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Homogeneous Catalysis

# Supramolecular Control of the Oxidative Addition as a Way To Improve the Catalytic Efficiency of Pincer-Rhodium (I) Complexes

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**Abstract:** $^1$H NMR studies using a cationic complex with a pyridine-di-imidazolylidene pincer ligand of formula $[Rh(CNC)(CO)]^+$ revealed that this compound showed high binding affinity with coronene in $CH_2Cl_2$. The interaction between coronene and the planar $Rh^I$ complex is established by means of π-stacking interactions. This interaction has a strong impact on the electron-donating strength of the pincer CNC ligand, which is increased significantly, as demonstrated by the shifting of the ν(CO) stretching bands to lower frequencies. The addition of coronene increases the reaction rate of the nucleophilic attack of methyl iodide on the rhodium (I) pincer complex, and also has a positive effect on the performance of the complex as a catalyst in the cycloisomerization of 4-pentynoic acid. These findings highlight the importance of supramolecular interactions for tuning the reactivity and catalytic activity of square-planar metal complexes.

Oxidative addition (OA) and reductive elimination (RE) are very likely the most important steps in the majority of transition-metal-based homogeneously catalyzed reactions.[1] A profound understanding of the factors that dictate the kinetics and thermodynamics of these fundamental steps in homogeneous catalysis is crucial for approaching a rational design of organometallic-based catalysts.[2] In the case of the oxidative addition, the common assumption is that is favored by electron-rich metal centers, thus by metals in low oxidation states bound to ligands that are strongly electron-donating. Consequently, the general strategy for promoting oxidative additions is to use strong electron-donating ligands,[3] while electron-withdrawing ligands are generally used for facilitating reductive eliminations.[4] Steric effects such as the presence of bulky ligands,[5] or the bite angle in chelating ligands,[6] have also been demonstrated to play a key role in both OA and RE processes. In traditional studies about the influence of the ligands on the OA and RE performances, the steric and electronic properties of the spectator ligands are used to control the performance of the catalyst. Such modifications are usually performed by introducing electron-donating or electron-withdrawing substituents at the ligand, which often requires tedious and laborious synthesis. Unfortunately, these studies cannot provide accurate information about the isolated influences that electronic and/or steric properties exert on the catalyst, as it is not possible to eliminate the potential role for ligand donor ability as a function of its substituents. Possibly, a more straightforward and convenient approach consists of the use of a redox-switchable ligand,[7] which can modify the Lewis acidity of the metal center without altering significantly the steric hindrance of the complex, and thus can provide an accurate view on how the modification of the electronic properties of the metal may influence the outcome of the OA and RE processes. We recently used the strategy of using redox-switchable ligands for uncovering useful information about the mechanism of several homogeneously catalysed reactions, and for designing improved catalysts for them.[8]

Pincer rhodium complexes have been widely used for performing studies for understanding how ligand steric size and electron-donor ability can be used for controlling the energetics of redox bond-breaking and bond-forming processes that normally involve interconversion between $Rh^I$ and $Rh^{III}$ organometallic species. Just to name a few examples, the first kinetic studies on the oxidative addition of MeI to a series of pincer rhodium complexes with pyridyl bis(NHC) ligands was performed by the group of Haynes in 2005.[9] Then, the Milstein group studied the effect PCP and PNP pincer ligands on the reductive elimination of methyl halides from $Rh^{III}$ complexes.[5b,10] Gunnoe and co-workers made detailed studies on the reductive elimination of a series of [($^R$terpy)Rh(Me)(Cl)(I)] complexes, and showed how the reductive elimination of the methyl group is favored when R is the electron-withdrawing nitro group compared to the situation in which R is a tert-butyl group.[11] The same research group also reported how the 'axial steric bulk' can be used for destabilizing octahedral $Rh^{III}$ complexes, and thus facilitate the reductive elimination step.[5a] The Murakami group performed studies that allowed them to conclude that the propensity of rhodium(I) complexes with PBP pincer ligands to undergo C–C bond oxidative addition of cyclobutanones is ascribed to the highly electron-donating nature of the boron ligand.[12] Chaplin and co-workers developed an imaginative strategy to promote the oxidative addition of an interlocked 1,3-diyne with bulky substituents

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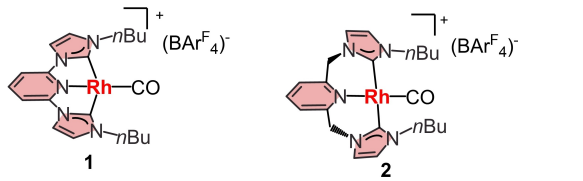
to a $Rh^I$ center with a macrocyclic phosphinite pincer ligand,[13] and made detailed thermodynamic and mechanistic studies on the oxidative addition of biphenylene and C–Cl bonds to Rh(PONOP)[14] and Rh(CNC)[15] complexes.

Herein, we show that the reactivity of a relatively simple a $[Rh(CNC)(CO)]^+$ pincer complex towards the nucleophilic oxidative addition of MeI is greatly enhanced by the addition of a π-π-stacking additive, such as coronene. As a proof of concept, the positive effect of the addition of coronene on the catalytic performance of the complex in the cycloisomerization of 4-pentynoic acid is also described.

Given the planar orientation of the aromatic rings of the CNC-pincer ligand in the rhodium complex **1** (Scheme 1), we sought to study if the complex would show any tendency to bind to polycyclic aromatic hydrocarbons (PAHs) by means of π-π-stacking interactions. We also thought that the positive charge of this cationic $Rh^I$ complex would facilitate the interaction when electron-rich PAHs were used. In order to test this hypothesis, we decided to perform a $^1H$ NMR titration of **1** with pyrene and coronene in $CD_2Cl_2$. The titrations were performed at a constant concentration of **1** (0.2 mM) and adding increasing amounts of pyrene or coronene. The $^1H$ NMR signals of the pincer rhodium complex did not show any significant changes when pyrene was added, thus indicating that the binding of pyrene with **1** was negligible under the conditions used (Figure S9 in ESI). By contrast, as can be observed in Figure 1, the $^1H$ NMR titration of **1** with coronene shows that the signals due to the protons of the pincer ligand are significantly shifted upfield upon the addition of coronene, thus indicating the formation of **1**-coronene π-stacking adducts within the range of concentrations used. The maximum shifts observed were −0.43 ppm for the resonances due to the protons of the imidazolylidene rings, −0.58 ppm for the singlet due to the protons of the pyridine ring, and −0.29 ppm for the protons of the N-C$H_2$- group of the wingtip of the imidazolylidenes. The analysis of the curve fitting and Job plot experiment allowed us to conclude that the data were best fitted to a 1:1 stoichiometry.[16] The binding constant was determined by global fitting analysis,[17] and gave a value of $270 \pm 9\ M^{-1}$, for the association of coronene with **1**. This large binding affinity is a consequence of the higher electron-richness and larger surface area of coronene compared to that shown by pyrene, thus making the π-π-stacking interaction to be more effective.

For comparative purposes, we also performed $^1H$ NMR studies in order to determine if the rhodium(I) complex with the lutidine-based CNC-ligand (**2**, in Scheme 1) would also show binding abilities with coronene. As expected, this complex did not show any tendency to bind coronene, as a consequence of the lack of a coplanar disposition of the three rings of the ligand (see Figure S13 in ESI).

Next, we wanted to investigate if the association of coronene with **1** would have any effect on the electron-donating strength of the pincer ligand. In order to address this point, we recorded the infrared spectra of **1** in $CH_2Cl_2$ in the presence of different concentrations of coronene. As can be observed in the series of IR spectra shown in Figure 2, the addition of increasing amounts of coronene is accompanied by the shifting of the C–O stretching band to lower frequencies, indicating that the association of coronene with the Rh(CNC) complex increases the electron-donating power of the pincer ligand. The maximum Δν(CO) observed




***Scheme 1.*** Pincer $[Rh(CNC)(CO)]^+$ complexes under study.

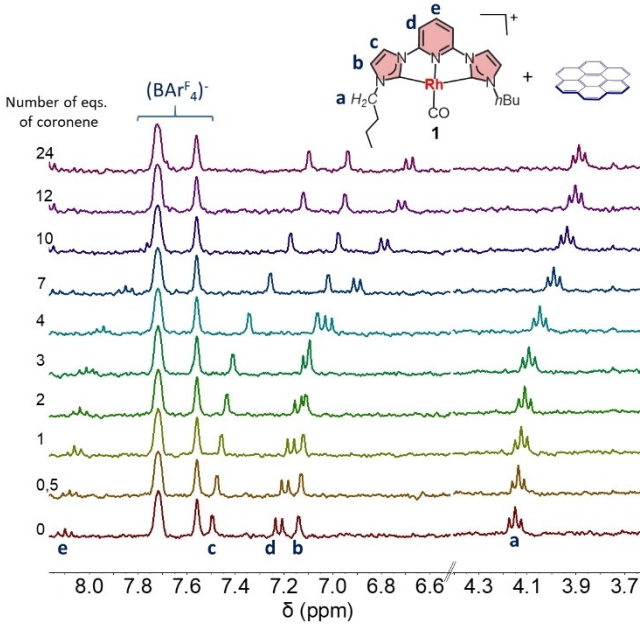



***Figure 1.*** Selected region of the $^1H$ NMR spectra resulting from the titration of **1** (0.2 mM) with coronene in $CD_2Cl_2$ at 293 K.

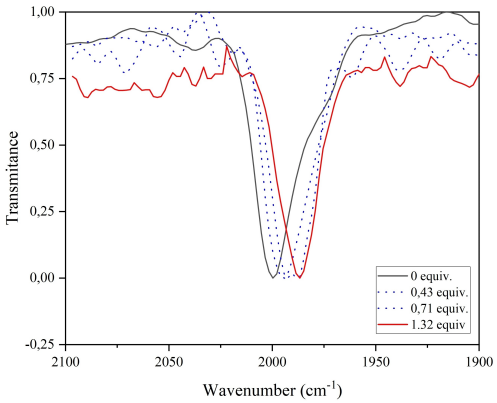



***Figure 2.*** Series of infrared spectra recorded for **1** in the presence of increasing amounts of coronene. The spectra were recorded at room temperature, after dissolving the Rh(CNC) complex and coronene in $CH_2Cl_2$.

was of −15 $cm^{-1}$, thus indicating a very significant increase of the electron-donor character of the ligand. As a control experiment, we performed the same experiment but adding increasing amounts of pyrene instead of coronene, and confirmed that under these conditions no change of the C–O stretching frequency was observed, in agreement with the negligible affinity found between pyrene and **1** (Figure S15). Likewise, addition of increasing amounts of coronene on a solution of the non-planar pincer complex **2**, showed no change of the frequency of the C–O stretching band, as should be expected for the lack of interaction between **2** and coronene (Figure S16). At this point it is important to mention that we previously studied the effect of adding π-stacking additives on the IR stretching frequencies of a series of iridium carbonyl complexes bearing NHC ligands decorated with polyaromatic moieties, but the maximum Δν(CO) values that we observed were in the range of 1–2 $cm^{-1}$,[18] therefore the 15 $cm^{-1}$ ν(CO) shift that we observe for **1** is remarkable, and made us think that it should be translated into an important effect on the reactivity of this pincer Rh(CNC) complex.

We next wondered whether the addition of coronene could have an effect on the oxidative addition abilities of the complex. In order to address this point, we decided to study the nucleophilic attack of **1** with MeI in the presence and in the absence of coronene. The reactions were carried out in $CD_2Cl_2$, with an initial concentration of the pincer Rh(CNC) complex of 4 mM and MeI (13 equivalents/Rh), and were monitored by $^1$H NMR spectroscopy. For the reaction carried out in the presence of coronene, a 8 mM concentration of this PAH was used. The analysis of the evolution of the process indicated that, in either case, only one of the three possible $Rh^{III}$ product isomer was formed. By comparing the NMR spectrum of the product with those reported in the literature for related $[Rh(CNC)(CO)(I)(Me)]^+$ complexes,[19] we concluded that the complex formed was the one with the CO ligand *trans* to the pyridine ring and the iodide and methyl ligands in a relative *trans* disposition, as in complex **3**, which is shown in Scheme 2.

As can be observed from the time-dependent reaction profiles for the reaction carried out at 40 °C shown in Figure 3, the plots are well fitted by exponential curves, from which pseudo-first-order rate constants ($k_{obs}$) were calculated. As can be observed from the observed kinetic constants shown in the figure, the addition of coronene increased the reaction rate by a factor of 2.6 [measured as $k_{obs(\mathbf{1}+coronene)}/k_{obs(\mathbf{1})}$]. When the reaction was performed in the presence of pyrene, instead of coronene, no improvement in the reaction rate was observed, in agreement with

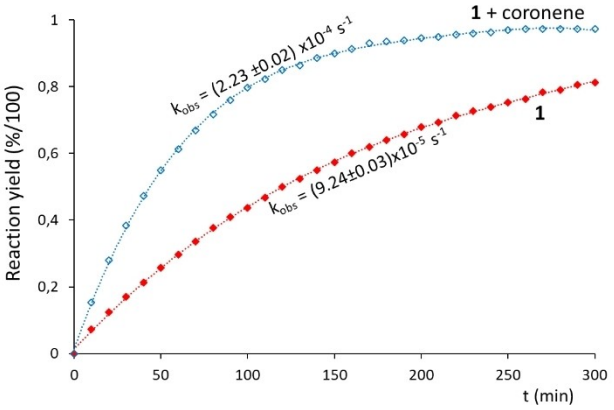
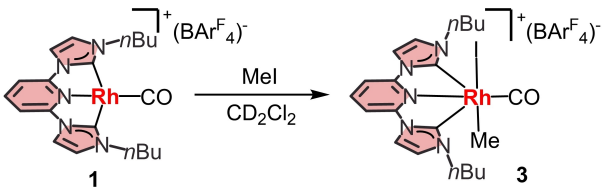



***Figure 3.*** Time-dependent reaction profiles of the reactions of **1** with MeI, in the presence and in the absence of coronene. The reactions were carried out in $CD_2Cl_2$ at 40 °C, using an initial concentration of the Rh(CNC) complex of 4 mM and a concentration of MeI of 52 mM. For the reactions performed with coronene, the concentration of coronene was of 8 mM. The evolution of the process was monitored by $^1$H NMR spectroscopy.

the negligible binding affinity of pyrene and complex **1** (see Figure S19 in ESI). We also performed the nucleophilic attack of **2** with MeI, and we observed that, for this complex, the addition of coronene did not have any effect on the reaction rate of the process (Figure S23). The lower reaction rate observed for **2** does not tally with the stronger electron-richness of the metal in **2** with respect to **1**, as observed form the frequencies of the C–O stretching bands in these two complexes (1992 $cm^{-1}$ for **1**; 1975.5 $cm^{-1}$ for **2**), but is in fully agreement with the results found by Chaplin and co-workers when comparing the reaction trends displayed by $Rh^I$ complexes with similar pyridine- and lutidine-centered bis-NHC ligands.[19] This observation indicates that steric effects and the bite angle of the ligand also play a key role on this reaction.

Variable-temperature kinetic data allowed to calculate the activation parameters obtained from the corresponding Eyring plots (see ESI for full details). As can be observed from the data shown in Table 1, the large negative $\Delta S^{\neq}$ values (−55 to −61 cal/molK) are consistent with an associative process, and are also in agreement with the reaction proceeding through a $S_N2$ mechanism, as it has been proposed.[9,20] More interesting is the fact that the addition of coronene does not affect significantly to the activation entropies, but has a large impact on the $\Delta H^{\neq}$ value, as this is reduced by 2.2 kcal/mol.




***Scheme 2.*** Reaction of **1** with MeI.

***Table 1:*** Activation parameters for the oxidative addition reaction of MeI to **1**.[a]

| Entry | Complex | $\Delta H^{\neq}$ (kcal/mol) | $\Delta S^{\neq}$ (cal/molK) |
|---|---|---|---|
| 1 | **1** | 6.8 ± 0.6 | -55 ± 2 |
| 2 | **1** + coronene | 4.6 ± 0.9 | -61 ± 3 |

[a] Data obtained from variable-temperature kinetic data in $CD_2Cl_2$, using the corresponding Eyring plots.

Can this supramolecular-induced enhancement on the nucleophilic oxidative addition be translated into an improvement of the catalytic performance of this complex? In order to answer to this question, we decided to test complex **1** in the cycloisomerization of alkynoic acids, and evaluate if the addition of coronene had an impact on the outcome of the process. We decided to study the cycloisomerization of alkynoic acids as model catalytic reaction for several reasons. First, for its inherent interest, as this reaction is an atom-economic process that constitutes one of the most effective methods for obtaining exocyclic enol lactones, which are versatile products in synthetic organic chemistry,[21] and are prevalent constituents of natural products with important biological activity.[22] And second -and probably more important for the purpose of this study- because as we recently demonstrated,[8c] the rate determining step (RDS) of this catalytic reaction is the oxidative addition of the alkynoic acid to the metal center, and therefore the enhancement of the oxidative addition by addition of coronene may be translated into a positive impact on the performance of the reaction. We studied the reaction of 4-pentynoic acid using complex **1** as catalyst, in the absence and in the presence of coronene. The reactions were performed in $CH_3CN$ at 80 °C, using a catalyst loading of 1 mol%, and the evolution of the reaction was monitored by $^1H$ NMR spectroscopy. The resulting reaction profiles are shown in Figure 4. As can be observed from the plots, the reactions follow a zeroth order dependence on the substrate, in agreement with previous studies.[8c,d,23] This zeroth order dependence of the reaction rate on the substrate concentration means that the resting state the substrate is already coordinated to the catalyst through the alkyne. By going from the resting state to the highest transition state, no substrate would enter the catalytic cycle, explaining the observed kinetics. As can be observed in the plots shown in Figure 4, the addition of coronene produces a significant improvement in the catalytic activity, which is manifested by a 2.7-fold increase of the reaction rate. It is also important to point out that this enhancement on the activity of the catalyst for this specific reaction is similar to that obtained using rhodium complexes with redox-switchable ligands,[8c,d] thus indicating that the supramolecular control of the process can compete in magnitude with the control provided by redox-switchable catalysts. Again, when we performed the reaction in the presence of pyrene, instead of coronene, no improvement in the reaction rate was observed, as a consequence of the negligible interaction between pyrene and complex **1** (Figure S26). For the same reason, the catalytic reaction carried out using **2** as catalyst, did not show any enhancement when coronene was added (Figure S27). These two control experiments confirm the need of a supramolecular interaction between the additive and the catalyst in order to produce an effect on the catalytic outcome.

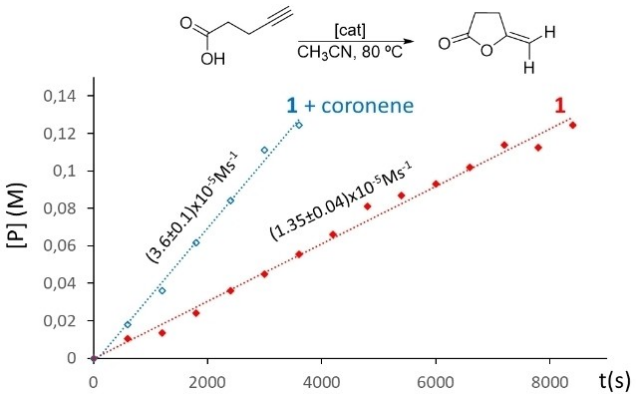



***Figure 4.*** Time-dependent reaction profiles for the cyclization of 4-pentynoic acid using catalyst **1** with and without addition of coronene. The reactions were carried out in acetonitrile, with an initial concentration of 4-pentynoic acid of 0.15 M, and a catalyst loading of 1 mol%. Coronene was added in a 10 mol% with respect to the substrate. Yields were determined by $^1H$ NMR spectroscopy, using 1,3,5-trimethoxybenzene as integration standard. The figure also shows the reaction rates for each reaction.

In summary, we showed that a planar $[Rh(CNC)(CO)]^+$ complex displays a high binding affinity with coronene. This observation is of great importance, since it anticipates that many other metal complexes with planar pincer ligands may display similar affinities, and therefore, may be prone to modifying their reactivities upon addition of supramolecular additives.

We also provided evidences that the binding of this complex with coronene had a large impact on the electron-donating strength of the pincer ligand, as the interaction of this ligand with coronene increased the electron-richness of the metal, as measured by the shift of the C–O stretching band to significantly lower frequencies. The addition of coronene also has an important effect on the reactivity of the $Rh^I$ complex, as demonstrated by the increase of the reaction rate in the nucleophilic attack of methyl iodide. Probably, the most relevant observation of our study is the impact that the addition of coronene has on the catalytic performance of the catalyst in the cyclization of 4-pentynoic acid. The addition of coronene to the pincer rhodium complex produced a significant improvement of its catalytic performance, a result that is directly connected to the facilitation of the oxidative addition of the alkynoic acid to the metal, which is the RDS of the process.

Our study highlights how supramolecular additives can be used to tune (in our case improve) the activity of homogeneous catalysts. We previously anticipated that the addition of π-stacking additives could be used for modulating the activity of catalysts bearing planar-polyaromatic moieties,[24] but our new results are more significant because they widen the scope to the more commonly used pincer planar catalysts, and reveals a much greater impact on the catalytic performances than those observed in all our previous studies. In fact, our findings indicate that the supramolecular-tuning of the reactivity and catalytic activity of planar complexes with pincer ligands may be an alternative to the use of ligands with stimuli-responsive units, such us redox,[7a–e] pH-,[25] or photo-switchable[26] ligands, whose preparation is normally accompanied by sophisticated synthetic protocols. In our case a very simple planar pincer ligand is already behaving as a stimuli-

responsive ligand. We are convinced that our study will have important implications in the design of further pincer planar catalysts whose performances can be modulated by the addition of easy-accessible and commercially available π-stacking additives, such as coronene.

## Supporting Information

The Supporting Information file contains all the experimental details dealing with the characterization, calculation of binding affinities, reactivity studies and catalytic experiments. This includes all NMR spectra, electrochemical measurements and description of methods for determining the association constants, observed kinetic constants and thermodynamic parameters.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** Homogeneous Catalysis · Oxidative Addition · Pincer Ligands · Rhodium · Supramolecular Chemistry

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