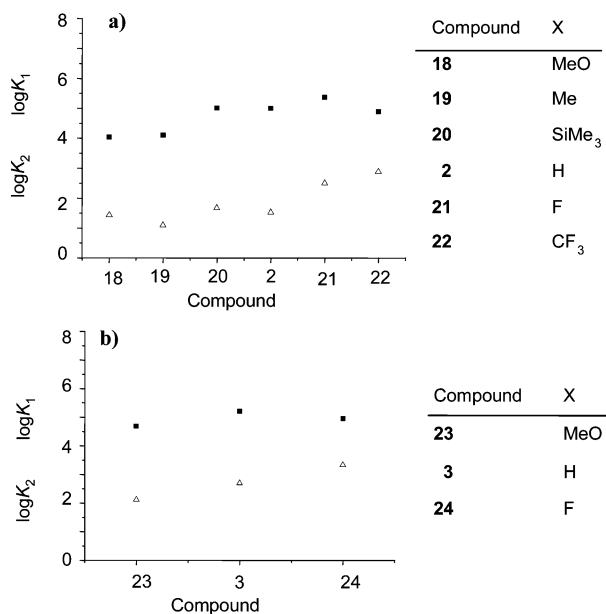


Figure 5. (a) $\log K_1$ and $\log K_2$ values for the para substitution of the phenyl rings in $\text{Rh}_2(\text{CH}_3\text{CO}_2)_2[(p\text{-XC}_6\text{H}_3)\text{P}(p\text{-XC}_6\text{H}_4)_2](\text{H}_2\text{O})_2$ complexes with pyridine as an incoming ligand. (b) $\log K_1$ and $\log K_2$ values for the para substitution of the phenyl rings in $\text{Rh}_2(\text{CF}_3\text{CO}_2)_2[(p\text{-XC}_6\text{H}_3)\text{P}(p\text{-XC}_6\text{H}_4)_2](\text{H}_2\text{O})_2$ complexes.

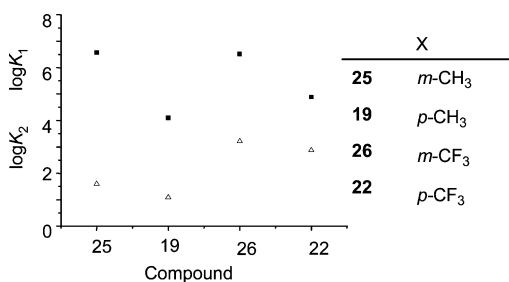


Figure 6. $\log K_1$ and $\log K_2$ values for the meta- and para-substituted phosphines in the $\text{Rh}_2(\text{CH}_3\text{CO}_2)_2[(\text{XC}_6\text{H}_3)\text{P}(\text{XC}_6\text{H}_4)_2](\text{H}_2\text{O})_2$ complexes.

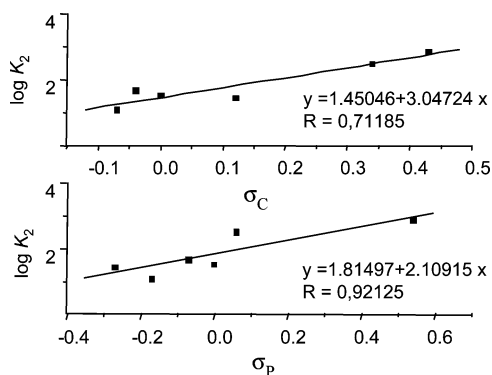


Figure 7. Hammett correlation analysis for the equilibrium constant K_2 according to the substitution site of the metalated ring in selected bis-cyclometalated compounds.

obtained for compound **9** are slightly different from those of the other compounds with aromatic rings in the carboxylate. This fact can be explained by the different structure of this compound related to the other aromatic carboxylate compounds. Because aromatic rings are more polarizable than aliphatic moieties, the aromatic rings can overlap through the π system with the metal centers. In this way, the orbital of the metal center and the carboxylate can interact

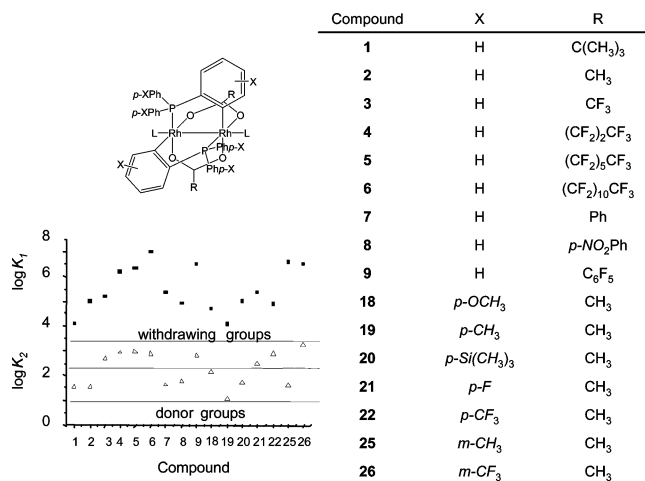


Figure 8. Comparison of the experimental $\log K_1$ and $\log K_2$ values for the bis-metalated $\text{Rh}_2(\text{RCO}_2)_2[(p\text{-XC}_6\text{H}_3)\text{P}(p\text{-XC}_6\text{H}_4)_2]$ compounds.

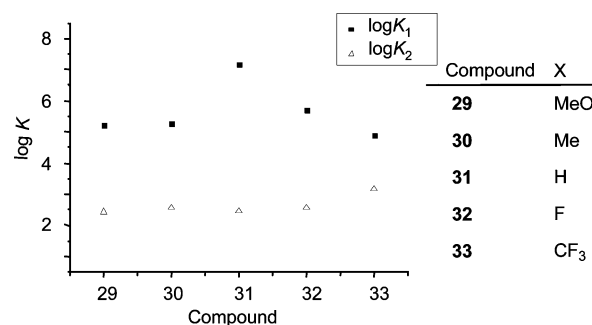
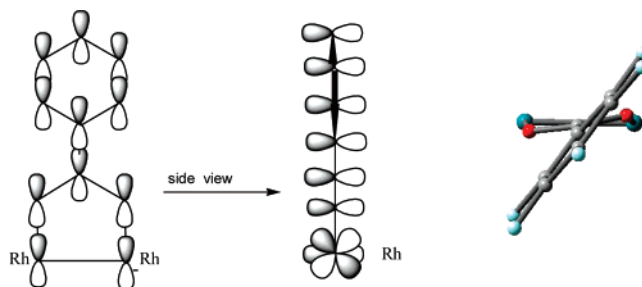


Figure 9. Experimental $\log K_1$ and $\log K_2$ values for selected mono-metalated dirhodium(II,II) compounds.

if they are in the same plane²⁷ (see below). However, when $\text{R} = \text{C}_6\text{F}_5\text{COO}$, the situation changes because the C_6F_5 ring and the carboxylate group are in a different plane, and thus an effective overlap is not possible. This affirmation is supported by the X-ray and ¹⁹F NMR information obtained for this compound²⁸ and also by computationally optimized geometries, where the fluorobenzene group was twisted by 42° from the plane of the carboxylate group (see below), in contrast to C_6H_5 , which was effectively planar with the carboxylate.



Trends very similar to those for the equilibrium constants can be found in the computational reaction energies (Table 1). Two main observations can be seen: the required energy for the first replacement reaction, ΔE_1 , is always smaller than ΔE_2 , and substituting carboxylates with more electron-

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Table 1. Computational Reaction Energies and Gibbs Free Energy Values for Pyridine Adducts with Selected Dirhodium(II,II) Complexes $Rh_2(RCO_2)_2[(C_6H_4)PPh_2]_2(H_2O)_2$

compd	R	ΔE_1 [kJ mol ⁻¹]	ΔE_2 [kJ mol ⁻¹]	$\Delta G_{1(298\text{ K})}$ [kJ mol ⁻¹]	$\Delta G_{2(298\text{ K})}$ [kJ mol ⁻¹]
1	C(CH ₃) ₃	26.6	31.9	31.4	43.9
2	CH ₃	21.1	28.4	31.1	40.8
3	CF ₃	15.9	18.7	26.3	31.7
7	Ph	21.5	24.7	29.0	35.6
8	<i>p</i> -NO ₂ Ph	14.4	20.0	28.1	
9	C ₆ F ₅	18.0	23.7	30.8	

Table 2. Computational Reaction Energies for Different Axial Ligand Adducts with the Complex $Rh_2(CH_3CO_2)_2[(C_6H_4)PPh_2]_2(H_2O)_2^a$

compd	L	ΔE_1 [kJ mol ⁻¹]	ΔE_2 [kJ mol ⁻¹]	$\Delta G_{1(298\text{ K})}$ [kJ mol ⁻¹]	$\Delta G_{2(298\text{ K})}$ [kJ mol ⁻¹]
10	icnt	-30.8	-9.3	-23.6	-3.3
11	4-MeCOpy	22.1	26.3	28.4	37.6
2	py	21.1	28.4	31.2	40.8
13	4-CF ₃ py	22.7	26.5	28.1	32.8

^a py = pyridine; icnt = *tert*-butylisocyanide; 4-MeCOpy = 4-acetylpyridine, 4-CF₃py = 4-(trifluoromethyl)pyridine.

withdrawing groups enhances the strength of the interaction at the axial site. Similar to the equilibrium constants, the latter effect is most clearly seen with the aliphatic carboxylates, where this is true for both reactions. Within aromatic rings, the preference for withdrawing groups is also more or less true, but here the steric effects make a complication, especially for the second substitution, and thus, for example, a very bulky C₆F₅ corresponds to the same amount of energy ΔE_2 as that of C₆H₅. It should be noted that the general trend is similar within the calculated Gibbs free energy values than with the relative energies even though the actual values are slightly larger.

3.1.2. Modification of the Axial Ligand. We also studied how different donor ligands coordinate the same dirhodium(II,II) compound $Rh_2(CH_3CO_2)_2[(C_6H_4)PPh_2]_2(H_2O)_2$. In addition to pyridine, we selected various ligands with different donor properties (Figure 3). Computational results for selected axial ligands are presented in Table 2.

We can observe how different axial ligands present very different values of the equilibrium constant. From these values, we can remark on the low coordinating ability of the NH₂Ph ligand compared to pyridine and substituted pyridine ligands. In fact, the NH₂Ph ligand is not able to completely form the bis-adduct even with a large excess of ligand, which is why the second equilibrium constant was not evaluated.

On the other hand, the isocyanide ligand showed the highest value for both K_1 and K_2 , compared with the other cases. These are consistent with the higher π -back-bonding ability of axial isocyanide ligands compared to other nitriles previously found in dirhodium tetracarboxylate complexes.²⁹

In addition to the DFT reaction energies presented in Table 2 for the $Rh_2(CH_3CO_2)_2[(C_6H_4)PPh_2]_2(H_2O)_2$ complex, we calculated the energies for the replacement reactions in a computationally less demanding phosphine $Rh_2(CH_3CO_2)_2-[(C_6H_4)P(CH_3)_2]_2(H_2O)_2$. This allowed us to extend the

Table 3. Computational Reaction Energies for Different Axial Ligand Adducts with $Rh_2(CH_3CO_2)_2[(p-XC_6H_3)P(p-XC_6H_4)_2]_2(H_2O)_2$ Complexes with Pyridine as an Incoming Ligand

compd	X	ΔE_1 [kJ mol ⁻¹]	ΔE_2 [kJ mol ⁻¹]
18	MeO	21.6	29.3
19	Me	22.5	30.1
20	SiMe ₃	22.8	29.4
2	H	21.1	28.4
22	CF ₃	14.5	21.1

selection of the axial ligands, which were again chosen to give information on the basic nature of the ligands. Figure 3b shows the results for the calculated reaction energies. The values for ΔE_1 and ΔE_2 are rather similar for all of the substituted pyridines as axial ligands but follow roughly the basicity of the ligands. The largest changes correspond to the isocyanide ligand, in agreement with the experimental equilibrium constants, and to 2-methylpyridine, where the relatively weaker interaction results from the steric bulk caused by the methyl group in the 2-position. Furthermore, the results show a cooperative effect that influences the relative values of the first and second equilibrium constants. Stronger interaction at the first axial site induces weaker interaction at the second one, and vice versa. It should be noted that the values for the smaller $Rh_2(CH_3CO_2)_2[(C_6H_4)P(CH_3)_2]_2(H_2O)_2$ differ only slightly from the values calculated for $Rh_2(CH_3CO_2)_2[(C_6H_4)PPh_2]_2(H_2O)_2$; thus, the conclusions are also valid for the larger phosphine.

As an extension of these studies, we have also evaluated the influence of the axial ligand on the bis-cyclometalated dirhodium(II,II) compounds $Rh_2(CF_3CO_2)_2[(C_6H_4)PPh_2]_2$. The logarithms of the equilibrium constants K_1 and K_2 are represented in Figure 4. In these compounds, a clear tendency for the K_1 and K_2 values could be observed with the character of the incoming ligand, and K values increase in the order 3-COMepy < py < 4-COMepy < Me-Im. Therefore, the constant values appear not to follow only the basicity order,³⁰ but the ability of the axial ligand to behave as a π acceptor could play an important role in the stability of the adduct. This effect is higher for the first coordination than for the second one in all of the cases.

3.2. Modification of the Phosphine. 3.2.1. Effect of the Substituent in the *Para* Position of the Aromatic Ring.

In this section, we will present the results oriented to study the influence of the metalated phosphine on the coordinating ability of the bis-cyclometalated dirhodium(II,II) compounds. We will present first the results obtained for compounds with different *para*-substituted phosphines of formula $Rh_2(CH_3CO_2)_2[(p-XC_6H_3)P(p-XC_6H_4)_2]$. The equilibrium constant values are plotted in Figure 5, and the computational reaction energies are shown in Table 3.

Only a small variation in the different X groups on the phosphine ligand was observed in values of K_1 (Figure 5a), but an increase of the K_1 and K_2 values with the withdrawing character of the X group could be known by intuition. Again,

(30) pK_b values: (a) 3-COMepy, 11.81. Bonire, J. J.; Jalil, N. S. N.; Ayoko, G. A.; Omachi, A. A. *Appl. Organomet. Chem.* **1996**, *10*, 369. (b) 4-COMepy, 10.50; py, 8.71. Steffen, W. L.; Palenik, G. J. *Inorg. Chem.* **1977**, *16*, 1119. (c) Imidazole, 7.2. Hayward, G. C.; Hill, H. A. O.; Pratt, J. M.; Williams, R. J. P. *J. Chem. Soc. A* **1971**, 196.

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Table 4. Experimental Equilibrium Constants and Computational Reaction Energies for Pyridine Adducts with Selected Dirhodium(II,II) Complexes

compd	X	R	$\log \beta_1$ ($\beta_1 = K_1$)	$\log \beta_2$	$\log K_2$	ΔE_1 [kJ mol ⁻¹]	ΔE_2 [kJ mol ⁻¹]
19	CH ₃	CH ₃	4.10 ± 0.03	5.19 ± 0.04	1.09 ± 0.05	22.5	30.1
22	CF ₃	CH ₃	4.89 ± 0.08	7.76 ± 0.08	2.87 ± 0.11	14.5	21.1
2	H	CH ₃	4.99 ± 0.03	6.52 ± 0.03	1.53 ± 0.04	21.1	28.4
3	H	CF ₃	5.207 ± 0.1	7.905 ± 0.1	2.70 ± 0.14	15.9	18.7
27^a	H	CF ₃				11.2	12.8
28^a	NO ₂	CF ₃				4.9	6.0

^a Modified phosphine: Rh₂(CF₃CO₂)₂[(*p*-XC₆H₃)P(CF₃)₂], computationally designed.

the effect is more clearly seen in the compounds of the formula Rh₂(CF₃CO₂)₂[(*p*-XC₆H₃)P(*p*-XC₆H₄)₂] (Figure 5b). If we compare the K_2 values of the CF₃CO₂ carboxylate for the analogue compounds with acetate, an increase of around 1 order of magnitude is observed. Also, computationally, the effect of *para* substitution is very small, except for the most electron-withdrawing group CF₃, which shows stronger interaction for both coordinations.

3.2.2. Effect of the Substituent in the *Meta* Position of the Aromatic Ring. Here we present the results obtained for compounds with different *meta*-substituted phosphines of formula Rh₂(CH₃CO₂)₂[(*m*-XC₆H₃)P(*m*-XC₆H₄)₂]. We can compare the results of these equilibrium constants with the K_1 and K_2 values obtained with the analogue compounds with *para*-substituted phosphines (Figure 6). In both cases, the K_1 values are larger for the *meta*-substituted phosphine complexes. This result agrees with the higher steric hindrance for the axial site promoted by the substituents in metalated *para*-substituted phosphines.

Further evidence for the larger values for the *meta*-substituted phosphine complexes was sought by calculating the energies for the corresponding mono-metalated phosphine derivatives of the type Rh₂(CH₃CO₂)₃[(*m*- or *p*-XC₆H₃)P(*m*- or *p*-XC₆H₄)₂](H₂O)₂, with X = CF₃. The energy difference between them was small, but the trend was clear; the interaction with the axial pyridine ligands entering by the side of the metalated ring was stronger for the *meta*-substituted phosphine than for the *para*-substituted one. The corresponding ΔE_1 values were -11.0 and -9.1 kJ mol⁻¹ for *meta*- and *para*-substituted compounds, respectively.

Additionally, electronic effects (Hammett σ values)³¹ for substituents at the aromatic rings on the equilibrium constants were considered. A better linear correlation was found when using σ values for substituents in its relative position to the phosphorus atom (σ_P) than to the metalated carbon atom (σ_C) (Figure 7).

3.3. Combined Effect of Introducing Electron-Withdrawing Groups in Both Phosphine and Carboxylate Ligands. In order to study the effect produced by the presence of a CF₃ group in the phosphine and carboxylate, we analyzed the equilibrium constants obtained for the reactions for pyridine adducts with the following compounds (Table 4).

While the observed values of $\log K_1$ are in a small range of units, the $\log K_2$ values are more dispersed. In both cases,

Table 5. Computational Reaction Energies for Pyridine Adducts with Selected Mono-metalated Rh₂(CH₃CO₂)₃[(*p*-XC₆H₃)P(*p*-XC₆H₄)₂] Complexes

compd	X	L	ΔE_1 [kJ mol ⁻¹]	ΔE_2 [kJ mol ⁻¹]
31	H	py	-8.1	13.8
33	CF ₃	py	-9.1	11.4

the K_1 and K_2 values increase when the CF₃ group is present. However, this increase is larger when the CF₃ group is present in the phosphine ring rather than in the carboxylate group.

Because both experimental and computational studies suggested that it would be favorable to introduce strongly electron-withdrawing groups in both phosphine and carboxylate groups in the dirhodium(II,II) compounds of the type Rh₂(RCO₂)₂[(*p*-XC₆H₃)PR'₂], we used DFT methods to design a compound in which both requirements would be fulfilled. In this compound, we used CF₃ groups directly in the phosphine, thus giving a formula Rh₂(CF₃CO₂)₂[(*p*-XC₆H₃)P(CF₃)₂]. The results for the reaction energies for pyridine adducts are presented in Table 5. As expected, the CF₃ groups bonding directly to phosphorus decrease the required energy and strengthen the interaction with the axial pyridine. The interaction is further enhanced by introducing very strongly electron-withdrawing NO₂ substituents in the metalated phosphine ring (compound **28**).

3.4. Comparative Results for the Bis-cyclometalated Compounds. Finally, in Figure 8, we plot $\log K_1$ (■) and $\log K_2$ (Δ) for pyridine adducts of all of the studied bis-metalated compounds containing substituents either in the carboxylate or the phosphine. While the values for $\log K_1$ seem to show a trend with the character of the substituent, the values for $\log K_2$ are segregated into two groups, a lower group with a value close to 2, including most of the compounds containing electron-donating substituents, and a second group with values larger than 2, including compounds with electron-withdrawing groups. The values are larger for compounds with electron-withdrawing groups independently of where these groups are located, in the carboxylate or in the phosphine.

3.5. Mono-cyclometalated Compounds. The effect of modifying the phosphine ligands in mono-cyclometalated compounds was also studied. The observed equilibrium constants are represented in Figure 9.

Considering that the size of the substituents at the metalated ring would affect the reaction equilibria, the equilibrium constants were subjected to correlation analysis with the steric effects (E_s),³² which can provoke the substituents at the coordinating position. The best correlation

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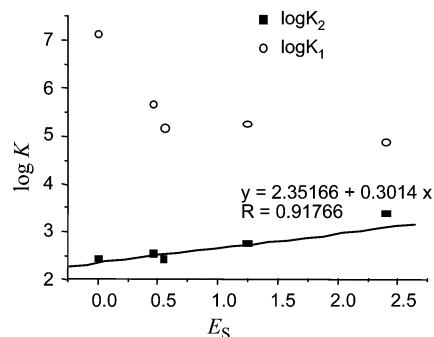


Figure 10. Correlation analysis between the experimental $\log K_1$ and $\log K_2$ values and the steric effects (E_s) for selected mono-metallated dirhodium-(II,II) compounds.

was obtained when considering, according to the previously found preferred coordination site,³³ that the axial ligand first coordinates to the rhodium atom attached to the metallated ring [see Figure 10; steric effect values E_s are -0.55 (m -OCH₃), -1.24 (m -CH₃), 0 (H), -0.46 (m -F), and -2.40 (m -CF₃)]. From the analysis, a decrease on K_1 with steric crowding was accompanied by an increase of the K_2 values. A lower value of K_1 would favor the second coordination (due to a smaller *trans* effect in the Rh–Rh bond).

3.6. Tetracarboxylates. We compared the results obtained for the cyclometalated compounds with the results for $Rh_2(RCO_2)_4$, where $R = C(CH_3)_3$ and CF_3 . Two different ligands were used for the reactions, pyridine (py) and *tert*-butylisocyanide (icnt) (Table 6).

The isocyanide ligand gives considerably higher values of the constants and also larger interaction energies, as was already observed for the bis-cyclometalated rhodium compound $Rh_2(CH_3CO_2)_2[(C_6H_4)PPh_2]_2$. The K_1 values are comparatively similar to those obtained for the mono- and bis-metallated compounds with the same incoming ligand. More important differences are observed for the K_2 values.

Comparing the K_1 values for the compounds with different carboxylates [$R = CF_3$, $C(CH_3)_3$], we could observe that introducing a donor ligand in the carboxylate produces an increase of the value by 2 orders of magnitude (Table 6). The opposite trend was observed for the rhodium phosphine compound $Rh_2(RCO_2)_2[(C_6H_4)PPh_2]_2$. However, computationally the trend is the same for the tetracarboxylate compounds and for the phosphine derivatives; introducing electron-withdrawing groups in the carboxylate enhances the strength of the interaction.

3.7. Computational Natural Population Analysis (NPA) Charges. To acquire more information on the electron-transfer properties of the ligand core, we calculated the NPA charges³⁴ of the active rhodium atoms in selected bis-metallated phosphines and compared the values with those for dirhodium tetracarboxylate. The results are shown in Table 7.

A very similar trend is found in all of the calculated dirhodium(II,II) compounds. Upon replacement of the first

axial water ligand with pyridine, the positive charge of the first rhodium atom (Rh1) increases and the charge of the opposite rhodium decreases. Therefore, as was previously found in the study of the $Rh_2(O_2CCH_3)_4$ catalyst,^{11,35} the second rhodium acts as a “storage” of electron density. The fact that Rh2 accepts the electron density makes it less electrophilic, and thus the second replacement reaction is not as favorable as the first one. A comparison of the change in the rhodium charge upon the first ligand replacement for bis-cyclometalated compounds and dirhodium tetracarboxylate shows a much higher increase of the positive charge of Rh1 for the phosphine compounds, in spite of their similar decrease of charge at Rh2. This could be an indication of a higher ability of the bis-cyclometalated compounds for back-donation from Rh1 to the ligand and would be in agreement with selectivity results previously found.^{1,7,36}

Upon the second replacement, the electron density flows back to Rh1, and with the bis-metallated phosphine complexes, the net change in charge is minimal. However, in the dirhodium tetracarboxylate, Rh1 has more electron density than it has initially.

The only exception from the general trend shown by the bis-cyclometalated compounds is obtained when the axial ligand is changed to a very strongly electron-donating compound, such as *tert*-butylisocyanide. Also, in this case, there is a charge-transfer effect along the axial core to the second rhodium atom, whose positive charge reduces considerably. The donation from the axial icnt ligand is so strong that also the charge of the first rhodium is reduced. Furthermore, unlike the pyridine ligands, the second icnt ligand does not balance the charge back to the original values; instead, the resulting rhodium charge is much less positive than that with the water ligands. The strong electron transfer is reflected in the much larger interaction energies of the adduct formation.

4. Conclusions

Properties of $Rh_2(RCO_2)_{4-n}(PC)_n$ chiral dirhodium catalysts with different *ortho*-metallated aryl phosphine and carboxylate ligands have been evaluated by determining the equilibrium constants (K_1 and K_2) and computational interaction energies (ΔE_1 and ΔE_2) for their mono-adduct and bis-adduct with Lewis bases. The main aim in the current work was to systematically modify the ligand core of the $Rh_2(RCO_2)_{4-n}(PC)_n$ catalysts ($n = 0-2$) in order to find structural and electronic trends in the reactions with different basic axial ligands. The results obtained are collected in Figures 2–9 and Tables 1–6.

Concerning the equilibrium constants, statistical consideration for noninteracting metal centers would lead to $K_1 = 4K_2$ if the metal centers were uncoupled.²⁰ In the currently studied dinuclear rhodium compounds $Rh_2(RCO_2)_{4-n}(PC)_n$ ($n = 0-2$), the observed ratio is considerably larger (Tables S1–S8; see the Supporting Information). We can explain

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Table 6. Experimental Equilibrium Constants and Computational Reaction Energies for Different Axial Ligand Adducts with Dirhodium(II,II) Tetracarboxylate

compd	R	L	$\log \beta_1$ ($\beta_1 = K_1$)	$\log \beta_2$	$\log K_2$	ΔE_1 [kJ mol ⁻¹]	ΔE_2 [kJ mol ⁻¹]
34	C(CH ₃) ₃	py	6.49 ± 0.04	9.38 ± 0.05	2.8888 ± 0.06	-12.5	-7.1
35	CF ₃	py	4.57 ± 0.08	7.63 ± 0.09	3.06 ± 0.12	-26.9	-19.8
36	CF ₃	icnt	7.14 ± 0.1	11.52 ± 0.1	4.38 ± 0.14	-44.4	-35.4

Table 7. NPA Charge of the Active Rhodium Atoms for Different Bis-metalated Rh₂(RCO₂)₂[(*p*-XC₆H₃)P(*p*-XC₆H₄)₂]₂L₂ Complexes^a

compd	R	X	L	2(H ₂ O)	(H ₂ O)L	2L	$\Delta q(1)$	$\Delta q(2)$
				<i>q</i> (Rh1)				
Rh ₂ (O ₂ CR) ₄	CH ₃		Py	0.827	0.845	0.805	0.018	-0.040
1	C(CH ₃) ₃	H	Py	0.341	0.377	0.336	0.036	-0.041
2	CH ₃	H	Py	0.340	0.374	0.336	0.034	-0.039
3	CF ₃	H	Py	0.324	0.352	0.315	0.028	-0.037
7	Ph	H	Py	0.341	0.374	0.336	0.033	-0.038
8	<i>p</i> -NO ₂ Ph	H	Py	0.337	0.367	0.330	0.030	-0.037
9	C ₆ F ₅	H	Py	0.332	0.360	0.324	0.028	-0.036
18	CH ₃	OCH ₃	Py	0.336	0.373	0.333	0.037	-0.041
19	CH ₃	CH ₃	Py	0.339	0.374	0.336	0.035	-0.038
20	CH ₃	Si(CH ₃) ₃	Py	0.339	0.373	0.335	0.034	-0.038
22	CH ₃	CF ₃	Py	0.346	0.375	0.341	0.029	-0.034
27 ^b	CH ₃	H	Py	0.322	0.345	0.317	0.023	-0.029
28 ^b	CH ₃	NO ₂	Py	0.329	0.349	0.323	0.020	-0.026
10	CH ₃	H	icnt	0.340	0.316	0.242	-0.024	-0.074
11	CH ₃	H	4-CH ₃ COPY	0.340	0.373	0.337	0.033	-0.036
				<i>q</i> (Rh2)				
Rh ₂ (O ₂ CR) ₄	CH ₃		Py	0.826	0.778	0.805	-0.048	0.027
1	C(CH ₃) ₃	H	Py	0.341	0.286	0.336	-0.055	0.050
2	CH ₃	H	Py	0.340	0.291	0.336	-0.049	0.044
3	CF ₃	H	Py	0.324	0.279	0.315	-0.045	0.036
7	Ph	H	Py	0.341	0.294	0.336	-0.047	0.042
8	<i>p</i> -NO ₂ Ph	H	Py	0.337	0.291	0.330	-0.046	0.039
9	C ₆ F ₅	H	Py	0.332	0.287	0.324	-0.045	0.037
18	CH ₃	OCH ₃	Py	0.336	0.285	0.333	-0.051	0.048
19	CH ₃	CH ₃	Py	0.339	0.290	0.336	-0.049	0.046
20	CH ₃	Si(CH ₃) ₃	Py	0.339	0.290	0.335	-0.049	0.045
22	CH ₃	CF ₃	Py	0.345	0.303	0.340	-0.042	0.037
27 ^b	CH ₃	H	Py	0.322	0.290	0.317	-0.037	0.026
28 ^b	CH ₃	NO ₂	Py	0.329	0.300	0.323	-0.029	0.022
10	CH ₃	H	icnt	0.340	0.224	0.242	-0.116	0.018
11	CH ₃	H	4-CH ₃ COPY	0.340	0.294	0.337	-0.046	0.043

^a $\Delta q(1)$ and $\Delta q(2)$ represent the change in the charge upon the first and second axial ligand replacement, respectively. ^b Modified phosphine: Rh₂(CF₃CO₂)₂[(*p*-XC₆H₃)P(CF₃)₂], computationally designed.

this fact by considering the inductive effect of base coordination, which is effectively transferred through the metal–metal bond to weaken the Lewis acidity of the second center. The same trend can be obtained by comparing the charge distribution of the active rhodium atoms; upon coordination of the first axial base, the electron density flows to the second active site, thus reducing its ability to coordinate to the second axial ligand. A less important effect, when $n = 2$, can be seen from the experimental equilibrium constants for the axial *tert*-butylisocyanide ligand (Figure 3). In this case, both constants are very similar (the ratio K_1/K_2 is only 1.27×10^1), producing a smaller ratio than in the other cases. Also, computationally, there is a strong net electron transfer from both of the axial ligands to both of the rhodium atoms, which increases the strength of the interaction. When the incoming ligand is NH₂Ph, the K_2 value is not calculated. The reason is the weak coordination ability of the ligand, which effectively prevents the second coordination.

The metal–metal interaction in the rhodium dimer seems to concentrate an important amount of π electron density in the metal–axial ligand bonding region, as has been observed with the tetracarboxylate compounds.³⁷ This phenomenon is similar to the *trans* effect, but in this case, the *trans* ligand

is the other rhodium. With an increase in the basicity or the π -donating ability of the axial ligands, the interaction with the active rhodium sites is further enhanced (Figures 3 and 4).

A comparison of the change in the rhodium charge upon the first ligand replacement for bis-cyclometalated compounds and dirhodium tetracarboxylate agrees with a higher ability of the bis-cyclometalated compounds for back-donation from Rh1 to the ligand and would be in agreement with selectivity results previously found. Computational reaction energies support the observations, thus providing the possibility for a “quick search” among the different modifications and their effect on the properties of the active sites.

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Supporting Information Available: Tables S1–S8 including experimental values of equilibrium constants and computational reaction energies for the acid–base reactions of Rh₂(RCO₂)₂(PC)₂-(H₂O)₂ catalysts (PC = cyclometalated aryl phosphine). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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