Coordination of α,β-unsaturated aldehydes on d^6 Ru and Rh complexes: A DFT study

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Abstract

The coordination modes of various α,β-unsaturated aldehydes on d^6 ML_4 and ML_5 complexes of rhodium and ruthenium have been compared by means of density functional theory (DFT) calculations. The studied aldehydes were acrolein, crotonaldehyde, prenal and cinnamaldehyde and the metallic fragments $RuH_2(PH_3)_2$, $RuH_2(PH_3)_3$ and $RhH_2Cl(PH_3)_2$. On the d^6 ML_4 Ru fragment, the best coordination geometry is η^4, where both double bonds are involved. On the d^6 ML_5 Ru fragment, the η^2CC geometry is preferred to the η^1O and to the η^2CO ones. Finally on the d^6 ML_5 Rh fragment, the η^2CO mode is not stable and only η^1O and η^2CC exist, the former being favored. In conclusion, the η^2CO coordination geometry is never favored even if the energy gap between η^2CC and η^2CO is reduced by the use of bulky ligands (PPh_3) or alkyl substituents on the C=C bond. The Ru and Rh complexes behave differently: in the case of Ru, η^2CC and η^2CO can be in competition and in the case of Rh, the best form is η^1O. This different behavior can explain the results obtained in the hydrogenation reaction of α,β-unsaturated aldehydes.
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Keywords: Unsaturated aldehydes; Complexes; Ruthenium; Rhodium; DFT calculations

1. Introduction

The hydrogenation of α,β-unsaturated aldehydes is of great importance in industry particularly for fragrance and pharmaceutical production. These aldehydes can lead selectively to unsaturated alcohols or to saturated aldehydes depending on their structures and on the catalyst nature. In homogeneous catalysis, a lot of various catalysts have been tested to obtain selectively the unsaturated alcohols that are the most useful products. It has been observed that ruthenium complexes give rather the unsaturated alcohols and rhodium complexes rather the saturated aldehydes [1]. Moreover, in the last 10 years, the use of a biphasic medium has largely improved the selectivity to the unsaturated alcohols [1,2]. In order to understand the origin of the selectivity and the role of the metallic com-

plex, it is necessary to know how an unsaturated aldehyde coordinates to a metallic fragment.

Such molecules possess two double bonds which can interact with the metal and also an oxygen atom with lone pairs. Therefore, four possibilities exist for the coordination: η^2CC (or π_{CC}), η^2CO (or π_{CO}), η^4 and η^1O (or σ) as illustrated in Scheme 1.

The coordination of alkenes in organometallic chemistry has been widely studied both experimentally and theoretically since Hoffmann's work [3–5]. The coordination of simple aldehydes and ketones, although less studied, has given rise to some theoretical studies [6–9].

The experimental structure of the α,β-unsaturated aldehyde complexes has been investigated since a long time. The coordination depends on the metal and on the ligand nature. In most of these complexes, the aldehydes are η^2CC or η^1O bound. As examples of η^2CC coordination, one can cite Ni and Fe complexes [10–12] and as examples of η^1O coordination Fe, Rh, Ir and W complexes [13–16]. A study of the dependence of the η^2 versus η^1 coordination
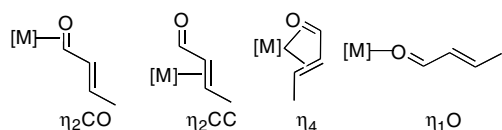
Scheme 1. Various coordination geometries of an unsaturated aldehyde on a metallic fragment.

on the metal and ligand nature appeared recently [17]. Depending on the number of ligands, the coordination can change from η^2CC to η^4 [18–20]. In rare cases the η^2CO coordination has been found with Re and Os complexes [21,22]. In these cases, the η^2CO complex is the kinetic one, which means that it is produced first and is transformed into the thermodynamic complex η^2CC. As far as we know, very few theoretical studies have been done on the complexes of α,β-unsaturated aldehydes: an Extended Hückel one on Fe(CO)$_4$L(η^4enone) [23] and density functional theory (DFT) calculations on Co(CO)$_3$-(acrolein) [24].

In the present work, we will give the results of DFT calculations on Ru and Rh complexes of acrolein (CH$_2$=CH−CHO), crotonaldehyde (CH$_3$CH=CH−CHO), prenal ((CH$_3$)$_2$CH=CH−CHO) and cinnamaldehyde (PhCH=CH−CHO). The catalysts often used for the hydrogenation reactions contain phosphine ligands and two hydrides [1]. Hence, we have focused our study on RuH$_2$(PH$_3$)$_2$(ald), RuH$_2$(PH$_3$)$_3$(ald) and RuH$_2$Cl(PH$_3$)$_2$(ald) where real phosphines have been modeled by PH$_3$.

2. Computation method

The calculations were based on the density functional theory (DFT) at the generalized gradient approximation (GGA) level. They were performed with the GAUSSIAN98 and GAUSSIAN03 codes [25]. We used the hybrid B3LYP functional. For the Ru, Rh, P and Cl atoms, we used the relativistic effective core potentials of Hay and Wadt (with 4s and 4p in the valence) and the corresponding double ζ basis set [26]. For P and Cl a d function was added (α = 0.37 and 0.6, respectively). For the other atoms, the Dunning–Huzinaga valence double-ζ basis set was used with polarization d functions on C and O (D95V*) and polarization p functions on the two hydrides (D95V**). The geometries were fully optimized using the gradient technique. In some cases, the complexes with real ligands (PPh$_3$) have been calculated using the QM/MM method as implemented in the GAUSSIAN code (ONIOM) [27].

3. The d^6 ML$_5$ RuH$_2$(PH$_3$)$_2$(ald) complexes

The coordination of a ligand on the RuH$_2$(PH$_3$)$_2$ fragment can yield several isomers depending on the position of the ligands. Various isomers of the complexes formed by coordination of formaldehyde (CH$_2$O) or ethylene (C$_2$H$_4$), models for C=O and C=C bonds, have been first considered. A d^6 ML$_5$ complex can have either a trigonal

bipyramid (TBP) or a square pyramid (SP) structure. During the geometry optimization, the TBP geometry of RuH$_2$(PH$_3$)$_2$(CH$_2$O) evolved to the SP geometry as shown in Scheme 2 in agreement with the structure of most d^6 ML$_5$ complexes [27]. The trend is enhanced here by the better overlap of π^*_{CO} with the HOMO of the SP geometry (d_{xy}) than with the HOMO of the TPB geometry ($d_{x^2-y^2}$).

Various positions of the ligands have been tested for the SP structure as well as different orientations of the formaldehyde moiety. The best isomers are those where one H is axial in agreement with the observation that the most donor ligand (here the hydrides) occupies the axial direction [28]. Hence, the two possible isomers are 1 and 2 depicted in Fig. 1.

The phosphine ligands prefer to be *trans* to each other. Effectively, it is energetically unfavorable for two σ-donor ligands to share the same metal orbital [29]. Since H is a much stronger σ-donor than a phosphine, the *trans* arrangement of phosphines is better than the *trans* arrangement of one H and one phosphine or of two H. Hence the metallic RuH$_2$(PH$_3$)$_2$ fragment in 1 is more stable than in 2 by 38 kJ/mol. The LUMO of the RuH$_2$(PH$_3$)$_2$ fragment in 2 is developed *trans* to the phosphine (see Scheme 3) so that the fifth ligand (here formaldehyde) prefers to coordinate in this position rather than *trans* to the hydride. The orbitals of the metallic fragment in 1 are higher than in 2. Therefore, the donation from the π_{CO} orbital to the metal LUMO is weaker and the back-donation to π^*_{CO} from the metal HOMO is stronger in 1 than in 2. The balance between these two effects results in a better interaction in 2 than in 1, which reduces the gap to only 4 kJ/mol, 1 remaining the most stable. This better interaction in 2 is reflected in the bond lengths: the Ru–C and Ru–O bonds are shorter and the C–O bond is longer in 2.
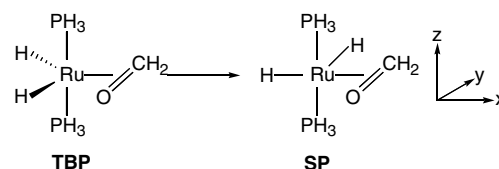
Scheme 2. Evolution of the trigonal bipyramid (TBP) to the square pyramid (SP) geometry for complex RuH$_2$(PH$_3$)$_2$(CH$_2$O).
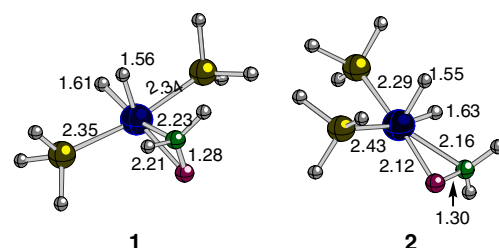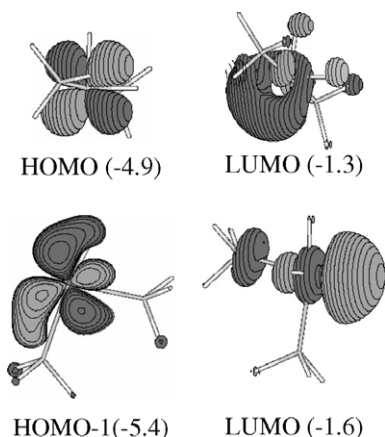

Fig. 1. Coordination geometries of formaldehyde on RuH$_2$(PH$_3$)$_2$. Bond lengths in Å.

Scheme 3. Interacting metal orbitals for **1** (top) and **2** (bottom). Energies in eV.

In **1** the C=O bond is parallel to the axial direction (the basal position being 6 kJ/mol less stable) and in **2** it is in the basal plane (the axial position being 23 kJ/mol less stable). In each case, the orientation of C=O allows the interaction of an occupied orbital of the metallic fragment with π^*_{CO} (HOMO in the case of **1** and HOMO − 1 in the case of **2**, the HOMO being in the HRuH plane). The role of this type of interactions in the orientation of a π ligand has already been pointed out [3]. Moreover, there are two possible orientations with the oxygen atom pointing towards the hydride or in the opposite direction. In the case of **2**, the latter is the most stable by 29 kJ/mol. In the case of **1**, the orientation with the oxygen atom towards the hydride does not exist and evolves to the position in the basal plane during the optimization. In **1**, when O is directed towards H, a negative overlap population exists between them, indicating a repulsive interaction. In the other orientation, with the carbon towards H, the C–H overlap population is positive. This partly explains the orientation in **1**. However one cannot exclude a possible dipole–dipole interaction between the Ru–H bond and the C=O bond, attractive or repulsive depending on the orientation. In **2**, the repulsive effect is not as strong when O is directed towards H (small positive overlap population) and this orientation is stable. This is due to the fact that the s orbital of the hydride is more delocalized in **2** than in **1** by the presence of the *trans* phosphine.

In the case of the η^1 coordination of formaldehyde through the oxygen atom, the **SP** geometry is also preferred and the best isomer has the oxygen atom *trans* to a phosphine. Such a complex is less stable than **1** by 39 kJ/mol. Effectively, the LUMO of the metallic fragment is high and hence the energy difference between this LUMO and the oxygen lone pair is larger than the energy difference between the HOMO of the metallic fragment and π^*_{CO}, which induces a stronger interaction in the latter case and explains the stability of the η^2 form compared to η^1. This result confirms those obtained with semi-empirical calculations [9].

The various possible complexes of ethylene have also been considered. Similarly to formaldehyde, the **SP** geometry is favored. Two isoenergetic structures were found and are depicted in Fig. 2.

The π_{CC} and π^*_{CC} orbitals are higher in energy than the π_{CO} and π^*_{CO} ones. Hence, the interaction of π_{CC} with the LUMO of the metallic fragment becomes important. The LUMO of the metallic fragment being lower in **4**, this isomer is favored. For the same reason as before, ethylene is *trans* to a phosphine in this isomer. One notices the same geometry difference between **3** and **4** as between **1** and **2**: the coordination of ethylene in **4** is stronger.

Contrary to the case of formaldehyde, the C=C bond is in the basal plane for both structures. In **3**, positive overlap populations exist between the carbons and the phosphorous atoms when ethylene is in the basal plane. On the contrary, when ethylene is perpendicular to this plane, these overlaps are negative, which indicates repulsive interactions. The shape of the orbitals depicted in Scheme 4 explains this result. For each orientation, the low-lying occupied orbital having the largest coefficient on the phosphorous atoms and on ethylene is represented. On the left (ethylene perpendicular to the basal plane), one observes an antibonding combination of the π orbital with the phosphorous atoms. On the right (ethylene in the basal plane), there is, on the contrary, a bonding combination between π^* and the phosphorous atoms. Due to the higher energy of the π^*_{CC} orbital compared to π^*_{CO}, the interaction of the metallic HOMO with π^*_{CC} plays a smaller role in the determination of the molecule orientation than in the case of the C=O bond and the destabilizing interactions are dominant.
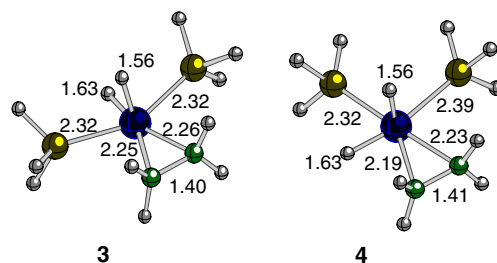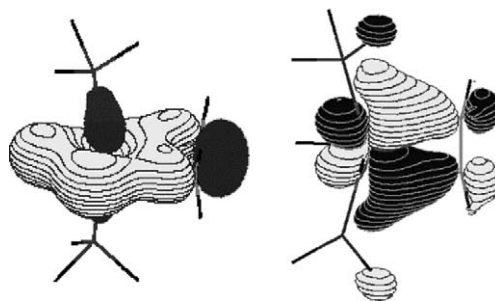

Fig. 2. Coordination geometries of ethylene on RuH$_2$(PH$_3$)$_2$. Bond lengths in Å.

Scheme 4. Low-lying occupied orbitals of **3** having the largest coefficients on the phosphorous atoms and on ethylene: on the left, with ethylene perpendicular to the basal plane; on the right, with ethylene in the basal plane.

Table 1
Energy of the coordination modes of acrolein, crotonaldehyde, prenal and cinnamaldehyde (in kJ/mol) relative to the most stable one (η^4)

	$\eta^1 O$	$\eta^2 CC$	$\eta^2 CO$	η^4
Acrolein	66	7	55	0
Crotonaldehyde	52	8	40	0
Prenal	28	2	18	0
Cinnamaldehyde	49	8	37	0

In the case of formaldehyde, these destabilizing interactions also exist but the stabilizing interaction between the HOMO and π^*_{CO} is the dominant factor. Moreover, for the orientation in the basal plane, only the overlap population between C and P is positive, the one between O and P being negative. Hence, the latter orientation is less favored than in the case of ethylene. To conclude, the orientation of the molecule depends on the balance between two effects: the interaction cited above between a high lying metallic occupied orbital and π^* and the destabilizing four-electrons interactions between ligands that occur through low-lying occupied metal orbitals. Such interactions have already been pointed out in our semi-empirical study [9].

The results obtained for the complexes of ethylene and formaldehyde are in agreement with the previous extended
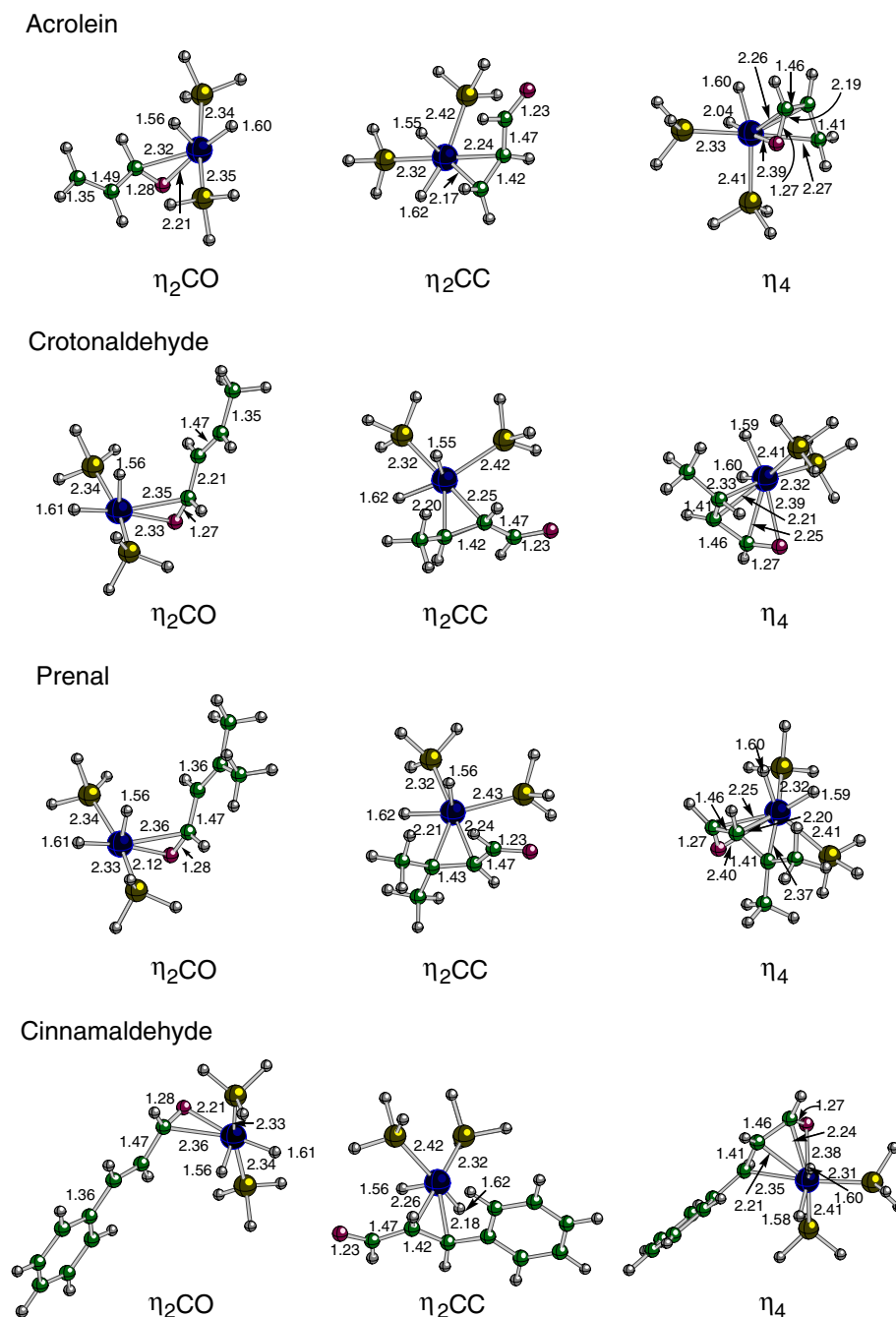

Fig. 3. $\eta^2 CO$, $\eta^2 CC$ and η^4 geometries for the coordination of acrolein, crotonaldehyde, prenal and cinnamaldehyde on RuH$_2$(PH$_3$)$_2$. Bond lengths in Å.
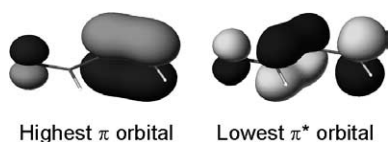
Hückel calculations [28] which state that, in **SP** d^6 ML$_5$ complexes, the donor ligands (H) prefer the axial position and the acceptor ligands (C=O or C=C) the basal position. As predicted also, the **SP** geometry is flat.

Let us consider now the coordination of the α,β-unsaturated aldehydes. For each, an exhaustive study of the possible structures has been done: several ligand positions and several orientations of the molecule have been tested. The η^{1}O coordination is never favored and the η^{2}CC coordination is always more stable than the η^{2}CO one. Finally, the most stable geometry is the η^4 one where both the C=C and the C=O bonds interact with the metal. The results are summarized in Table 1 and the geometries of the various complexes are given in Fig. 3.

For the η^{2}CO and η^{2}CC forms, the same ligand arrangement is found as for formaldehyde and ethylene, i.e. phosphines in *trans* position and C=O perpendicular to the basal plane and phosphines in *cis* position and C=C in the basal plane. One of the hydrides is always axial. For the η^4 geometry, the best isomer respects also the trends observed previously: the hydrides are *cis* with one of them in the apical position, the C=O bond is *trans* to a hydride and the C=C bond is *trans* to a phosphine.

When going from acrolein to prenal, a stabilization of the η^{1}O and η^{2}CO forms relative to η^{2}CC or η^4 is observed. When the molecule is substituted by donor groups like methyls in crotonaldehyde and prenal, all the orbitals are shifted toward higher energy. Hence, the interactions of the oxygen lone pairs or of the π orbitals with a metal vacant orbital are stronger and, in contrast, the interactions between the metal occupied orbitals and the π* orbitals are weaker. This explains the stabilization of the η^1 form. The highest π orbital and the lowest π* orbital of acrolein are represented in Scheme 5. They are delocalized over the C=C and C=O bonds. Those of crotonaldehyde and prenal are similar. The π orbital is more localized on C=C and the π* orbital is equally distributed on C=C and C=O. Hence the interaction of the metal occupied orbital with π* equally favors the η^{2}CC and the η^{2}CO coordination. The interaction of π with the vacant metal orbital contributes to favor the η^{2}CC geometry. The shift up of the orbitals toward higher energy would lead to a better interaction of the C=C bond (via π) and to a stabilization of both the η^{2}CC and η^4 geometries. This is not the case because of steric effects of the methyl groups that hinder the C=C coordination. The role of through-bond and through-space destabilizing interactions has already been pointed out in earlier study [9].

The effect of the phosphine nature on the relative stability of the forms has been tested with crotonaldehyde. The replacement of PH$_3$ by PMe$_3$ gives slightly different relative energies. The η^{2}CO geometry is less stable than the η^{2}CC one by 26 instead of 32 kJ/mol. PMe$_3$ being more electron-donor, the orbitals of the metallic fragment are higher in energy. Their interaction with the π* orbital is better which favors equally η^{2}CO and η^{2}CC. On the contrary, the interaction of the π orbital with the metal LUMO is weaker, which is unfavorable to η^{2}CC. The two effects add. With PPh$_3$ as ligands, the difference decreases to 17 kJ/mol. In that case, only the steric effects are taken into account since the phenyl groups are treated in molecular mechanics (MM).

4. The d^6 ML$_6$ RuH$_2$(PH$_3$)$_3$(ald) complexes

We have first compared various isomers of the d^6 ML$_5$ RuH$_2$(PH$_3$)$_3$ fragment (Scheme 6).

By optimization, **7** evolves to **5**, since having two hydrides *trans* to each other is not a favorable situation. **5** and **6** give geometries close to the ideal ones as shown in Fig. 4. **6** is less stable than **5** by 39 kJ/mol, since we have seen before that H prefers the apical position. The comparison of **5** and **6** is a good illustration of the *trans* influence (Fig. 4): in **6** there is no *trans* influence for the apical phosphine and the Ru–P distance is the smallest (2.21 Å). In **5** one observes the known stronger *trans* influence of H compared to PH$_3$, since the Ru–P bond *trans* to the hydride is longer (2.39 versus 2.32 Å).

On the fragments **5** and **6**, formaldehyde and ethylene have been coordinated in various orientations, as illustrated in **8**–**11** (Scheme 7).
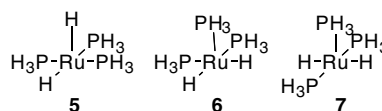
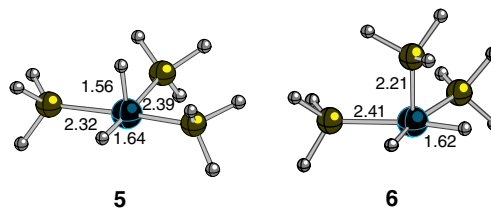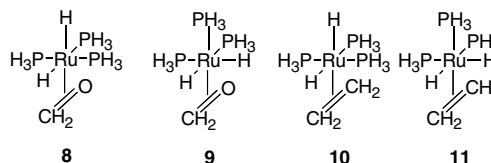Scheme 6. Various isomers of the RuH$_2$(PH$_3$)$_3$ fragment.

Fig. 4. Optimized geometries of the most stable RuH$_2$(PH$_3$)$_3$ fragments.

Scheme 7. Various isomers for the coordination of formaldehyde and ethylene on the RuH$_2$(PH$_3$)$_3$ fragment.

Scheme 5. Frontier orbitals of acrolein.

8 is more stable than **9** and **10** is more stable than **11** by 24 and 16 kJ/mol, respectively, which reflects the relative stability of **5** and **6**. In both cases, the unsaturated ligand prefers to be *trans* to the hydride and parallel to the H–Ru–P bond. This is explained in **8** and **10** by the nature of the HOMO (d_{yz} in the HHP plane).

Crotonaldehyde has been chosen in the following as model for α,β-unsaturated aldehydes because its hydroge-

nation has been studied extensively. Coordinations η^1O, η^2CC and η^2CO have been considered on fragments **5** and **6**. For the η^2 coordination, many isomers have been compared differing by the orientation of the molecule as illustrated in Fig. 5. In all cases, the molecule prefers to coordinate *trans* to the hydride, following the stability order of **5** and **6**. As do ethylene and formaldehyde, the C=C and C=O bonds prefer to be parallel to the H–
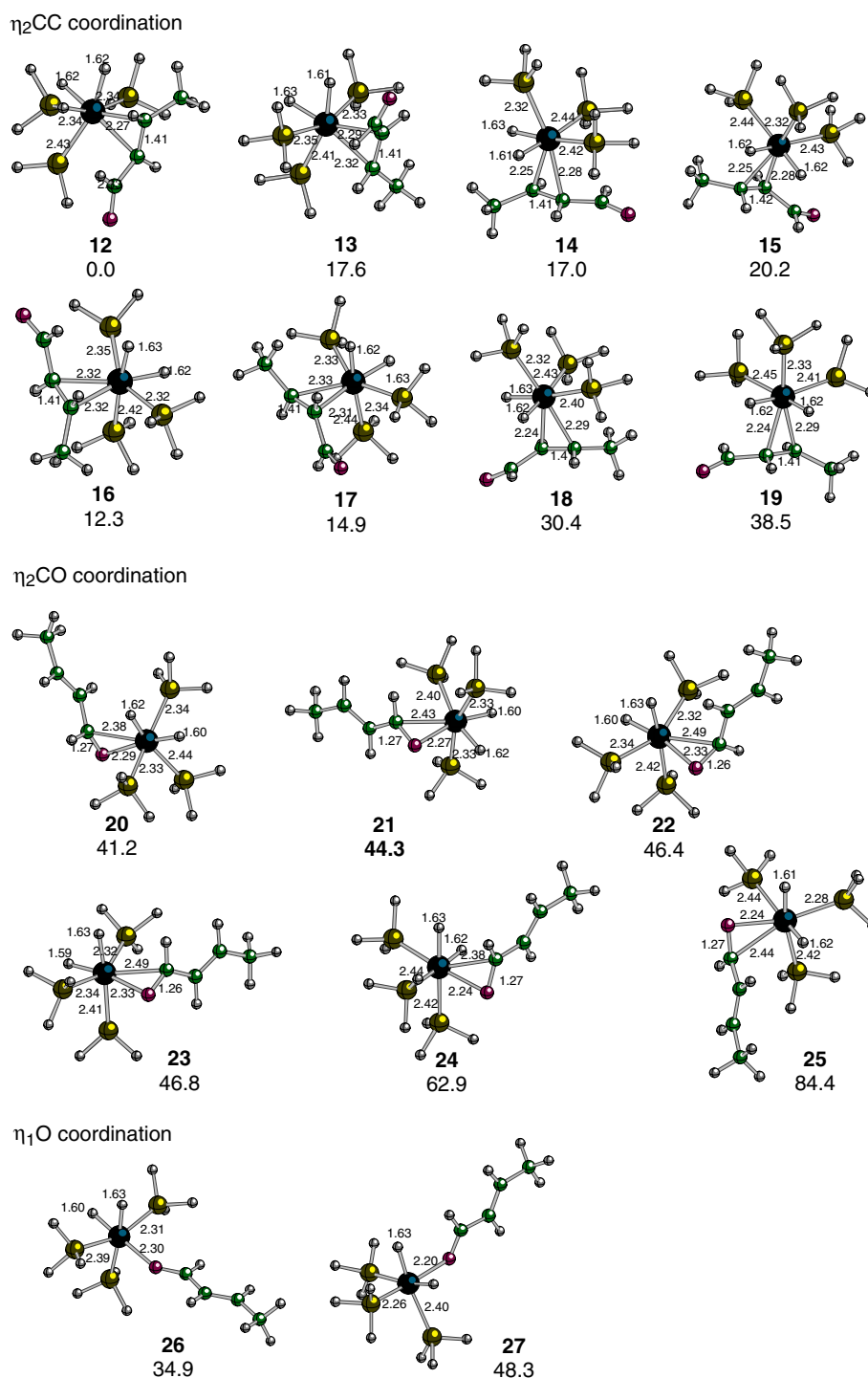

Fig. 5. Various geometries for the coordination of crotonaldehyde on RuH$_2$(PH$_3$)$_3$. Bond lengths in Å, relative energies in kJ/mol.

Ru–P direction rather than to the P–Ru–P direction. In the case of η^2CO coordination, the oxygen atom prefers to be opposite to H. The relative energies of all the structures are given in the figure. The most important feature is that all η^2CC geometries are more stable than all η^2CO ones, the difference between the most stable of each type being 41 kJ/mol. As before, the shape of the molecule orbitals explains this general preference for the η^2CC coordination.

The best isomers for the η^1O geometry are **26** and **27**, which differ by 13 kJ/mol. The stability order of fragments **5** and **6** is respected although the difference is reduced. The reason is that the LUMO of **6** is lower in energy than the one of **5**, which results in a better interaction with the oxygen lone pair. Due to the *trans* influence, the coordination *trans* to the hydride corresponds to a longer Ru–O bond than *trans* to a phosphine (2.30 versus 2.20 Å). The η^1O coordination is more stable than the η^2CO one by 6 kJ/mol. We saw above that the inverse is true for the coordination on $RuH_2(PH_3)_2$ for which the η^2CO form is more stable than the η^1O one by 12 kJ/mol. The HOMO of $RuH_2(PH_3)_2$ is higher than the one of $RuH_2(PH_3)_3$, which gives a better interaction with π^*_{CO}. Moreover beside electronic factors, the steric effects also play an important role, as we have pointed out before. These steric effects are larger in the ML_6 than in the ML_5 complex, which favors the η^1O coordination. In fact, the experimental aldehyde complexes on ML_5 fragments are usually η^1O.

The effect of the ligand nature on the energy difference between η^2CC and η^2CO has also been checked. If the phosphines PH_3 are replaced by PMe_3, the difference between **12** and **20** is only reduced to 36 kJ/mol. The reason is the same as before (higher HOMO). The replacement of PH_3 by PPh_3 has also been considered with the phenyls treated at the MM level. Some of the isomers shown in Fig. 5 are not stable and evolve to ML_5 $RuH_2(PPh_3)_2$(crotonaldehyde) by decoordination of a phosphine. However, the energy difference between the most stable isomers for the η^2CC and the η^2CO coordination (corresponding to **12** and **20**) is only 16 kJ/mol. The η^1O coordination has also been calculated with PPh_3. It is isoelectronic with η^2CO. However, with the QM/MM method, the electronic properties of the phenyl substituents are not taken into account, which can bias the result.

In conclusion, the nature of the ligands and particularly their size, plays an important role in the relative stability of the η^2CC and η^2CO coordination modes of crotonaldehyde on a $RuH_2(PR_3)_3$ fragment. This follows the trend already observed for simple aldehydes and ketones [9].

5. The d^6 ML_6 $RhH_2Cl(PH_3)_2$(ald) complexes

The RhH_2ClL_2 fragment has already been calculated by Dedieu et al. [4] in the study of the olefin hydrogenation. Three possible isomers **28–30** have been optimized (Scheme 8), with either the donor ligands H or Cl in the apical position, the isomer having the phosphine at the apical position
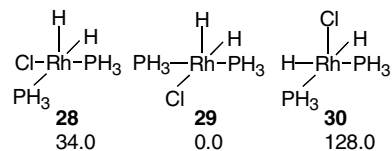
Scheme 8. Various possible isomers of the $RhH_2Cl(PH_3)_2$ fragment. Relative energies in kJ/mol.

giving **28** during the optimization. The best isomer **29** has H and Cl *trans* to each other as found in the case of Ru complexes. The strong σ-donor H prefers to be *trans* to the cylindrical π donor Cl than to a good σ-donor phosphine, which leads to the favorable *trans* arrangement of phosphines.

There are some differences with the results of Dedieu because his fragments were not optimized. Nevertheless the same trend is observed. After optimization, fragment **29** does not keep the **SP** geometry but evolves to a Y-shaped geometry (symmetry C_{2v}) with a HRhH angle of 64°. The same structure has been found by Morokuma et al. [30]. A qualitative analysis based on EHT calculations [31] has shown that such a structure is favored over the **SP** one when a poor σ-donor and good π-donor is *trans* to the acute angle, which is the case of Cl in **29**. The strong σ-donor H ligand prefers the apical position and the π-donor Cl ligand prefers the basal position, following Hoffmann's rules [27], hence **30** is far less stable than **29**.

The coordination of crotonaldehyde has been examined on these fragments. A lot of various structures have been considered, depending on the ligand nature *trans* to the aldehyde and on the orientation of the molecule. For each type of metallic fragment, the best geometries for the C=C and C=O coordination are given in Fig. 6. The η^2CO coordination is stable only in the case of **34** even if the Rh–C distance is long (2.52 Å). In all the other cases, this coordination evolves during the optimization to the η^1O coordination by the oxygen atom. The stability order of **38** and **32** reflects the one of the fragments **28** and **29**. Isomer **36** corresponds to the non stable fragment where PH_3 is apical and it is far in energy. The best isomer for the η^2CC coordination **37** corresponds also to the most stable fragment **29**, with H *trans* to Cl and the two phosphines *trans* to each other. Isomer **38** where the coordination is η^1O is more stable than the best η^2CC isomer **37** by 27 kJ/mol.

Hence, the coordination of the α,β-unsaturated aldehydes on the two d^6 ML_5 fragments studied in this work, $RuH_2(PH_3)_3$ and $RhH_2Cl(PH_3)_2$, does not lead to the same preferred structure. In the latter case, the η^1O coordination is the most stable and the η^2CO coordination does not exist. In the former case, the η^2CC form is the most stable, followed by η^1CO and η^2O. This is due to the energetic position of the fragment orbitals. The orbitals of $RhH_2Cl(PH_3)_2$ are much lower (by 1 eV) than those of $RuH_2(PH_3)_3$. Hence, the interactions of the occupied metal orbitals with the vacant orbital of the molecule are weaker. The coordinations where these interactions are important
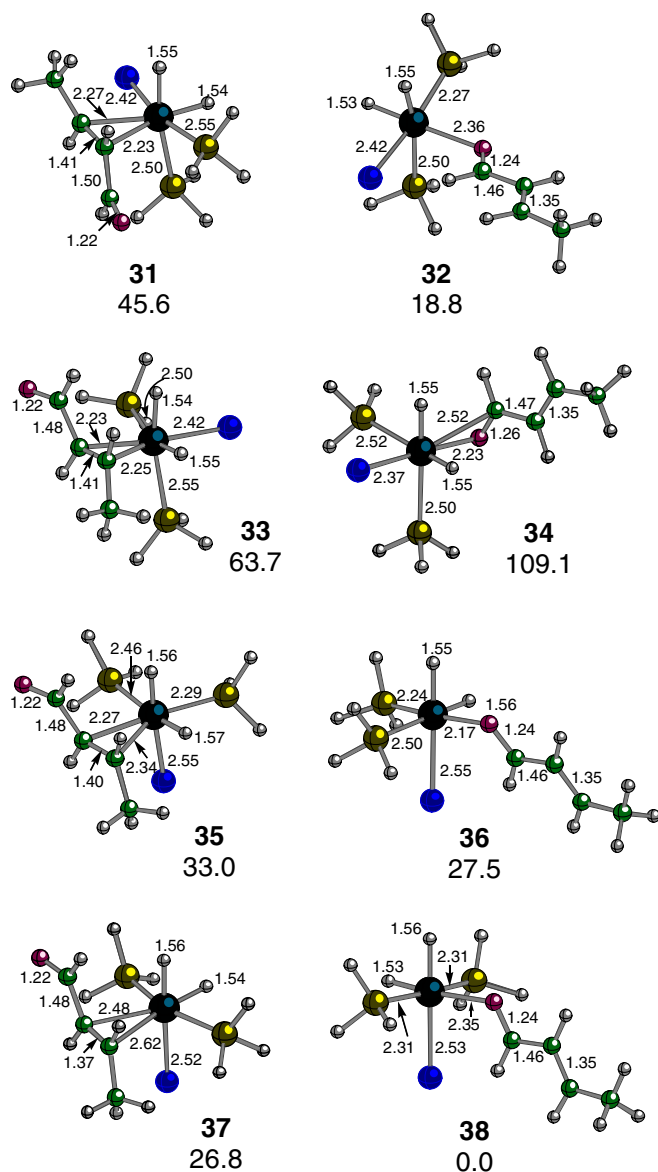
Fig. 6. Various geometries for the coordination of crotonaldehyde on $RhH_2Cl(PH_3)_2$. Bond lengths in Å, relative energies in kJ/mol.

(for example with π^*_{CC} or π^*_{CO}), are therefore less favored. On the contrary, the donation from the molecule into the metal vacant orbitals is stronger, which explains the stability of the η^1O geometry. These results confirm the previous semi-empirical ones [9] on the influence of the energy position of the fragments orbitals.

6. Conclusion

We have examined the coordination of various α,β-unsaturated aldehydes on Ru and Rh complexes and compared the relative stability of the four possible geometries: η^2CC, η^2CO, η^4 and η^1O. The substitution of the aldehyde (by methyls), the nature of the metal (Ru, Rh), the nature and the number of the ligands (PH_3, PMe_3, PPh_3) have a

great influence on the relative stability. The substitution of the C=C bond by methyls stabilizes the η^2CO and η^1O forms relatively to the η^4 and η^2CC geometries. The replacement of the model phosphines PH_3 by PMe_3 and more by PPh_3 reduces the gap between η^2CC and η^2CO. For the d^6 ML_5 $RuH_2(PH_3)_2$(ald) complex, the best geometry for all aldehydes is η^4. In the case of the d^6 ML_5 $RuH_2(PH_3)_3$(ald) complex, the η^2CC coordination is the most stable followed by η^1O and then η^2CO (for ald = crotonaldehyde). Finally, for the $RhH_2Cl(PH_3)_2$(ald) complex, the η^2CO geometry does not exist and the η^1O coordination is the most stable, even more than the η^2CC one.

Generally speaking, the η^2CO geometry is never preferred. The behavior of the Ru and Rh complexes is different. In the case of Ru, the best geometry is η^2CC even if, in some cases (substituted C=C bond and bulky ligands), the η^2CO geometry is not far in energy and in the case of Rh it is η^1O. This different coordination certainly plays a role in the selectivity of the hydrogenation of the α,β-unsaturated aldehydes and could explain the different experimental results.

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