

Isomerization Processes on Mixed Ortho-Metalated Phosphine/Succinimidato $[\text{Rh}_2(\text{P}(\text{C}_5\text{CH}_4)\text{Ph}_2)_2(\text{OC}_4\text{NH}_4\text{O})_2]$ Complexes. A Sliding Movement of the Succinimidato Ligand

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An improved preparation of mixed ortho-metalated phosphine/succinimidato dirhodium(II) complexes, $[\text{Rh}_2(\text{P}(\text{C}_5\text{CH}_4)\text{Ph}_2)_2(\text{OC}_4\text{NH}_4\text{O})_2]$, allowed the isolation and characterization of a new isomeric form having both imidato N donors trans to P, **1'**, that adds up to the two already known having both, **1**, or only one, **2**, of the imidato N donors trans to the metalated C (Chart 3). The new complex, **1'**, isomerizes to the thermodynamically stable complex **2** similarly to what had already been observed for isomer **1**. Stoichiometric and kineticomechanistic studies of both isomerization processes have been carried out. The reactions have been shown to occur via an intramolecular dissociatively activated process, despite the involvement of the labile axial Rh_2 coordination sites in the formation of intermolecular adducts in solution that do not affect the processes. Density functional theory calculations show two transition states with similar energies for the isomerizations, in very good agreement with the kineticomechanistic measurements. The calculation of the charge generation in the two distinct transition states, **TS1** and **TS1'**, indicates an important increase in the N negative charge from the reactants, more pronounced for **TS1'**. This fact agrees very well with the acceleration observed for the processes in polar solvents, especially for the **1'** to **2** reaction, when compared that for the reactions carried out in toluene.

Introduction

As an extension of our previous studies on bis-cyclometalated complexes of general formula $[\text{Rh}_2(\text{PC})_2(\text{O}_2\text{CR})_2]$ (PC = ortho-metalated triarylphosphine),^{1–3} including a kineticomechanistic interpretation of the processes.^{4–7} We explored the replacement of the carboxylates by succinimi-

date groups,⁸ which were expected to act as O,N donor ligands, with a dangling noncoordinated O atom oriented toward the axial sites of the Rh_2 unit (Chart 1). The aim was to study the effect of possible modifications in the selectivity of the catalysts derived from these compounds by the presence of the above-mentioned dangling O group, given the fact that these $[\text{Rh}_2(\text{PC})_2(\text{O}_2\text{CR})_2]$ compounds have inherent backbone chirality. It is expected that, as described for 1-methyluracilato complexes,^{10,11} deprotonation of the N atom increases the electron density at the exocyclic O. The favorable electron density, as well as the geometry in the

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Chart 1

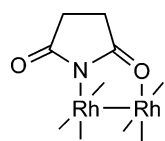


Chart 2

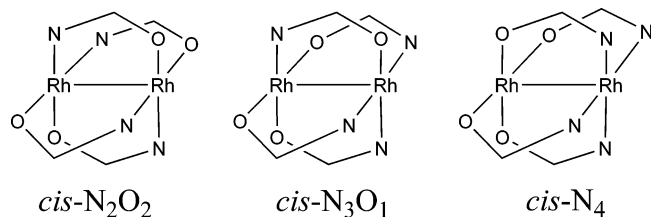
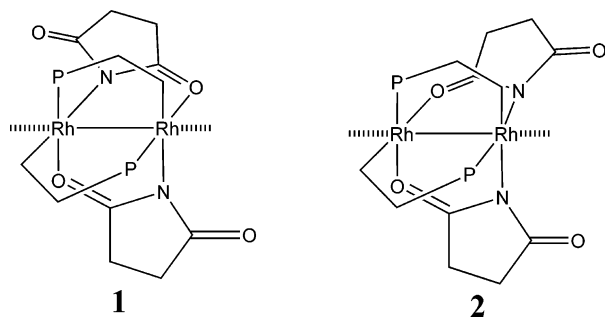


Chart 3



complexes, should enable the interaction with a possible reactive intermediate complex containing a carbene axially coordinated to the Rh₂ unit.

Interestingly, because of the unsymmetric character of the amidate ligand, the resulting [Rh₂(O,N)₄] units are frequently obtained as a mixture of isomers (Chart 2).¹² Chemical evolution between isomers has been observed after long thermal treatment of these mixtures, finally producing isomer *cis*-N₂O₂ as the major product in solution. Several [Rh₂(O,N)₄] complexes have been structurally characterized, but no kinetic study on this particular isomerization process has been reported.

Substitution of the carboxylate groups in the above-mentioned [Rh₂(PC)₂(O₂CR)₂] complexes leads to the formation of two fairly inert isomeric compounds having two succinimidato bridges plus the two cyclometalated phosphine ligands. Two [Rh₂(PC)₂(C₄H₄NO₂)₂] species have been isolated and structurally characterized. Chart 3 indicates the simplified structures showing only the backbone of the bridging phosphine ligand.⁹ Isomeric form **1** has the two succinimidate groups symmetrically located with the N atoms trans to C, while form **2** contains both O,N ligands, with the uncoordinated O atom oriented toward the same axial site.

Given the fact that kinetic/mechanistic studies on isomerizations of dinuclear compounds of this type have not been reported and that isomer **1** in solution rearranges to form isomer **2**, we decided to explore the solution chemistry and mechanistic aspects involved in this process. The process can occur via an inter- or intramolecular fashion; the latter

process could be of interest because it involves the movement of two donors of the chelating ligand. Very few studies of this type are available, and they are generally related to a non-metal–metal-bonded Pd or Pt dinuclear center.^{13,14}

We present here (i) an improved synthetic method for the preparation of compounds **1** and **2**, (ii) the preparation of an additional isomer **1'**, also showing a symmetrical structure that rapidly rearranges to form isomer **2**, and (iii) the kinetic study of the transformation of isomeric forms **1** and **1'** to **2**. Scheme 1 shows the simplified different isomeric forms indicated.

Results

Compounds. Modifications to the initial reported methods for the preparation of [Rh₂(P(C₅CH₄)Ph₂)₂(OC₄NH₄O)₂] in the two known isomeric forms **1** and **2** are already available. Isomer **2** had been conveniently prepared quantitatively by thermal exchange of the acetate groups by succinimidate anions in [Rh₂(P(C₅CH₄)Ph₂)₂(O₂CCH₃)₂].⁹ Given the fact that isomer **1** is always obtained together with a similar amount of **2**, we explored the direct reaction of [Rh₂(P(C₅CH₄)Ph₂)₂(O₂CCH₃)₂] in a chloroform solution with a mixture of succinimide/KOH (1:1 in methanol). After the solution was stirred for 5 min at room temperature, it was analyzed by ³¹P NMR spectroscopy. Surprisingly, in addition to isomers **1** and **2**, a new species was also detected in solution, **1'**, showing a single P resonance at 18.6 ppm (*J*_{Rh–P} = 144 Hz). The three isomers are present approximately in a ratio of **1:2:1'** = 2:1:1. Changes neither in temperature nor in the amount of ligand significantly changed the resulting product distribution. From the relatively low value for the Rh–P coupling constant, we conclude that this new isomer of [Rh₂(P(C₅CH₄)Ph₂)₂(OC₄NH₄O)₂] must contain the two succinimidate ligands bridging symmetrically the binuclear Rh unit, with the N trans to P of the metalated phosphine, rather than to C, as in isomer **1**.¹⁵ When the same preparative process was carried out from complex [Rh₂(P(C₅CH₄)Ph₂)₂(O₂CCF₃)₂], having more labile CF₃COO[–] ligands, only isomers **1** and **1'** were formed in a 4:1 ratio. No other resonances with significant intensity were observed in the spectrum of the reaction mixture. Although subsequent workup allowed the isolation of pure isomer **1**, all efforts to isolate pure isomer **1'** failed. ³¹P NMR monitoring of the mixture indicated that compound **1'** in solution isomerizes to form **2** during workup at a much faster rate than the process producing **2** from **1**. Given the fact that the reaction rates observed for the isomerization of compounds **1** and **1'** are very different and allow for an independent kinetic treatment (see the following sections), no further attempts to isolate **1'** were pursued.

Solution Behavior. To establish their relative stability, the time evolution of toluene solutions containing mixtures of complexes **1** and **1'** was monitored by ³¹P NMR

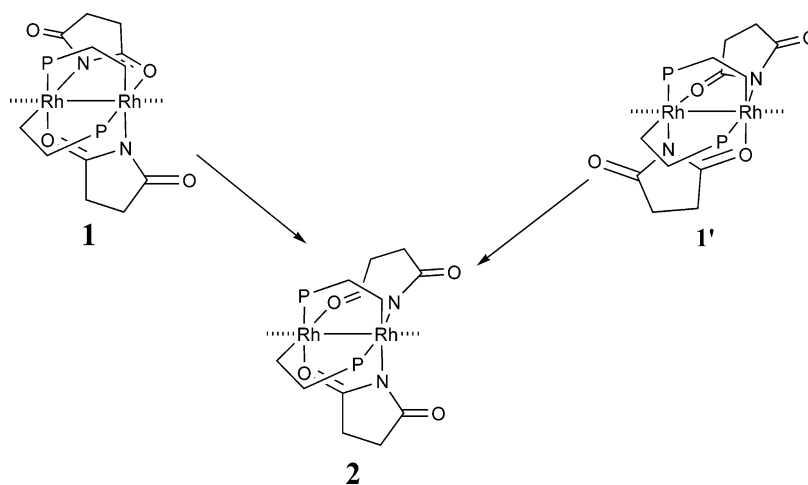
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Scheme 1



spectroscopy. At room-temperature complex **1'** evolves completely to **2** in a period of 30–40 h, as indicated by the disappearance of the corresponding resonance at 18.6 ppm ($J_{\text{RhP}} = 144$ Hz) in the ^{31}P NMR spectrum. Under these conditions, complex **1** does not evolve significantly. The resonance at 23.9 ppm ($J_{\text{RhP}} = 164$ Hz), corresponding to complex **1**, only shows a significant decrease in intensity upon heating of the system at 70 °C. Appearance of the subsequent two signals corresponding to the unsymmetrical complex **2** takes place during a period of ca. 3–4 h under these conditions. During both processes, no other signals were observed in the ^{31}P NMR spectrum, indicating that no intermediate species can be detected during the isomerization of both complexes **1** and **1'**. These reactivity patterns were observed independently of the concentration of the species present and the presence of free succinimide (a common compound present in the reaction mixture) in the reaction medium.

Monitoring of the reactions in UV–vis cells via electronic spectroscopy produced similar results. Surprisingly, though, the spectra of the different species in toluene solution did not follow Lambert–Beer's law; the electronic spectral characteristics were found to be dependent on the concentration. Figure 1 collects the changes observed on dilution of a toluene solution of complex **1**; similar changes were observed for solutions containing complexes **1'** and **2**. The greenish dilute samples of the complexes show a spectrum with a peak at ca. 600 nm, while the absorption of the concentrated samples is shifted toward the red, having only a single maximum at 535 nm. The same hypsochromic shift is observed in dilute solutions when succinimide is present in solution. These shifts are in good agreement with those observed for the complexes upon complexation to different Lewis bases through the axial Rh^{II}_2 coordinating sites.¹⁶ In this respect, the shift observed is found to be more concentration-dependent for the complexes, allowing a less strained coordination of an oxo group in the axial positions, i.e., **1'** and **2**, than for complex **1**. Quantification has not been further pursued.

Even with this variable response, the isomerization processes produced definite changes in the UV–vis spectra of the solutions. Its amplitude was found to be dependent on the presence of free succinimide and dirhodium(II) complex concentration, as shown in Figure 2. This result was expected, given the different response to concentration mentioned before. Nevertheless, joint ^{31}P NMR and UV–vis spectroscopy monitoring indicated that the processes could be checked by any of these two procedures and that the time required for the complete transformations is independent of any of the concentrations used in the experiments (see the Kinetics section).

Kinetics. Both processes leading to **2** from **1** and **1'** have been monitored kinetically by standard UV–vis spectroscopy in toluene solution. Figure 2 shows the spectroscopic changes observed during some of the isomerization processes studied. The absorbance variations at any wavelength are good first-order traces, as expected from the presence of isosbestic points during full spectrum monitoring. The values for the observed rate constants are collected in Table S1 of the Supporting Information as a function of the complexes, concentrations, and different variables used for the study. The observed rate constants are found to be independent of the concentration of the Rh_2 complex and that of the added succinimide ligand. Figure 3 shows this independence for the reaction from **1** to **2** at different temperatures. This fact is a clear indication of the intramolecular nature of the two isomerization processes, requiring a ligand dissociative process to take place.¹⁷

The dependences of the first-order rate constants with temperature and pressure were determined in the usual way.¹⁸ Figure 4 and Table 1 collect the values for ΔH^\ddagger , ΔS^\ddagger , and ΔV^\ddagger for the systems studied. The values of the activation enthalpies are large and very similar for the two systems studied, indicative of a highly dissociative activation mode. ΔS^\ddagger and ΔV^\ddagger for the **1'** → **2** process are also within the range of values expected for this sort of activation process. On

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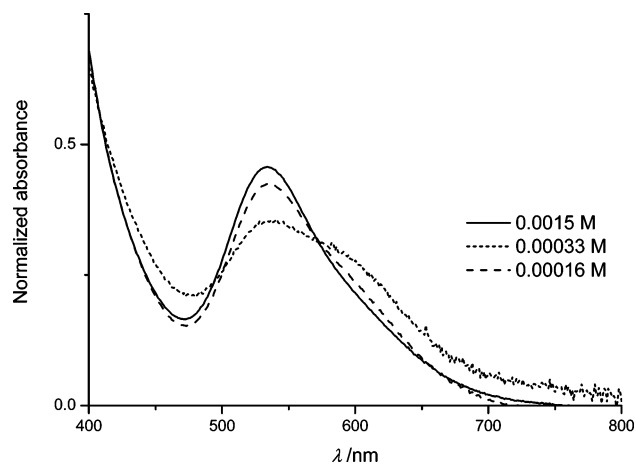


Figure 1. UV-vis spectral changes obtained upon dilution of a toluene solution of complex **1** (initial normalized $[\text{Rh}^{\text{II}}_2] = 1.5 \times 10^{-3}$ M).

the contrary, the values of the volume and entropy of activation for the $\mathbf{1} \rightarrow \mathbf{2}$ isomerization process are zero or slightly positive, in disagreement with the expected dissociative activation intramolecular process. The dramatic differences in the reaction rate constants observed have an entropic origin, related with a more important disordering expansion occurring in the $\mathbf{1}' \rightarrow \mathbf{2}$ process. The results obtained prompted us to determine the rate constants for the reaction in a more polar solvent, such as chloroform, to establish if an important degree of charge separation is occurring on going to the transition state. Effectively, the rate constants obtained in this more polar medium for the $\mathbf{1} \rightarrow \mathbf{2}$ and $\mathbf{1}' \rightarrow \mathbf{2}$ reactions were 5.5×10^{-5} and $1.1 \times 10^{-4} \text{ s}^{-1}$, at 50 and 25 °C, respectively. These values represent 2- and 4-fold accelerations for the reactions, in good agreement with important charge generation in the transition state of the isomerization processes.

Density Functional Theory (DFT) Calculations. To shed further light on the mechanisms involved in the isomerization processes, we performed computational DFT calculations of isomers **1**, **1'**, and **2**. Computationally, all of the isomers exhibited very similar energies, with isomer **1'** having the lowest energy. However, the energy difference was too small to rule out any of the options; the maximum difference between the isomers was only about 18 kJ mol⁻¹, which indicates the probable coexistence of all of the isomeric forms in the reaction mixtures. Two different transition structures (Scheme 2) were located in the reactions corresponding to the sliding movement of the two succinimidato ligands.

The first reaction path, $\mathbf{1} \rightarrow \text{TS1} \rightarrow \mathbf{2}$, corresponds to the shift of the succinimidato N from a *trans*-C to a *trans*-P position, while the second, $\mathbf{1}' \rightarrow \text{TS1}' \rightarrow \mathbf{2}$, represents the shift of the other succinimidato ligand, with the N moving from a *trans*-P to a *trans*-C position. This difference makes the movement of the two ligands unequal, and therefore two different transition states can be located. However, the calculations showed very similar activation enthalpies for the two processes.

Because the energetic considerations did not give further information on the mechanisms, we studied the charge-transfer properties of the different compounds. Figure 5

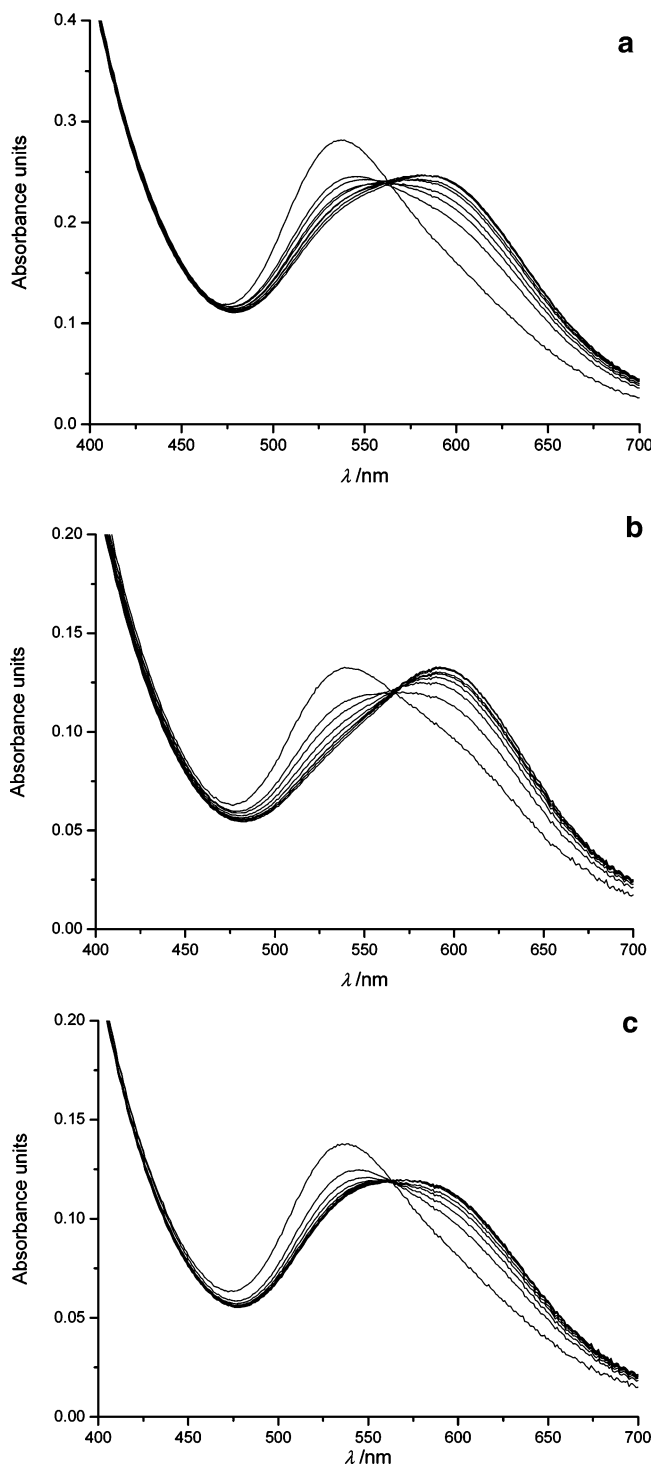


Figure 2. UV-vis spectral changes obtained upon reaction of a toluene solution of complex **1'** to produce complex **2** at 60 °C: (a) $[\text{Rh}^{\text{II}}_2] = 1.3 \times 10^{-3}$ M; (b) $[\text{Rh}^{\text{II}}_2] = 5.0 \times 10^{-4}$ M; (c) $[\text{Rh}^{\text{II}}_2] = 6.2 \times 10^{-4}$ M, $[\text{succinimide}] = 5.0 \times 10^{-3}$ M.

shows the NPA (natural population analysis) charges for selected atoms involved in the isomerization process, calculated in chloroform. During the movement of the succinimidato ligands, considerable charge transfer can be obtained, most clearly seen in the N donor (Figure 5a,b). As the N moves from the isomer **1**, or **1'**, to the transition state, the negative charge of the sliding N increases notably. When the reaction proceeds to isomer **2**, the negative charge of

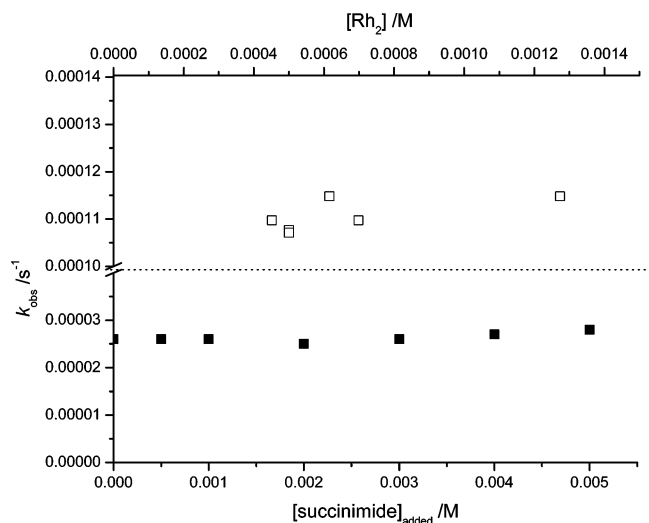


Figure 3. Plots of the changes of the values of k_{obs} for the $1 \rightarrow 2$ reaction in a toluene solution versus the concentrations of added succinimide (50 °C, ■) or the Rh^{II} starting material (60 °C, □).

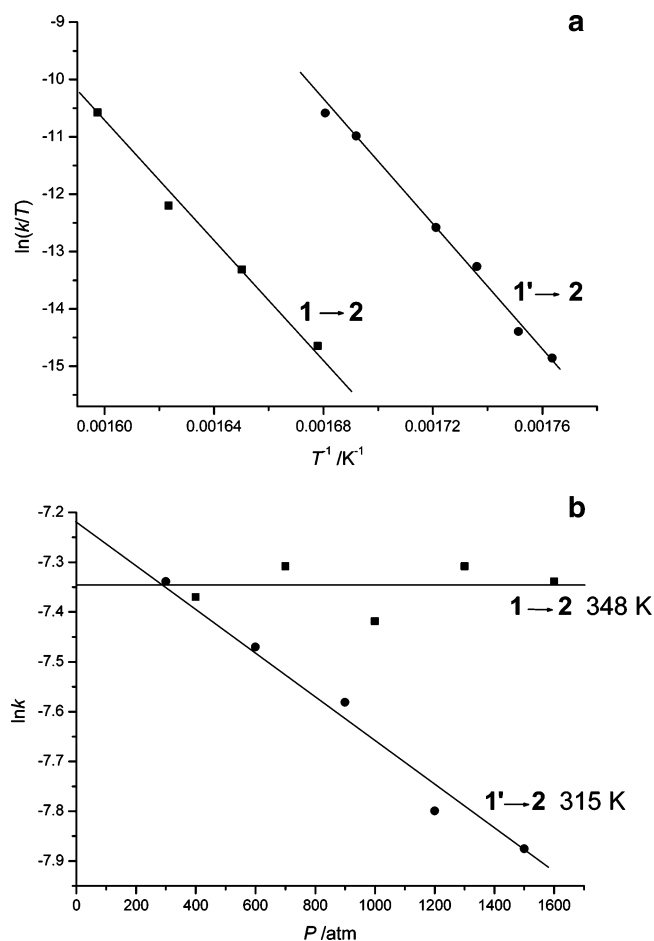


Figure 4. (a) Eyring plots for the two isomerization processes studied in toluene solution. (b) Plots of $\ln k$ versus pressure for the two processes studied.

the active N decreases again, although not to the original value given the different trans influence for the two moving succinimidates. The degree of charge transfer is larger for the transition state $\text{TS1}'$, where N moves from a *trans*-P position to a *trans*-C position, than for TS1 , where the shift is the opposite. When the transitions $\text{TS1}' \rightarrow 2$ and $\text{TS1} \rightarrow$

Table 1. First-Order Rate Constants and Activation Parameters for the Isomerization Processes Studied in Toluene Solution

reaction	$10^5 \times {}^{298}k$ s^{-1}	ΔH^\ddagger (kJ mol^{-1})	ΔS^\ddagger ($\text{J K}^{-1} \text{mol}^{-1}$)	$\Delta V^\ddagger(T)$ ($\text{cm}^3 \text{mol}^{-1}$) (K)
$1 \rightarrow 2$	0.074 ^a	120 ± 5	40 ± 20	~ 0 (348)
$1' \rightarrow 2$	3.1	125 ± 5	90 ± 10	12 ± 1 (315)

^a Extrapolated from Eyring plots.

2 are considered, a very similar net charge transfer results. Parts c and d of Figure 5 show NPA charges for the succinimidato O atoms. Here again the charge-transfer process is clear: when the O moves from a bonding (O1) to a dangling position (O2), the negative charge decreases, and vice versa. Again, the charge of the bonding O depends mostly on the nature of its trans ligand.

As for the Rh centers on the parent compound (Figure 5e,f), the whole ligand environment affects in an important way the charge of both Rh atoms. In the first transition $1 \rightarrow \text{TS1} \rightarrow 2$, the movement of the succinimidato ligand increases the positive charge of Rh1 while the charge of Rh2 is reduced. However, in the transition $1' \rightarrow \text{TS1}' \rightarrow 2$, where the succinimidato N is originally located trans to P, the larger change in the negative charge of N reduces the positive charge of Rh1 while the charge of Rh2 remains the same in the transition structure. Consequently, in the transition state $\text{TS1}'$, the charge distribution of the two Rh atoms is more symmetric and the charge-transfer process is more concentrated on the moving N atom than in TS1 .

We have also compared the effect of the isomerization on selected geometrical parameters, listed in Table 2, where the values of $\Delta H^\ddagger(298 \text{ K})$ are also collected. There is a clear trans influence from the ligand core in the bonding distances. The Rh–N distance shortens in the $1 \rightarrow 2$ process from 2.141 to 2.076 Å, while it increases from 2.065 to 2.154 Å in the $1' \rightarrow 2$ reaction. The change in the O bonding distances is also larger for the $1' \rightarrow 2$ reaction, which indicates a slightly larger overall geometrical change for this process. The Rh–Rh distance shortens similarly in both transition structures, indicating an increase in the metal–metal interaction resulting from the reduced metal–ligand interaction.

Discussion

Complexes. The syntheses of compounds 1 and 2 have been previously described.⁹ Both compounds were obtained together from the reaction of $[\text{Rh}_2(\text{P}(\text{C}_5\text{CH}_4)\text{Ph}_2)_2(\text{O}_2\text{CCH}_3)_2]$ with ClSiMe_3 , followed by the addition of succinimide/KOH (1:1) in MeOH, and were isolated by column chromatography. The modified synthetic procedure described here improves the yield of 1 and allows, as well, the observation of a new isomer $1'$. At 0 °C, the addition of succinimide/KOH (1:1) in MeOH to a solution of $[\text{Rh}_2(\text{P}(\text{C}_5\text{CH}_4)\text{Ph}_2)_2(\text{O}_2\text{CCF}_3)_2]$ in CHCl_3 provided selectively isomers 1 and $1'$ of the general formula $[\text{Rh}_2(\text{P}(\text{C}_5\text{CH}_4)\text{Ph}_2)_2(\text{OC}_4\text{NH}_4\text{O})_2]$.

Both isomers undergo chemical evolution to form 2 on standing in solution. In fact, the poor stability of $1'$ in solution prevented us from obtaining single crystals for X-ray structure determination. The structure of this isomer has been so established from the ^{31}P NMR data. Both 1 and $1'$

Scheme 2

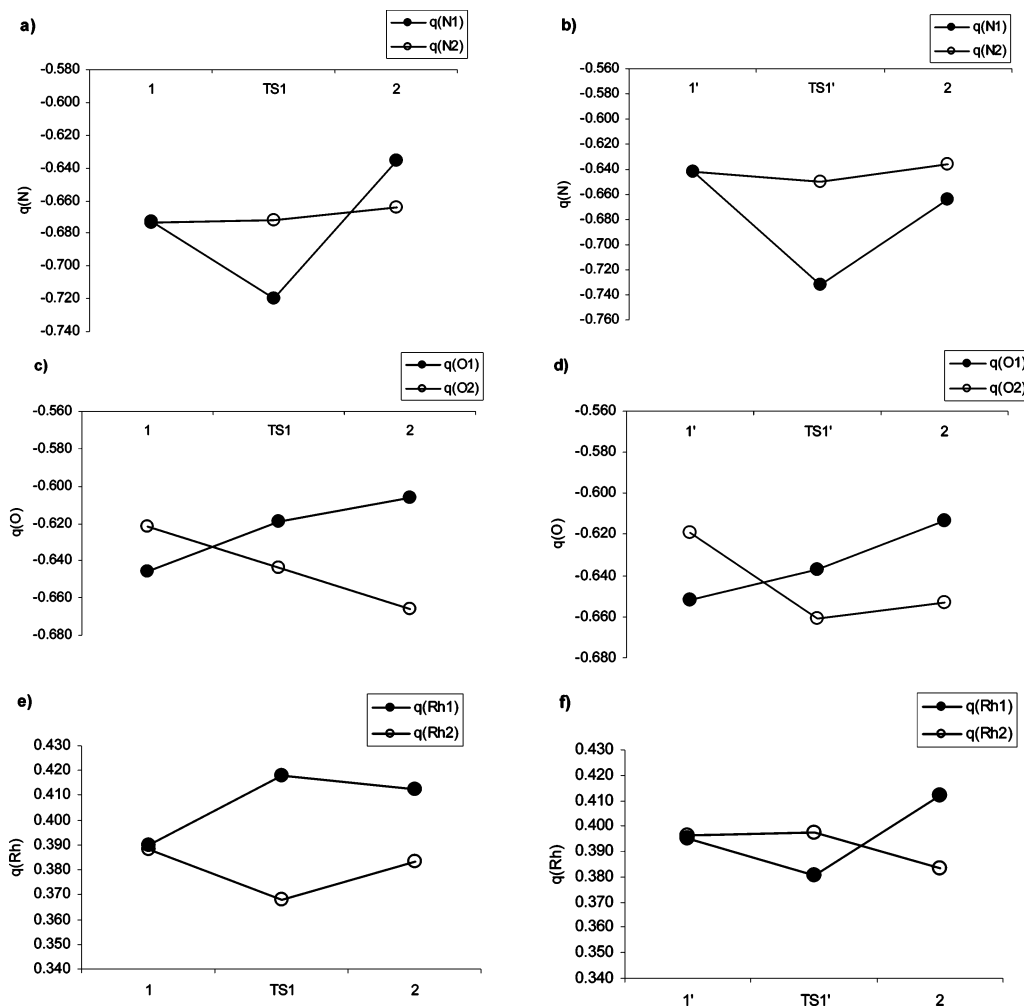
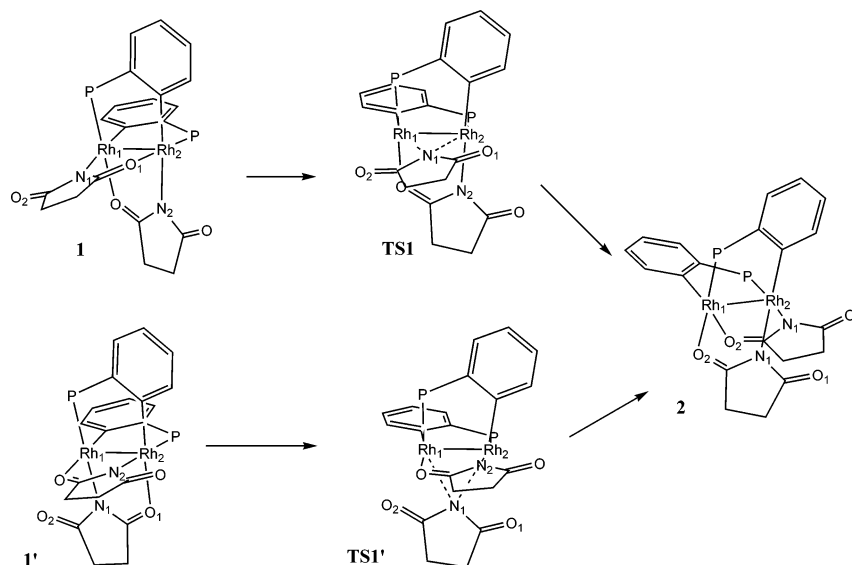


Figure 5. Computational NPA charges in a chloroform solution for selected atoms directly involved in the isomerization process. (a and b) Charge of N in the succinimidato ligands. q(N1) corresponds to the moving succinimidato ligand and q(N2) to the unsliding one. (c and d) Charge of O in the succinimidato ligands. q(O1) corresponds to the shift from bonding to a dangling position and q(O2) to the inverse shift. (e and f) Charge of Rh atoms. The numbering scheme and the structures of the compounds are presented in Scheme 2.

compounds have a symmetric spectrum, showing only one ^{31}P NMR resonance. However, the $J_{\text{Rh-P}}$ coupling constants

have very different values, 171 and 146 Hz for **1** and **1'**, respectively. This difference can only be attributed to the

Table 2. Selected Bond Lengths for the Compounds Calculated at the DFT Level^a

species	$d(\text{Rh}-\text{N})/\text{\AA}$	$d(\text{Rh}-\text{O1})/\text{\AA}$	$d(\text{Rh}-\text{O2})/\text{\AA}$	$d(\text{Rh}-\text{Rh})/\text{\AA}$
1	2.141	2.131	3.440	2.513
TS1 ^b	2.535	2.589	2.759	2.476
2	2.076	3.375	2.196	2.514
1'	2.065	2.219	3.290	2.521
TS1' ^c	2.461	2.887	2.487	2.477
2	2.154	3.449	2.121	2.514

^a The distance for the moving atoms is measured from the nearest Rh atoms. O1 represents the originally bonding O and O2 the dangling one (see Scheme 2). ^b $\Delta H^\ddagger(298\text{ K}) = 109.7\text{ kJ mol}^{-1}$ in toluene. ^c $\Delta H^\ddagger(298\text{ K}) = 108.5\text{ kJ mol}^{-1}$ in toluene.

presence in each compound of a different trans atom to P, that is, O in **1** and N in **1'**. Considering that compound **2**, which has the two P nonequivalent nuclei in precisely these two environments, shows similar coupling constant values, 178 and 146 Hz, the structural assignment made for **1'** is corroborated.

The distribution of complexes obtained on the preparative substitution of trifluoroacetate by succinimide merits some further comments. The absence of complex **2** in the final reaction medium, before thermodynamic equilibration, can be explained if the substitution process involves a sort of zip movement from the succinimidato, starting from the coordination of an O to the axial position of the dinuclear Rh₂ core. Further coordination of the N to the same Rh center should then allow for the decoordination of the former O atom and the coordination of the second one across the Rh–Rh bond. The carboxylato ligand will be displaced at the same time. The process is de facto parallel to that observed for the cyclometalation of phosphines in dirhodium tetraacetate.^{4,7} Steric hindrance does not allow for the coordination of a second succinimide ligand in the same axial position, thus inhibiting the formation of **2**. Similarly, the fact that complex **1** is obtained with preference to **1'** can be directly related to the high trans effect of the metalated C present in [Rh₂(P(C₅H₄)Ph₂)₂(O₂CCH₃)₂]. This effect labilizes the carboxylato group in a way that the preferred (faster) reaction path should correspond to a O_{axial} → O_{axial} + N_{trans_to_C} → N_{trans_to_C} + O'_{trans_to_P} sequence.

Isomerization Behavior. The results collected for the static behavior of the toluene solutions of the compounds indicate the formation of intermolecular adducts such as those found in similar complexes;¹⁹ quantification of these equilibria as a function of the solvent and temperature is currently underway. Fortunately, the isomerization processes studied were found to proceed independently from the existence of any donors in the axial position of the Rh^{II}₂ core (Scheme 1). The intramolecular nature of the rate-determining step of the process is clearly established; the results indicate that coordination of neither an external succinimide nor a dangling O from another dinuclear molecule affects the process. This is rather surprising; the general processes in which these Rh^{II}₂ complexes are involved tend to include these axial coordination sites as important anchoring points

for further reactivity.⁷ For other reactions studied on this type of complexes, which involved C–H bond activation via electrophilic substitution, the use of the axial coordination sites proved to be crucial for both stoichiometric and electronic catalytic reasons.⁴ Nevertheless, although for the isomerization reactions studied these positions are not involved in the rate-determining step of the reaction, their involvement in non-rate-determining processes cannot be ruled out. The neat nature of the processes observed by UV–vis and ³¹P NMR spectroscopies indicates that no buildup of intermediates exists in these reactions.

The kinetic and activation parameters obtained for the reactions studied are indicative of a dissociative activation of the process taking place in an intramolecular manner. The process has to involve, as shown in the DFT calculations, the dissociation of both the Rh–N and Rh–O bonds, although the dissociation of the stronger Rh–N⁽⁻⁾ bond has to be reasonably associated with the rate-determining step. For both the **1** → **2** and **1'** → **2** reactions, the values determined for the activation enthalpy are very large (120–125 kJ mol⁻¹), as expected for the dissociation process of a strong Rh–N ligand. There is a very good agreement between these values and those obtained by DFT calculation (Table 2). The process generates thus a charge separation between the anionic succinimide ligand and the Rh^{II} metal in the transition state, which agrees with the observed increase in the reaction rate upon an increase in the polarity of the solvent.²⁰ This charge separation has also been found computationally as an important feature in the formation of the transition structures (Figure 5). Furthermore, calculations showed the unequal nature of the two transition states, where the degree of charge distribution was found to depend on the original and final positions of the bonding N and O, therefore explaining the more important acceleration observed when the reaction **1'** → **2** is carried out in chloroform.

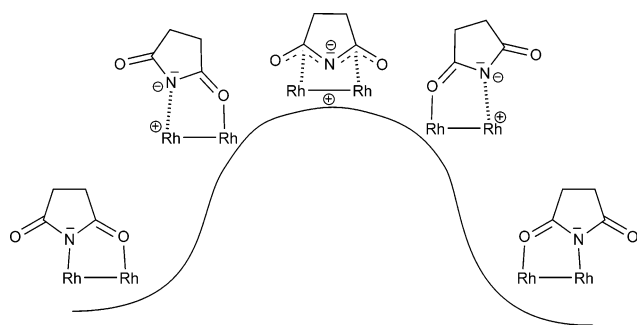
The values found for the volumes and entropies of activation are more surprising. Even though for the **1'** → **2** reaction the values found ($\Delta V^\ddagger = 12\text{ cm}^3\text{ mol}^{-1}$ and $\Delta S^\ddagger = 90\text{ J K}^{-1}\text{ mol}^{-1}$) agree very well with the expected increase in the volume and deorganization upon partial dissociation of the succinimide ligand, the same parameters for the **1** → **2** process ($\Delta V^\ddagger \approx 0\text{ cm}^3\text{ mol}^{-1}$ and $\Delta S^\ddagger = 40\text{ J K}^{-1}\text{ mol}^{-1}$) are not as large and positive as would be expected for such an activation. Nevertheless, the DFT data collected in Table 2 agree with the overall trend: the total bond lengthening for **TS1'** is 1.6 times larger than that for **TS1**. Considering the X-ray crystal structures determined for complexes **1** and **2**, this fact is related to the higher trans influence of the phenyl ring C with respect to the phosphine P, already responsible for the **1:1'** complex distribution ratio.^{17,21} The lengths of the Rh–N bonds trans to Rh–C in complexes **1** and **2** are considerably longer than those trans to Rh–P in complex **2**.⁹ The degree of Rh–N bond lengthening for complex **1'** to reach the transition state has

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Chart 4



to be more important, given the fact that it is trans to a P ligand (Scheme 1). As a consequence, the system should produce a more substantial increase in the entropy and volume, as seen in the data in Table 1.

The nature of the isomerization process studied seems very complex, but the nature of the changes observed leads to a rather straightforward *pictorial* sliding sequence of the succinimidato ligand (Chart 4). Although dissociative activation of the Rh–N bond seems clear, a Rh–O bond also has to dissociate to reach the final complex (Scheme 2). From there, the movement of the N and dangling O donors to the thermodynamically favored final geometrical arrangement in complex **2** has to occur.

Experimental Section

Instruments. ^1H and ^{31}P NMR spectra were recorded on a Bruker 300 spectrometer in CDCl_3 at room temperature unless specified otherwise. Chemical shifts are reported in ppm, referred to tetramethylsilane (^1H) and phosphoric acid (^{31}P , external), and coupling constants (J) in Hertz (Hz). All Rh^{II} compounds show ^{31}P NMR spectra corresponding to an AA'XX' system.

The UV–vis spectra and the kinetic monitoring of the reactions were recorded in a Hewlett-Packard 8452A, a Cary 50, or a J&M TIDAS instrument, depending on the experiments. The pressurizing system used for the experiments run at variable pressure has already been described.^{22,23} In all cases, a pill-box cell has been chosen for the experiments.²⁴

Compounds. Rh^{II} complexes with ortho-metalated arylphosphine ligands, $[\text{Rh}_2(\text{P}(\text{C}_5\text{CH}_4)\text{Ph}_2)_2(\text{O}_2\text{CR})_2]$ ($\text{R} = \text{CH}_3, \text{CF}_3$), were prepared by literature procedures.^{25–27} Coupling constants were obtained from a *gNMR*-simulated spectrum.²⁸ Commercially available PPh_3 and CF_3COOH were used as purchased (Aldrich). Column chromatography was carried out on silica gel (70–230 mesh); indicated solvents are volume/volume mixtures.

(a) Synthesis of 1. This compound was prepared by synthetic methods slightly modified from those previously reported.⁹ To a

solution of $[\text{Rh}_2(\text{P}(\text{C}_5\text{CH}_4)\text{Ph}_2)_2(\text{O}_2\text{CCF}_3)_2] \cdot 2\text{H}_2\text{O}$ (0.10 g, 1×10^{-4} mol) in 10 cm^3 of dichloromethane at 0°C was slowly added a solution of succinimide in methanol (0.041 g, 4.16×10^{-4} mol) and KOH (0.026 g, 4.16×10^{-4} mol), and the mixture was stirred for 5 min. The ^{31}P NMR spectrum of the crude product showed two different products, **1** and **1'** in a 4:1 ratio. Isomer **1** was isolated by column chromatography using ethyl acetate/hexane (3:1) as the eluent; elimination of the solvent at reduced pressure produced the desired compound in a 60% yield. ^1H NMR (CDCl_3 , 400 MHz): 1.20 (m, 2H), 1.45 (m, 2H), 1.78 (m, 2H), 2.08 (m, 2H), 6.52 (m, 4H), 6.68 (m, 4H), 6.92 (m, 10H), 7.18 (m, 2H), 7.28 (m, 6H), 7.52 (m, 4H). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 121 MHz): 23.9 ($^1J_{\text{Rh-P}} = 171 \text{ Hz}$, $^2J_{\text{Rh-P}} = 9 \text{ Hz}$).

(b) Synthesis of 2. Some modifications to the previously reported method of preparation⁹ have been applied. To a solution of $[\text{Rh}_2(\text{P}(\text{C}_5\text{CH}_4)\text{Ph}_2)_2(\text{O}_2\text{CCH}_3)_2] \cdot 2\text{HO}_2\text{CCH}_3$ (0.024 g, 2×10^{-5} mol) in toluene (15 cm^3) succinimide was added (0.012 g, 1.2×10^{-4} mol), and the resulting mixture was refluxed for 15 min. The solvent was evaporated in a vacuum, and 15 cm^3 of toluene was added again; the procedure was repeated three more times to eliminate any remains of acetic acid. The resulting residue was purified by column chromatography using CH_2Cl_2 as the eluent; elimination of the solvent at reduced pressure produced the desired compound in a 90% yield. ^1H NMR (CDCl_3 , 400 MHz): 1.4–2.4 (m, 8H), 6.49 (m, 1H), 6.60–7.25 (m, 17H), 7.36 (m, 6H), 7.56 (m, 4H). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 121 MHz): 14.7 ($^1J_{\text{Rh-P}} = 146 \text{ Hz}$, $^2J_{\text{Rh-P}} = 8 \text{ Hz}$), 25.0 ($^1J_{\text{Rh-P}} = 178 \text{ Hz}$, $^2J_{\text{Rh-P}} = 7 \text{ Hz}$).

(c) Synthesis of 1'. This isomer was obtained as a side product in the synthesis of compound **1**. All efforts to obtain it separately were unsuccessful given its relatively fast isomerization to **2**. Given this fact, the reaction mixture containing compounds **1** and **1'** was evaporated at low temperature and the mixture obtained was used in all further studies. Alternatively, chromatographic separation of **1** from these reaction mixtures gave mixtures of **1'** and **2**. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 90.75 MHz): 18.6 ($^1J_{\text{Rh-P}} = 144 \text{ Hz}$, $^2J_{\text{Rh-P}} = 8 \text{ Hz}$).

Kinetic Measurements. The isomerization processes in toluene solution were followed by UV–vis spectroscopy in the wavelength range where the solvent does not absorb. All of the reactions at atmospheric pressure were monitored on instruments equipped with thermostated multicell transports. The general kinetic technique for this type of processes has been described elsewhere.^{4,28} For the kinetic runs at elevated pressure, a previously described pressurizing system attached to a J&M TIDAS instrument was used.²⁹ Observed rate constants were derived from absorbance versus time traces at the wavelength where a maximum increase and/or decrease of absorbance was observed. No dependence of the observed rate constant values on the selected wavelength was detected, as is expected for reactions where a good retention of isosbestic points is observed (Figure 1).³⁰ Table S1 (Supporting Information) collects the obtained kinetic constant values for all of the reactions studied, as a function of succinimide concentration, starting product, pressure, and temperature.

Computational Methods. All calculations were carried out with the *Gaussian03* program package.³¹ The DFT level of theory with the nonlocal hybrid density functional B3PW91 was selected for the quantum chemical studies.^{32,33} The basis set was comprised of

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a Stuttgart–Dresden effective small-core potential³⁴ augmented with an extra p-polarization function for Rh [SDD(p)] and a standard all-electron basis set 6-31G* for other atoms. The system was found to be reliable in the previous preliminary study on the structural and electronic trends in Rh^{II}₂ compounds.³⁵ Frequency analysis with no scaling was performed to ensure ground-state optimization or first-order saddle-point optimization for the transition structures, which were obtained using the QST3 algorithm. NPA³⁶ was used for obtaining the charge distribution for the models. Solvent effects were calculated on the optimized structures with a polarizable continuum model.^{37–41}

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Supporting Information Available: Optimized calculated structures for the complexes studied in PDB format and values of k_{obs} determined as a function of the complexes, concentration, temperature, and pressure. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(35) The basis set was obtained from the Extensible Computational Chemistry Environment Basis Set Database, version 9/12/01, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory, which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multiprogram laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830. Contact David Feller or Karen Schuchardt for further information.

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