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DFT-studies of *cis*- and *trans*-$[Rh(CO)_2X_2]^+$ ($X = PH_3$, PF_3, PCl_3, PBr_3, PI_3 or $P(CH_3)_3$) and oxidative addition of CH_3I to them

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Abstract

We have performed B3LYB density functional calculations for oxidative addition of CH_3I to $[Rh(CO)_2X_2]^+$ ($X = PH_3$, PF_3, PCl_3, PBr_3, PI_3 or $P(CH_3)_3$). This species is similar to the catalyst used in industrially important Monsanto process. Our goal is to see if the catalytic process could be enhanced by modifying the ligands. We have taken a set of phophine ligands and calculated the oxidative addition of methyl iodide to both the *cis*- and *trans*-forms of the modified catalysts. In our calculations, we found concerted mechanisms for the oxidative additions studied. Our results show that the activation parameters of the oxidative additions have a clear correlation to the ligand type and ligand size. With PCl_3 and PBr_3, our results show lower activation parameters than for the experimentally observed *cis*-$[Rh(CO)_2I_2]^-$.

Keywords: Rhodium; Density functional theory; Carbonylation; Catalysis; Oxidative addition; Phosphine

1. Introduction

The Monsanto and Cativa processes, employing the catalytic carbonylation of methanol by rhodium or iridium catalysts, are one of the most effective procedures to manufacture acetic acid by industrial means. The basic reaction mechanisms and structures involved in the catalysis cycles have been studied for a long time to understand the system as a whole and to find improvement possibilities for the processes. There are both experimental [1–5] and computational [6–11] studies dealing with these systems. Part of the experimental studies have been concerned with the active catalytic species and the search for even better catalysts still continues. In our previous computational studies, we have explored the catalytic cycles of the Monsanto and Cativa processes systematically, studying also the species that have been so far unobserved experimentally [8–10]. With our prior knowledge of these systems, we have taken a challenge to customize the actual active catalytic species and to test if some improvements could be found. This is the obvious advantage of the computational chemistry; we are able to browse through vast series of different structures and see if any enhancements could be achieved.

Our previous calculations suggest that the rate determining step of the Monsanto process could be accelerated by the experimentally unobserved *trans*-$[Rh(CO)_2I_2]^-$ [9] but the *trans*-form is relatively more unstable than the corresponding *cis*-form. This study has shown a clear difference in the molecular orbital interactions while comparing the oxidative addition to *cis*-$[Rh(CO)_2I_2]^-$ or *trans*-$[Rh(CO)_2I_2]^-$. The experimentally verified key feature of an efficient carbonylation catalyst is a presence of electron-donor ligands. These lead to the idea of ligand modification, so that the active species should obtain the *trans*-form with the electron-donors present. The use of phosphines instead of iodides could provide the electron donating capability and proper steric effects to favor the *trans*-form of the active species. The idea of using phosphines in the carbonylation catalyst is not a new one [12] but a simple and systematic computational study will provide a new aspects to the topic. Our goal here is to see if a rather

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simple modifications of the default catalyst $[Rh(CO)_2I_2]^-$ with a set of simple phosphines PH_3, PF_3, PCl_3, PBr_3, PI_3 or $P(CH_3)_3$ could provide enhancement possibilities for a very important industrial process. The replacement of the iodides with the phosphines changes the total charge of the catalyst species but the relevance to the Monsanto process is preserved since in the experimental study where the phosphines were used, the total charge and the ligands also changed [12]. The idea is to test the *cis*- and *trans*-forms of a series of modified catalysts and to find the ones where the *trans*-forms are favored. Then the oxidative addition is tested with these modified catalysts. The results will tell, if oxidative addition, the rate-determining step of the Monsanto process could be enhanced this way.

2. Computational details

Our work is based on the density functional theory with the hybrid B3LYP exchange and correlation functional [13,14]. All the calculations have been performed with the GAUSSIAN-98 program package [15] using the basis set that is denoted SDD. The SDD consist of a D95V for carbon, oxygen and hydrogen atoms. The Stuttgart/Dresden effective core potentials (ECP) with scalar relativistic corrections have been used for rhodium and all the halogens used, except fluorine. In our calculation, the integration grid has been extra fine. The methods used here are the same as in our preceding studies.

The default optimization algorithm of the GAUSSIAN-98 has been used in the minimum energy and transition state searches. Approximate structures of the transition states have been determined with the potential energy surface (PES) scans with a constrained optimization along a chosen reaction coordinate.

The frequency analyses have been performed to verify the minimum energy and the transition state geometries. The transition states have one imaginary frequency. In the minimum energy structures all modes are real. The entropy approximation has also been acquired through the frequency analyses and the reported free energies are obtained at 298.15 K. The calculations have been performed without any symmetry constraints and all structures have been calculated as a singlet states.

The optimized structures reported here are obtained from the gas phase calculations. However, the effect of solvation has been added with the PCM [16] calculations using dichloromethane as a solvent. The solvent has been selected according to the experimental studies of these systems. To save the crucial computation time, the PCM calculations have been performed with the single-point energy evaluations for the gas phase geometries. The zero-point corrections and entropy approximation are from the gas phase frequency calculations.

In this study, the basis set superposition error (BSSE) has been corrected by the counterpoise approximation [17].

3. Results and discussion

3.1. Structures and energy differences of *cis*- and *trans*-$[Rh(CO)_2X_2]^+$ ($X = PH_3$, PF_3, PCl_3, PBr_3, PI_3 or $P(CH_3)_3$)

In the first part of this study, we optimized the *cis*- and *trans*-structures of the catalyst $[Rh(CO)_2X_2]^+$ ($X = PH_3$, PF_3, PCl_3, PBr_3, PI_3 or $P(CH_3)_3$). In our custom structures, the total charge is +1 whereas in the original catalytic species of the Monsanto process the total charge is −1. However, the electron-rich phosphines balance the reduced nucleophility introduced by the positive total charge. The change of the charge is of course a crucial change but also in the experimental studies of the phosphine modified systems [12], the change of the charge has occurred. We found that the *cis*- and *trans*-structures of $[Rh(CO)_2X_2]^+$ ($X = PH_3$, PF_3, PCl_3, PBr_3, PI_3 or $P(CH_3)_3$) can obtain various conformations very near in energy. To our analysis, we took the most stable ones. The effect of solvation was tested with the PCM model. In these calculations, we computed the PCM single point energy for the relatively most stable structures we use in our analysis. Schematic structures of the catalyst species are introduced in Fig. 1. The relative gas phase and PCM energy differences of the *cis*- and *trans*-species of $[Rh(CO)_2X_2]^+$ ($X = PH_3$, PF_3, PCl_3, PBr_3, PI_3 or $P(CH_3)_3$) are in Figs. 2 and 3 where they are compared with the *cis*–*trans* energy difference of $[Rh(CO)_2I_2]^-$ [8].

The calculations verify our original assumption by showing increasing relative stability of the *trans*-structures when ligand size gets larger. The PCM-model introduces some deviation from the gas phase results but there are no radical changes in the *cis*–*trans* energy differences. All the *cis*-forms of the structures are square-planar. Also the *trans*-forms apart from $[Rh(CO)_2X_2]^+$ ($X = PI_3$, $P(CH_3)_3$) are planar. The twisted structures when $X = PI_3$ or $P(CH_3)_3$ are analogous to the original catalysts of the Monsanto- and Cativa-processes [8,9].

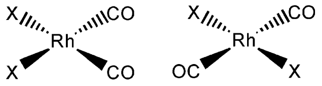

Fig. 1. The schematic illustration of the modified catalytic species *cis*- and *trans*-$[Rh(CO)_2X_2]^+$ ($X = PH_3$, PF_3, PCl_3, PBr_3, PI_3 or $P(CH_3)_3$).

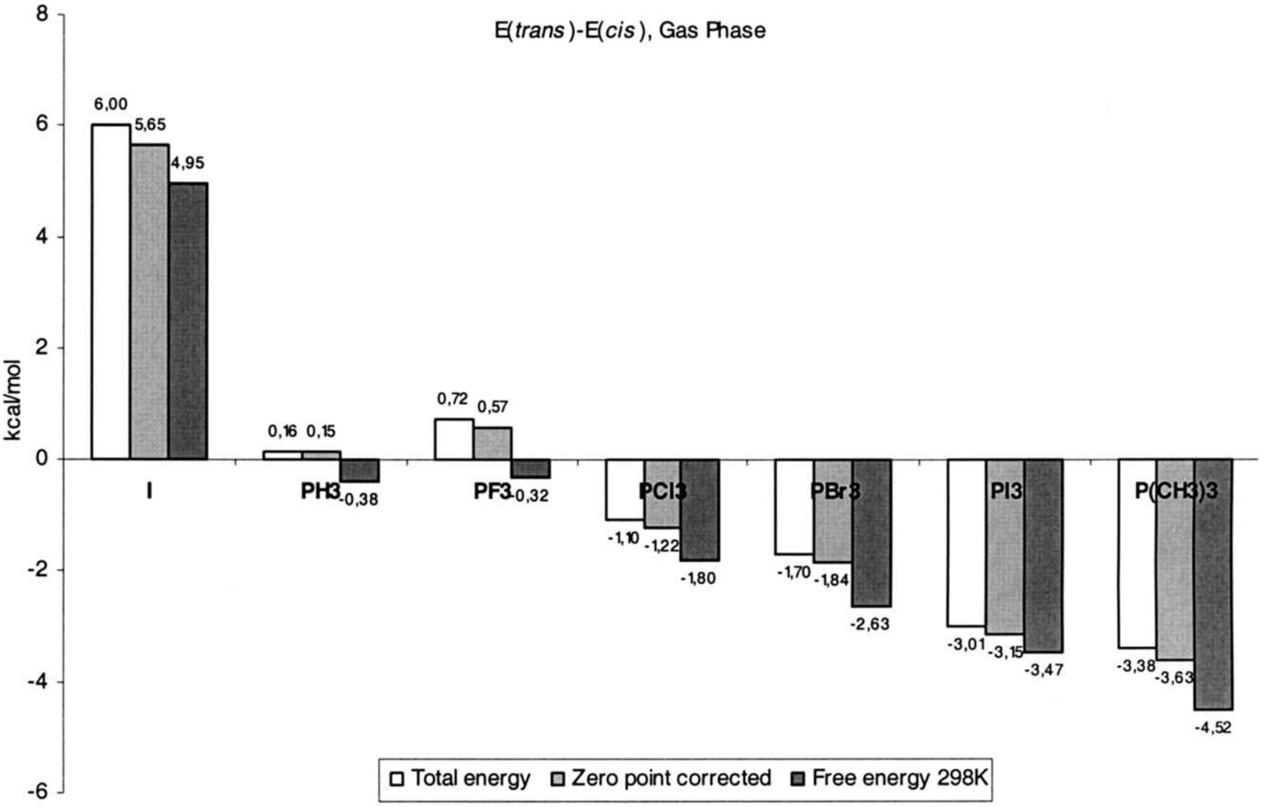

Fig. 2. The relative gas phase energy differences of the *cis*- and *trans*-species of $[Rh(CO)_2X_2]^+$ ($X = PH_3$, PF_3, PCl_3, PBr_3, PI_3 or $P(CH_3)_3$) compared to the *cis–trans* energy difference of $[Rh(CO)_2I_2]^-$. The values are given in kcal mol^{-1}.

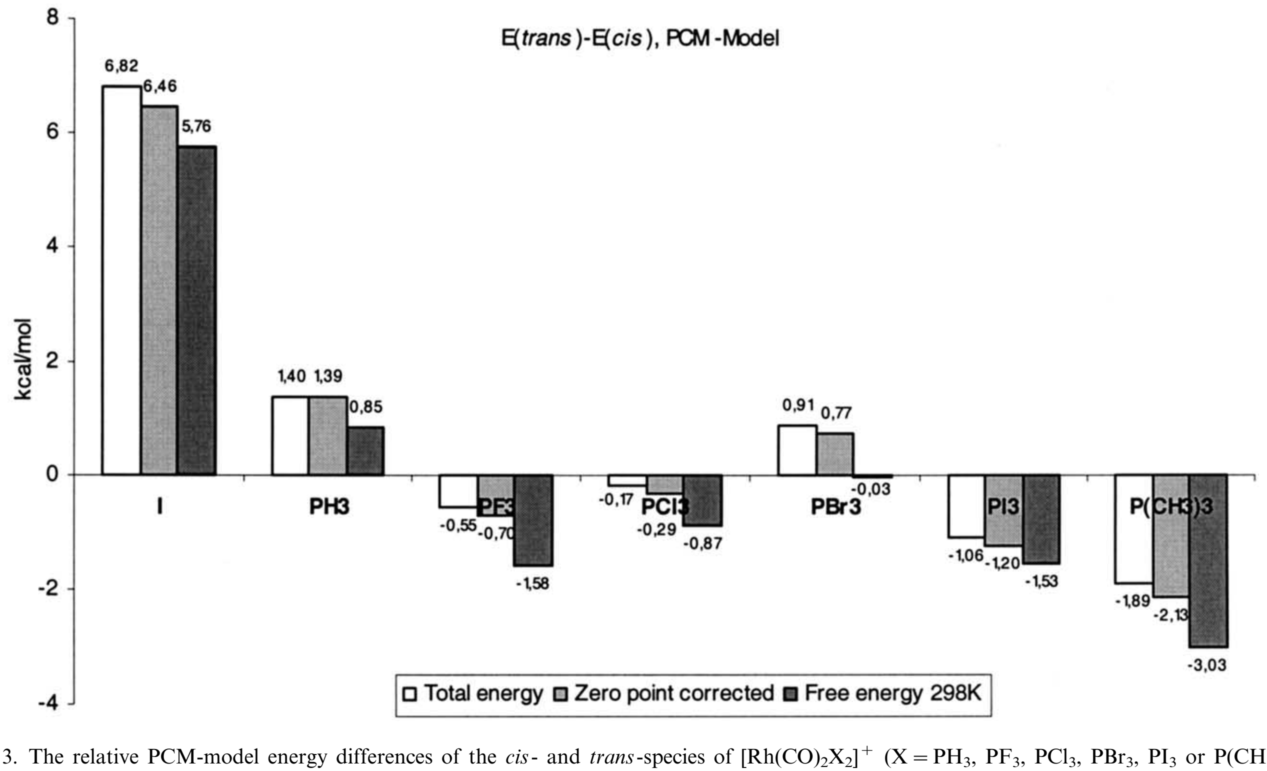

Fig. 3. The relative PCM-model energy differences of the *cis*- and *trans*-species of $[Rh(CO)_2X_2]^+$ ($X = PH_3$, PF_3, PCl_3, PBr_3, PI_3 or $P(CH_3)_3$) compared to the *cis–trans* energy difference of $[Rh(CO)_2I_2]^-$. The values are given in kcal mol^{-1}.

3.2. Oxidative addition of methyl iodide to cis- and trans-$[Rh(CO)_2X_2]^+$ ($X = PH_3$, PF_3, PCl_3, PBr_3, PI_3 or $P(CH_3)_3$)

At first, in the second part of this study, we searched for the reactant complexes where methyl iodide would be in vicinity of the catalyst species [8–10]. However, in these systems such states were not found so we decided to use a catalyst and methyl iodide at infinite separation, as the starting points for the oxidative additions. The approximate structures for the transition states were determined using PES-scans as mentioned in Section 2.

All the ligands selected to modify the original rhodium catalyst, provided a transition state in the oxidative addition except for PF_3. Neither *cis*- nor *trans*-forms of $[Rh(CO)_2(PF_3)_2]^+$ were stable during the attempted oxidative addition. All the other reactions studied result in three-centered transition states, so the mechanism is concerted oxidative addition not the S_N2-type addition as in the original catalysts. This is most likely due to the net positive charge of the modified catalysts; metal center is not electron-rich enough for the nucleophilic attack. Schematic illustration of the concerted transition states are presented in Fig. 4. The calculated activation parameters are presented in Table 1.

Activation energies of the different reactions vary. Our results in Table 1 show that the total energy barriers to the *cis*- and *trans*-forms of the catalysts are very similar and the *cis–trans* difference is less significant here than in the original catalysts. This is due to lack of the orbital effects that were found in the default catalysts [9] where in the transition state of the oxidative addition the *trans*-form of the active species has a clear linear bonding overlap with the methyl iodide orbitals whereas in the *cis*-system the transition state has a twisted structure and poorer overlap; the lack is caused by the concerted transition states that have very different symmetry than in S_N2 transition states. In the *trans*-systems, there are slightly greater negative entropy change than in the *cis*-systems which make the free energy barriers slightly higher in the oxidative additions to the *trans*-species. In the systems studied, the ligands have a large effect on the activation energies. To put the different phosphine ligands in order according to their donor capability, we have investigated the CO-stretching modes of the different structures, which are presented in Table 2. The analysis here is based on the assumption that when there are electron-donors present, the metal center is electron-rich. This allows the more efficient metal–ligand back-bonding effect that strengthens the C–O-bonds which is shown as the lowering of the CO-stretching modes. According to the previous, we order the ligands in the following way according to their donor capability: $PF_3 < PCl_3 < PBr_3 < PI_3 < PH_3 < P(CH_3)_3$. First, the lack of the transition state in $[Rh(CO)_2(PF_3)_2]^+$ can understood with poor donor capability when compared to other phosphines used. In the other systems studied, the transition states exist and analysis can be made according to the donor capabilities of the ligands and their

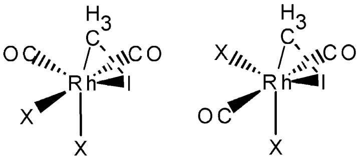

Fig. 4. The schematic illustration of the concerted transition states for the oxidative addition of CH_3I to *cis*- and *trans*-$[Rh(CO)_2X_2]^+$ ($X = PH_3$, PCl_3, PBr_3, PI_3 or $P(CH_3)_3$).

Table 1
Activation parameters of the oxidative additions studied. The values are given in kcal mol^{-1}. Total energy values include zero-point corrections. Superscript ‡ denotes for activation parameter. Activation parameters for $[Rh(CO)_2I_2]^-$ are from Refs. [9] (computational) and [3] (experimental)

Oxidative addition of CH_3I to	$\Delta E^{\ddagger}$	$\Delta G^{\ddagger}$
trans-$[Rh(CO)_2I_2]^-$	10.4	15
cis-$[Rh(CO)_2I_2]^-$	16.3 [a] 12–17 [b]	20.8 [a] ∼25 [b]
trans-$[Rh(CO)_2(PH_3)_2]^+$	28.7	40.3
cis-$[Rh(CO)_2(PH_3)_2]^+$	28.6	40.1
trans-$[Rh(CO)_2(PCl_3)_2]^+$	8.2	20.1
cis-$[Rh(CO)_2(PCl_3)_2]^+$	8.9	19.9
Trans-$[Rh(CO)_2(PBr_3)_2]^+$	11.5	24.7
cis-$[Rh(CO)_2(PBr_3)_2]^+$	12.2	24.2
Trans-$[Rh(CO)_2(PI_3)_2]^+$	14.8	28.0
cis-$[Rh(CO)_2(PI_3)_2]^+$	15.1	27.3
Trans-$[Rh(CO)_2(P(CH_3)_3)_2]^+$	33.0	46.2
cis-$[Rh(CO)_2(P(CH_3)_3)_2]^+$	32.9	45.3

[a] Computational.
[b] Experimental.

Table 2
The calculated wave numbers of the CO-stretching modes for the *cis*- and *trans*-$[Rh(CO)_2X_2]^+$ ($X = PH_3$, PF_3, PCl_3, PBr_3, PI_3 or $P(CH_3)_3$). $\nu_{(CO)sym}$ is the symmetric stretch and $\nu_{(CO)antisym}$ the antisymmetric stretch

Species	$\nu_{(CO)sym}$	$\nu_{(CO)antisym}$
trans-$[Rh(CO)_2(PH_3)_2]^+$	2082.7	2007.1
cis-$[Rh(CO)_2(PH_3)_2]^+$	2071.0	2022.9
trans-$[Rh(CO)_2(PF_3)_2]^+$	2139.0	2086.1
cis-$[Rh(CO)_2(PF_3)_2]^+$	2126.9	2094.3
trans-$[Rh(CO)_2(PCl_3)_2]^+$	2116.4	2059.5
cis-$[Rh(CO)_2(PCl_3)_2]^+$	2100.7	2064.4
trans-$[Rh(CO)_2(PBr_3)_2]^+$	2104.0	2043.8
cis-$[Rh(CO)_2(PBr_3)_2]^+$	2087.4	2048.1
trans-$[Rh(CO)_2(PI_3)_2]^+$	2081.9	2021.4
cis-$[Rh(CO)_2(PI_3)_2]^+$	2073.2	2030.7
trans-$[Rh(CO)_2(P(CH_3)_3)_2]^+$	2040.9	1965.6
cis-$[Rh(CO)_2(P(CH_3)_3)_2]^+$	2046.9	1994.8

steric effects. According to the data of the Table 2, the *cis*- and *trans*-forms of the species have very similar donor capability and, as mentioned earlier, the transition states of the additions both to *cis*- and *trans*-forms have similar structures. The previous also explains the similar activation energies to the *cis*- and *trans*-species. When comparing the activation barriers to the data of the Table 2, we see that the barriers do not solely depend on the donor capability of the phosphine. The lowest activation energies calculated, are for the PCl_3. For PBr_3 and PI_3 which are stronger donors, the barriers are slightly higher. Here the steric effects of the ligands raise the barriers, consecutively. The highest activation energy calculated, is for the $P(CH_3)_3$-modified catalyst. Although this ligand is strongest electron-donor, its steric effect raises the activation energy, especially because of the concerted addition mechanism. Interestingly PH_3-ligand that is a strong donor and has low steric effect, has larger activation energy than PCl_3, PBr_3 and PI_3-modified catalysts although the latter ligands have lesser donor capability and larger steric effects. To explain this phenomenon, we compared the PI_3- and PH_3-modified catalysts by comparing energy values $E_{TOT}([Rh(CO)_2(PI_3)_2]^+ + 2*E_{TOT}(PH_3)$ and $E_{TOT}([Rh(CO)_2(PH_3)_2]^+ + 2*E_{TOT}(PI_3)$. This calculation shows the PH_3-modified catalyst to be relatively more stable structure than PI_3-modified species. In addition, we compared Rh–P bond length in the catalyst complex and the transition state of the oxidative addition. In the of the PH_3-modified catalyst, the Rh–P bond lengthens less than it lengthens in the case of the other phosphines, also indicating stronger binding of the PH_3 ligands to the metal center. From these, we can conclude that in the system under study, PH_3 ligand is too strong donor for this reaction leading to high activation energy in the oxidative addition. Important feature in our results is that for PCl_3- and PBr_3-modified catalysts, the activation energies are smaller than for the experimentally observed *cis*-$[Rh(CO)_2I_2]^-$.

From the computational point of view the BSSE, in general, is not very large in these systems. It raises the activation energies from ~1.5 to ~4 kcal mol^{-1}, so the BSSE is not very significant in the systems studied.

4. Conclusions

We have studied a set of simple phosphine modified catalytic species *cis*- and *trans*-$[Rh(CO)_2X_2]^+$ ($X = PH_3$, PF_3, PCl_3, PBr_3, PI_3 or $P(CH_3)_3$) and the oxidative addition of CH_3I to them. Our goal has been to see if some enhancements for the industrially important Monsanto process could be found. Our idea of these calculations is based on the experimental study of the catalytic cycle, where the iodides of the default catalyst of the Monsanto process have been replaced affecting the total charge of the catalyst.

Our results show that the phosphine modified complexes studied here are quite fluxional but the energy differences between the different conformations are not large. Calculations performed here verify our original assumption that with increasing ligand size, the *trans*-forms are relatively more stable than the *cis*-forms.

The oxidative additions with the modified catalysts show concerted mechanisms instead of S_N2. As mentioned earlier in Section 3.2, this is effect of the net positive charge of the complexes studied. As with the original catalyst $[Rh(CO)_2I_2]^-$ of the Monsanto process, also here the oxidative additions to the *trans*-forms have slightly lower total energy barriers than to the *cis*-forms, although the differences here are much smaller due lack of the orbital effects observed in the original catalysts [9] which is introduced by the concerted transition states. In general and more importantly, ligand donor capability and ligand size seem to affect greatly on the activation energies. The donor type ligands seem to lower the barrier but with increasing ligand size the barriers rise due to the steric effects of the ligands that becomes important by the concerted mechanisms. Also in the case of the $[Rh(CO)_2(PH_3)_2]^+$ that has low steric effect, the phosphine ligand shows to be too strong donor for the reaction.

From these results, we can propose that some of the ligands studied here, could provide enhancements for the industrially important Monsanto process. When suitable combination of the ligand donor capability and the ligand size is selected, the *trans*-forms of the active species are more stable and also in the concerted mechanisms, they seem to result in lower activation energies than the corresponding *cis*-structures. In this study, both the *cis*- and *trans*-forms of the PCl_3- and PBr_3-modified catalysts result in lower activation energies for the experimentally observed *cis*-$[Rh(CO)_2I_2]^-$. The next step in the catalyst modification could be the restoration of the net negative charge for the catalyst complex. By this way, the S_N2-mechanism could be obtained for the oxidative addition.

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