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The mechanism of transition metal catalyzed carbonylation of allyl halides: A theoretical investigation

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Abstract

The mechanism of the carbonylation reaction of allyl halides catalyzed by nickel ($Ni(CO)_4$) and palladium ($Cl_2Pd(PPh_3)_2$) complexes is theoretically investigated at the DFT level using the hybrid B3LYP functional. The favored reaction path to carbonylation corresponds, for both catalysts, to a direct attack of the halogen on the metal. This affords η^1 intermediates that can undergo the final carbonylation step. It is also possible to obtain the acyl product (β,γ-unsaturated acyl halides) from η^2 and/or η^3 intermediates. However, in this case, the barrier of the rate-determining step to carbonylation is much higher. Since a channel on the potential surface connects rather easily the η^2 or η^3 intermediates to the η^1 intermediates, an alternative and competitive path leading to the acyl products can originate from the η^2 or η^3 intermediates, follow the $\eta^2/\eta^3 \rightarrow \eta^1$ transformation, then undergo the final carbonylation step.
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1. Introduction

The carbonyl group certainly represents one of the most versatile functional groups in organic synthesis. However, in spite of the great utility of carbonyl compounds, conventional organic synthesis does not provide many clean, high-yielding and efficient direct routes from appropriate precursors to aldehydes, esters, acyl halides or anhydrides.

An alternative way to obtain carbonyl compounds is represented by catalytic procedures involving transition metal complexes. Transition metal based carbonylation chemistry, after the pioneering work by Roelen [1] who discovered the hydroformylation of ethene catalyzed by cobalt tetracarbonyl hydride $HCo(CO)_4$, has seen exceptional progress in the last half century and the employment of direct catalytic processes leading to organic carbonyl compounds has been continuously increasing at both aca-

demic and industrial level. An extensive research program in carbonylation chemistry was carried out by Reppe and co-workers [2]. These authors developed the well-known Reppe carbonylation [2] that consists of the reaction of an olefin, acetylene or diene with CO and a nucleophile in the presence of transition metal carbonyl complexes. In all cases, high temperature (in the range 50–150°) and high CO pressure are required.

The basic features of carbonylation chemistry remained very much those of Roelen and Reppe discoveries for more than 20 years. Thus, these reactions usually require high temperatures and pressures, expensive autoclave equipment and large quantities of dangerous volatile and unstable catalysts such as $HCo(CO)_4$, $Fe(CO)_5$ and $Ni(CO)_4$.

During the last three decades, however, the work of many researchers, in particular Wilkinson, Heck and Tsuji [3], led to the development of new stable and effective catalysts based on rhodium and palladium. Also, new techniques such as phase transfer, could be employed. As a result, it is now possible to carry out many carbonylation reactions under mild conditions i.e., low temperature and

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pressure and using very small amounts of stable catalyst precursors such as Pd(PPh$_3$)Cl$_2$ and RhCl(CO)$_4$P(Ph$_3$)$_2$ [4]. These complexes are converted in situ into the real active catalyst.

A particular interesting aspect of the carbonylation chemistry, which will be the subject of this review, is its application to unsaturated substrates such as allylic systems. The use of these substrates represents a powerful synthetic tool that allows to obtain β,γ-unsaturated acyl derivatives.

A number of papers, where different transition metal complexes are used as catalysts in the carbonylation of allyl halides, have appeared in the literature [5–20]. This process can be catalyzed by nickel tetracarbonyl Ni(CO)$_4$ [6,15–23] and it was first reported by Chiusoli [6–15]. Room temperature and atmospheric or low (2–3 atm) CO pressures [17] can be used to carry out this reaction, but large amount of nickel tetra-carbonyl is required. The products are acyl halides in the presence of inert solvents, such as ethers or aromatic compounds. In alcohol and other solvents, the reaction proceeds up to the formation of the corresponding acids and esters, depending on the media. The nickel tri-carbonyl complex Ni(CO)$_3$, in equilibrium with the Ni(CO)$_4$ species, is postulated to represent the "active" form of the catalyst [24]. However, since the decomposition of Ni(CO)$_4$ into Ni(CO)$_3$ and CO is an endothermic process (by 22.1 kcal mol^{-1} in *n*-hexane solutions [25] and by 35 kcal mol^{-1} when measured using calorimetric techniques [26]), only a small amount of Ni(CO)$_3$ is probably available in the reaction medium.

Because of the hazardous nature of Ni(CO)$_4$, chemists have replaced in many cases the nickel catalyzed carbonylation with palladium catalyzed carbonylation [7–14], even if this reaction has the disadvantage of requiring a very high carbon monoxide pressure. However, since alternative techniques that avoid the direct manipulation of the toxic Ni(CO)$_4$ have been quite recently proposed, the use of nickel complexes has known a renewed interest. Moreto and co-workers [22,23] have applied a new synthetic approach to the Ni-mediated cyclocarbonylation of allyl halides and alkynes, a reaction reported some time ago by Chiusoli [17–19]. These authors have shown that, if π-allyl nickel complexes (the hypothesized key-species of the process) are previously prepared (following a procedure suggested by Mackenzie et al. [27]), cyclopentanones can be efficiently and selectively obtained without any handling of nickel carbonyl.

Regarding the use of palladium-based catalysts, Long and co-workers [28], during the sixties, carried out one of the first examples of palladium catalyzed carbonylation of allyl chlorides. These authors proved that, when allylic chlorides are heated under pressure with carbon monoxide in the presence of small quantities of π-allylic palladium chloride complexes, the formation of alk-3-enoilchlorides is observed. Furthermore, it was demonstrated that the reaction is catalyzed by palladium chloride PdCl$_2$ and even

by metallic palladium. In the same period Tsuji et al. [29] investigated the reaction of allyl chloride and allyl alcohol with CO in ethanol using PdCl$_2$ as catalyst and proved that the main product of the reaction is ethyl 3-butenoate. Other allylic compounds, such as allylic esters and ethers, were found to react in the same way. However, this reaction, although synthetically useful, requires high CO pressure and high temperature (as above mentioned), it is very slow and can provide only modest yields of carbonylation products.

Various alternative synthetic procedures have been proposed to correct the unfavorable features of the palladium catalyzed carbonylation and to find more practical routes characterized by low pressure and low temperature. Mllstein proved that low pressure and temperature can be used to carry out the carbonylation of (π-allyl)palladium complexes in the presence of carboxylic acid anions [30]. Tsuji and co-workers [31] reported that a smooth palladium catalyzed carbonylation can be accomplished for allylic carbonates. Murahashi and co-workers [32] described similar results for allyl phosphates and allyl acetates. Then, different reaction conditions and different techniques were proposed by several researchers to improve the palladium-catalyzed carbonylation of allylic systems [33–36]. For instance, a two-phase system using phosphine palladium complexes such as Cl$_2$Pd(PPh$_3$)$_2$ or phosphine-free disodium tetra-chloropalladate complexes Na$_2$(PdCl$_4$), was proposed by Okano and Okabe [37] to accomplish a palladium-catalyzed carbonylation of allylic halides under atmospheric pressure.

The commonly postulated catalytic cycle for the carbonylation of allyl halides is schematically represented in Scheme 1. After the formation of the "active" catalytic species from the starting complex, three major steps can be recognized: (1) the oxidative addition of allyl halides XCH$_2$–CH=CH$_2$ to the metal to form η^3, η^2 and/or η^1-allyl complexes; (2) the carbonylation step where a CO molecule formally inserts into a carbon–metal bond and metal–acyl complexes are obtained; (3) the reductive elimination, where the acyl product (acyl halide) and the regenerated catalyst are released.

A theoretical investigation of the mechanism of the above described synthetic routes to β,γ-unsaturated acyl derivatives has been recently carried out by our group at the DFT level [24,38,39]. The most important results are reported in this review. In particular we describe (i) the reaction of allyl bromide with CO in the presence of Ni(CO)$_4$; (ii) the reaction of allyl chloride with CO in the presence of Cl$_2$Pd(PH$_3$)$_2$.

Since in case (ii) our model-system clearly emulates a Pd(II) catalytic species, a few comments concerning the palladium oxidation state of the active catalytic complex are important. Even if the conversion of starting Pd(II) complexes to Pd(0) species is often postulated, there is no evidence that this process occurs whatever the reaction conditions are. For instance, a reducer [40] or suitable electrochemical techniques [41] are needed if Cl$_2$Pd(PR$_3$)$_2$ com-
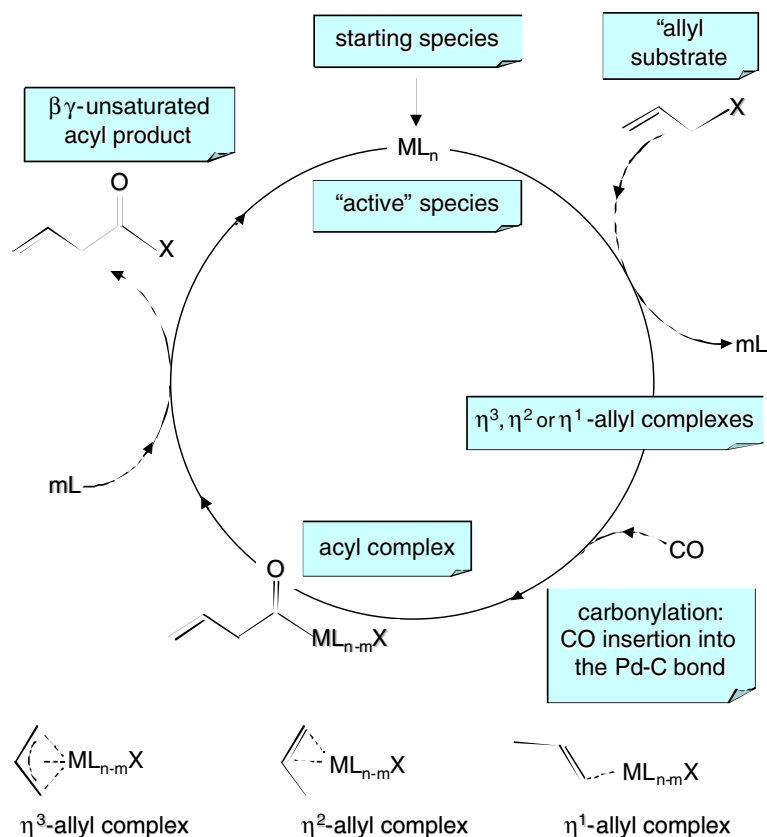
Scheme 1.

plexes are used as a source of Pd(0) species. Furthermore, some Pd(II) salts are reduced by phosphines only when oxygenated ligands or oxygenated substances are present in the reaction medium [42]. In many cases, it is difficult to establish the oxidation state of the active catalyst and several examples support the idea that the real catalyst is either a Pd(II) species or a Pd(0) intermediate [2,43–45]. On the other hand, a number of experimental results clearly point to a Pd(II) catalytic species. For instance, the deactivation of some Pd catalysts has been observed in the absence of a suitable stabilizer (these catalysts tend to decompose to Pd black or to form dinuclear complexes) [2]. Their activity is restored when they are treated with an acid HX, which is believed to stabilize Pd in the active divalent state as PdX_2 species [43–45].

Thus, an examination of the literature clearly indicates that the structure of the active species and its oxidation state have not been elucidated yet. It is reasonable to believe that, depending on the reaction conditions and the nature of the pre-catalyst complex, both Pd(0) and Pd(II) species can act as a true catalyst. In the present discussion we clearly emulate a Pd(II) species acting as a catalyst in the carbonylation of allyl-chloride. The involvement of a Pd(II) species is, in our opinion, a likely hypothesis when $Cl_2Pd(PPh_3)_2$ complexes are used in the absence of additional substances (suitable reducer or oxygenated ligands) in the reaction medium.

2. Computational details

All the DFT computations reported here have been performed with the GAUSSIAN-98 [46] series of programs using the non-local hybrid Becke's three-parameter exchange functional [47,48], denoted as B3LYP. This functional has been demonstrated to provide a reliable description (structures and energies) of transition metal complexes and of the potential surfaces associated with catalytic processes [38,39,49,50]. The geometry of the various critical points on the reaction surface has been fully optimized with the gradient method available in GAUSSIAN-98. In the case of the nickel catalyzed reaction we have used the DZVP basis sets, which is a local spin density (LSD)-optimized basis of double-zeta quality in the valence shell plus polarization functions [51]. To check the reliability of the DZVP basis, the structure of the most important critical points have been re-optimized at a more accurate level i.e., using the 6-31G* basis [46] for C and H atoms and the 6-311G* basis [46] for Ni and Br (6-31G*/6-311G* basis). In the case of the palladium catalysis a basis formed by the energy-adjusted pseudopotential basis set proposed by Preuss and co-workers [52] (denoted as sdd pseudopotentials in the GAUSSIAN-98 formalism) for the metal and the 6-31G* basis for the remaining atoms has been employed. This basis is denoted here as sdd/6-31G* basis and provides results that are very similar to the DZVP and 6-31G*/6-

311G* basis previously described. To roughly evaluate the effect of the solvent, we carried out single-point computations on the most important gas-phase optimized structures (reactants and more energetic transitions states) using the polarized continuous model (PCM) [53] method available in GAUSSIAN-98.

3. Carbonylation of allyl bromide catalyzed by Ni(CO)₄

In this section, we describe the most important steps of the catalytic cycle of Scheme 1 for the nickel catalyzed carbonylation of allyl bromide. A full description of the singlet potential energy surface for this reaction is given in Ref. [38]. The computational investigation of the decomposition reaction of the initial complex Ni(CO)₄:

$$Ni(CO)_4 \rightarrow Ni(CO)_3 + CO$$

that provides the catalytic active form, shows that this process is endothermic by 23.4 kcal mol⁻¹. This value is in rather good agreement with the experimental value of 22.1 kcal mol⁻¹ obtained by Day et al. [25] and reported in the introduction. It also agrees quite well with a bond

dissociation energy (Ni–CO bond) of 23.6 kcal mol⁻¹ obtained at the CCSD(T) level [54].

The oxidative addition leads to the formation of a preliminary η^2 π-complex (M1) where the terminal CC double bond interacts with the nickel atom. This complex, when we consider Ni(CO)₃ as the "active" form of the catalyst, forms without any barrier and is 7.6 kcal mol⁻¹ more stable than reactants (Ni(CO)₃ + allyl bromide). The barrier (E_a) to form M1 becomes 19.4 kcal mol⁻¹ in the assumption that Ni(CO)₄ is the "active" species. In a subsequent step the bromine atom can migrate from the carbon to the metal leading to a η^3 complex intermediate M2. This transformation, where a carbon-bromine bond is broken and one CO ligand is expelled from the metal coordination sphere, requires a rather large activation barrier of 25.9 kcal mol⁻¹. M1 and M2 are schematically represented in Fig. 1.

The oxidative addition can follow a different mechanism where the bromine atom directly attacks the metal atom. In the resulting complex M3 (see Fig. 2) the halogen is bridging the metal and the methylene group. Again, the addition does not have any activation energy when Ni(CO)₃ is involved as catalytic species, while a barrier
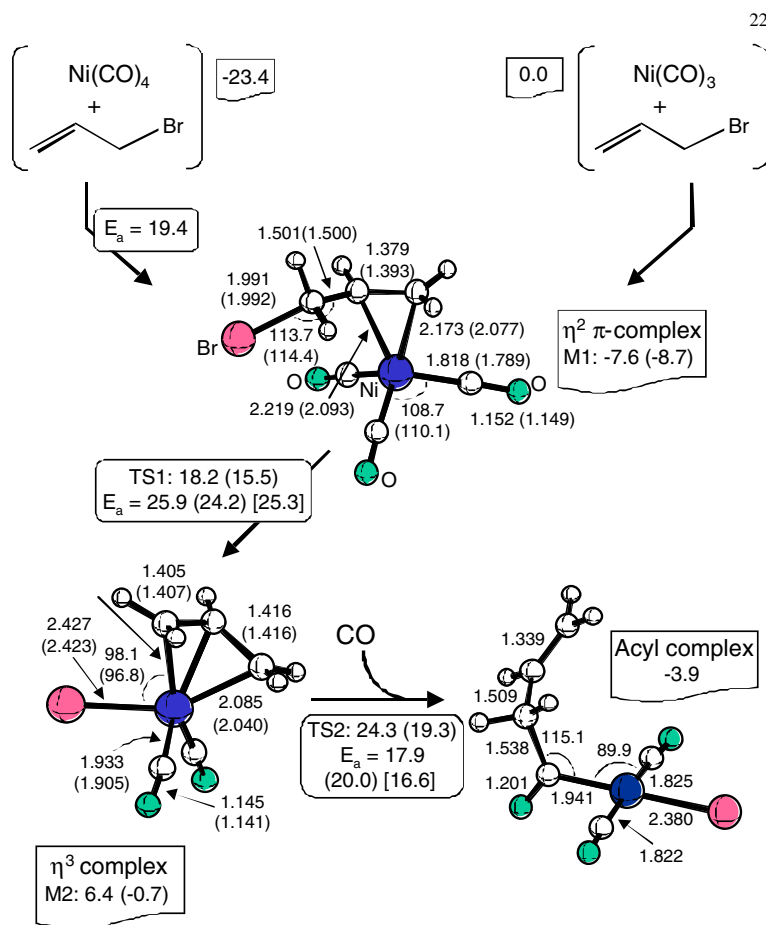

Fig. 1. Schematic representation of the structures of the η^2 (M1) and η^3 (M2) allyl–nickel complexes obtained with the DZVP basis. The energies (kcal mol⁻¹) are relative to reactants (Ni(CO)₃ + allyl bromide). The values in parenthesis have been obtained with the 6-31G*/6-311G* basis. Bond lengths are in Å and angles in °.
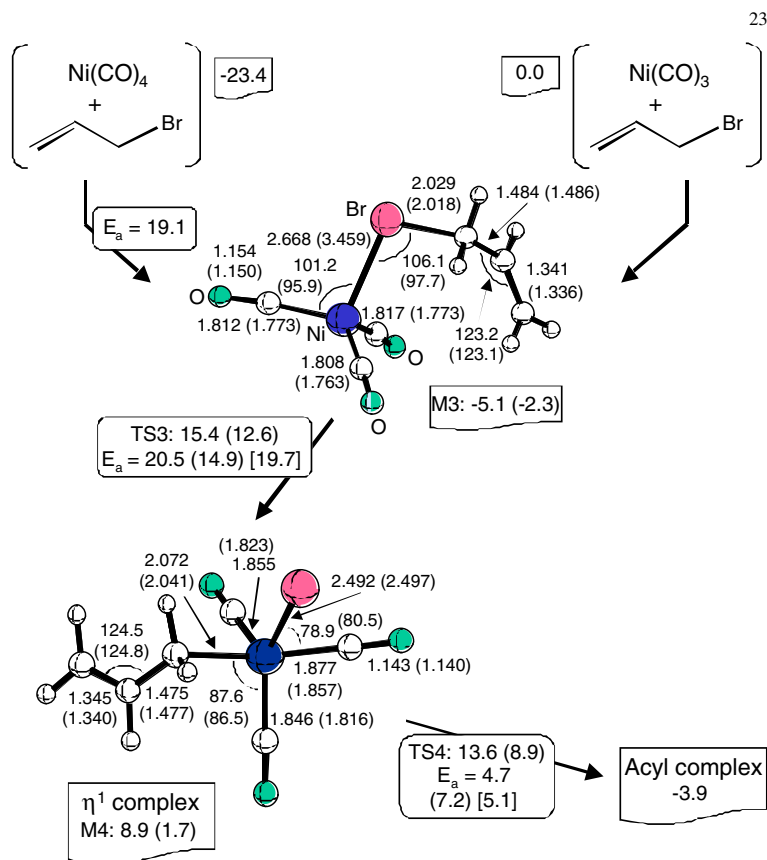
Fig. 2. Schematic representation of the structures of the M3 and η^1 (M4) allyl–nickel complexes obtained with the DZVP basis. The energies (kcal mol^{-1}) are relative to reactants (Ni(CO)$_3$ + allyl bromide). The values in parenthesis have been obtained with the 6-31G*/6-311G* basis. Bond lengths are in Å and angles in °.

of 19.1 kcal mol^{-1} must be overcome if the attack occurs on Ni(CO)$_4$. A further transition state TS3 (barrier of 20.5 kcal mol^{-1}), where the allyl fragment slides along a direction parallel to the Ni–Br bond, leads to the formation of a η^1 allyl–nickel complex (M4 in Fig. 2), which is 8.9 kcal mol^{-1} above the asymptotic limit represented by reactants.

The carbonylation process can occur on both the η^1 and η^3 complexes. In the former case the CO insertion requires an activation barrier of only 4.7 kcal mol^{-1}. Analysis of the

transition state structure (TS4) and the transition vector shows that the insertion of CO is actually a migration of the allyl unit from the metal to the carbon atom of one CO ligand. This transition state, which is schematically represented in Fig. 3, is 13.6 kcal mol^{-1} higher than the asymptotic limit. In the case of the η^3 complexes the carbonylation has a barrier of 17.9 kcal mol^{-1} (transition state TS2). Again, the formal insertion of CO into the metal–carbon bond is a migration of the allyl fragment as indicated by the shape of the transition vector obtained in the
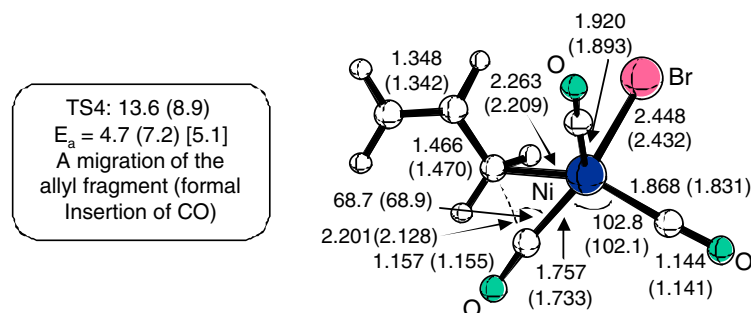

Fig. 3. Schematic representation of the structure of the transition state TS4 (a formal insertion of CO into the Ni–C bond) obtained with the DZVP basis. The energies (kcal mol^{-1}) are relative to reactants (Ni(CO)$_3$ + allyl bromide). The values in parenthesis have been obtained with the 6-31G*/6-311G* basis. Bond lengths are in Å and angles in °.

frequency computation. However, in this case the transition state is 24.3 kcal mol^{-1} higher than reactants, suggesting that the favored carbonylation path is that involving the direct attack of bromine on the metal and the formation of η^1 intermediates. The resulting nickel–acyl complex product, where the carbonyl group is σ-bonded to the metal, is 3.9 kcal mol^{-1} lower than reactants and is depicted in Fig. 1.

In the investigation of the potential surface, we have found a further interesting aspect that demonstrates the existence of an alternative path to carbonylation. The η^3 complexes can be converted to η^1 complexes after coordination of an additional CO ligand. This transformation requires the overcoming of a barrier of 8.0 kcal mol^{-1}. In the corresponding transition state, which is represented in Fig. 4, the metal has approximately a square planar structure and the incoming CO is approaching the metal along a direction orthogonal to the molecular plane. Since this transition state is 13.4 kcal mol^{-1} higher than reactants, an alternative carbonylation pathway could use this "gate" connecting the η^3 and η^1 regions on the potential surface. Thus, the system could first undergo the oxidative addition leading to the η^3 complexes (reactants → M2). Then, it could reach the more convenient η^1 region through the "gate" open on the potential surface (M2 → TS5 → M4) and afford the final acyl complexes.

The values of the most important activation barriers have been recomputed in the presence of the solvent effects and are reported in square brackets in Figs. 1 and 2 for the following transformations: (1) M1 → M2; (2) M2 → nickel–acyl complex; (3) M3 → M4; (4) M4 → nickel–acyl complex. The emulated solvent is CH$_2$Cl$_2$ (dielectric constant $\varepsilon = 8.93$), which is the solvent commonly used in the experiment. The solvent-corrected barriers are 25.3, 16.6, 19.7 and 5.1 kcal mol^{-1}. It is evident from a comparison with the corresponding gas-phase barriers (25.9, 17.9, 20.5 and 4.7 kcal mol^{-1}, respectively) that the presence of the solvent only slightly affects the entity of these quantities

and does not change the mechanistic scenario obtained with the gas-phase model.

Furthermore, it is interesting to comment briefly the results obtained using the more accurate basis set 6-31G*/6-311G*. The re-optimized geometrical parameters and the corresponding energy values relative to reactants and the activation barriers are reported in round parenthesis in Figs. 1–3. It is evident that the geometry of the various structures is very similar at the two computational levels. Also, since TS1 and TS2 are much higher in energy (15.5 and 19.3 kcal mol^{-1} above the asymptotic limit, respectively) than TS3 and TS4 (12.6 and 8.9 kcal mol^{-1}, respectively), the carbonylation path involving the formation of η^1 complexes is again highly favored. This finding indicates once again that the less expensive DZVP basis is adequate to describe this type of catalytic systems.

4. Carbonylation of allyl chloride catalyzed by Cl₂Pd(PH₃)₂

We examine in this section the results obtained for the carbonylation of allyl chloride catalyzed by palladium complexes. A detailed description of the corresponding singlet potential surface is given in Ref. [41]. Here, we summarize the most important aspects evidenced by the computations. The Cl$_2$Pd(PH$_3$)$_2$ model-catalyst that emulates the Cl$_2$Pd(PPh$_3$)$_2$ complex often employed in the real synthesis, exists in two forms, a *trans* and a *cis* isomer, the former being 6.4 kcal mol^{-1} more stable than the latter. A *trans–cis* isomerization can occur only when a third phosphine ligand is involved [39]. The new PH$_3$ ligand enters the metal coordination sphere and causes the expulsion of one of the two phosphine groups bonded to the metal. This transformation is characterized by a high energy barrier of 38.3 kcal mol^{-1}. We have examined the attack of allyl chloride on both *cis* and *trans* isomers. Since the reaction pathway involving the *cis* isomer remains at high energy, we describe here only the most important features of the path that originates from the more stable *trans-*
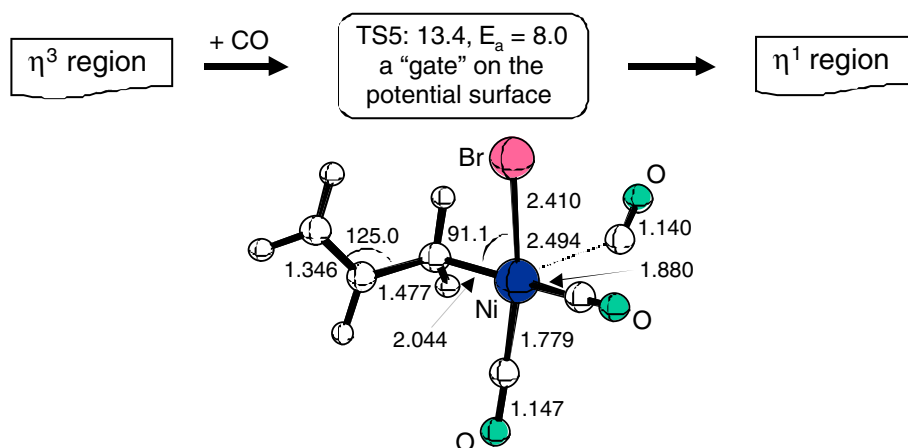

Fig. 4. Schematic representation of the structure of the transition state TS5 (connecting the η^2 and η^3 regions) obtained with the DZVP basis. The energies (kcal mol^{-1}) are relative to reactants (Ni(CO)$_3$ + allyl bromide). Bond lengths are in Å and angles in °.

$Cl_2Pd(PH_3)_2$ species. We have again investigated the existence of η^3 complexes, similar to those described in the previous section. Despite exhaustive exploration, we have not located any intermediate of this type. In place of the η^3 intermediates we have found only preliminary η^2 π-complexes (M5 in Fig. 5) that can form rather easily from the reaction of *trans*-$Cl_2Pd(PH_3)_2$ with allyl chloride by overcoming a barrier of 9.0 kcal mol^{-1}. M5 is 6.8 kcal mol^{-1} higher than the asymptotic limit represented by reactants (*trans*-$Cl_2Pd(PH_3)_2$ + allyl chloride).

The pathway leading from the η^2 complexes to the final acyl product involves multiple molecular transformations. The important step corresponds to the approach of a CO unit to the η^2 complex M5. The related transition state TS7 is quite high in energy (43.9 kcal mol^{-1} above the reactants). Here, the CO does not insert directly into the Pd–C bond, but simultaneously interacts with one of the two chlorine ligands and the terminal carbon of the substrate double bond. The resulting complex M6 (see Fig. 5) has a cyclic penta-atomic structure that includes palladium and one chlorine ligand, which is now bridging the metal and the carbonyl group. A cyclic structure such as M6 is

possible because the chlorine atom, after having formed a σ bond with the carbon of the CO unit, can use one of the lone-pairs to interact with the metal. A sequence of rather complex transformations leads to the final products (the β,γ-unsaturated acyl chloride, about 20 kcal mol^{-1} more stable than reactants) and the regenerated catalyst. All these transformation are characterized by small energy barriers (6.0, 1.1 and 3.2 kcal mol^{-1}) and involve the formation of a new four-member cycle (M7) and a η^2 π-complex (M8). In M7 one chlorine atom is again bridging the metal and the terminal methylene of the substrate molecule. In the final step an additional PH$_3$ ligand enters the metal coordination sphere and causes the expulsion of acyl chloride.

An alternative carbonylation pathway involves the direct attack of the chlorine atom on the metal. This is similar to the attack described in the previous section for Ni(CO)$_3$ reacting with allyl bromide. When $Cl_2Pd(PH_3)_2$ is used as a catalyst, the approaching of Cl causes the displacement of one PH$_3$ group from the metal coordination sphere and requires a barrier of 15.6 kcal mol^{-1}. Again, this leads to an intermediate (M9) where the chlorine is
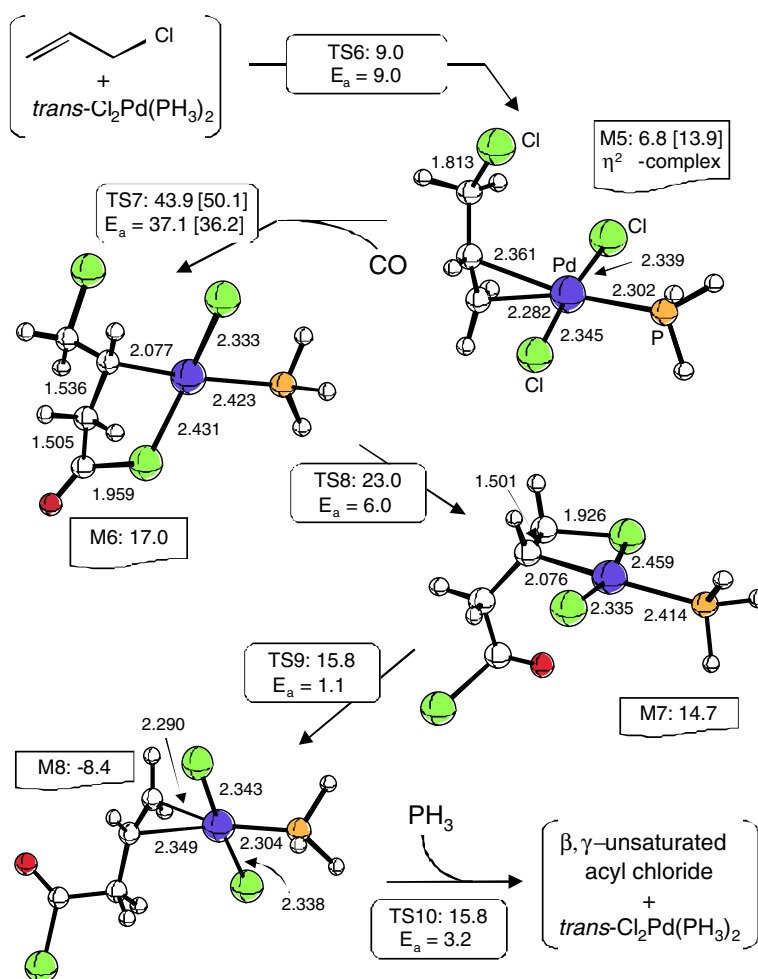

Fig. 5. Schematic representation of the structures of M5 (η^2 allyl-palladium complex) M6, M7 and M8 complexes obtained with the sdd/6-31G* basis. The energies (kcal mol^{-1}) are relative to reactants (*trans*-$Cl_2Pd(PH_3)_2$ + allyl chloride). Bond lengths are in Å and angles in °.
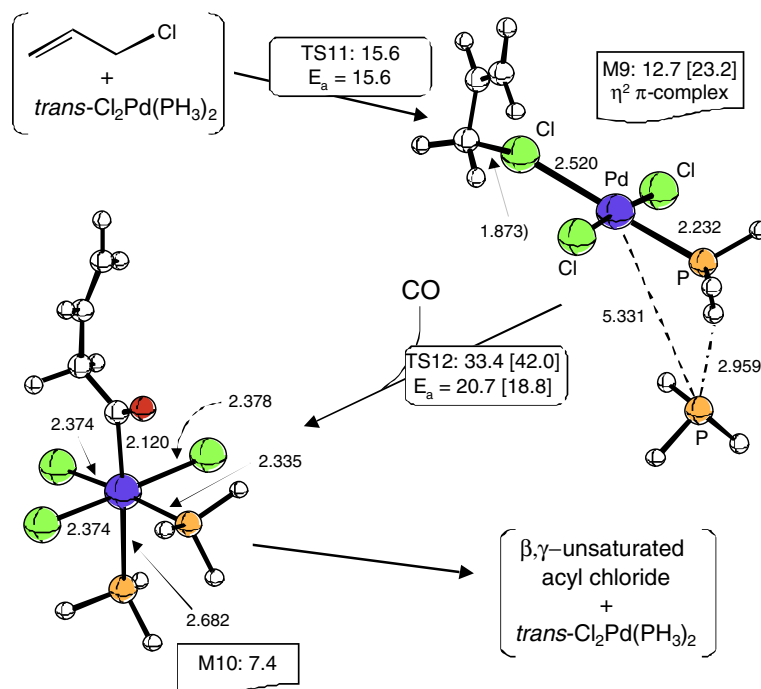
Fig. 6. Schematic representation of the structures of the M9 and M10 complexes obtained with the sdd/6-31G* basis. The energies (kcal mol^{-1}) are relative to reactants (*trans*-Cl$_2$Pd(PH$_3$)$_2$ + allyl chloride). Bond lengths are in Å and angles in °.

bridging one methylene carbon and the palladium atom. In this intermediate, represented in Fig. 6, the expelled PH$_3$ ligand is still slightly interacting with the metal, the H···P distance being 2.959 Å. The carbonylation occurs when a CO molecule approaches the intermediate. This step is the rate-determining step of the process with an activation barrier of 20.7 kcal mol^{-1}. The corresponding transition state TS12 is 33.4 kcal mol^{-1} higher than reactants and its main feature is a cyclic structure where CO simultaneously interacts with the metal and the free terminal methylene carbon of the substrate (see Fig. 7). The resulting intermediate (M10, schematically represented in Fig. 6)

has an octahedral structure where the acyl group and one PH$_3$ group are in axial positions. The migration of a chlorine ligand from the metal to the carbonyl carbon causes the breaking of the acyl-metal bond and the release of the allyl chloride product.

A comparison between the two reaction channels affording the acyl product, i.e., (a) η^2 complex formation and (b) direct attack of the chlorine atom, leads to conclusions that are very similar to those previously described for the nickel catalyzed carbonylation. The highest in energy transition state along the first path is 43.9 kcal mol^{-1} above the reactants while along the second path this energy amount is
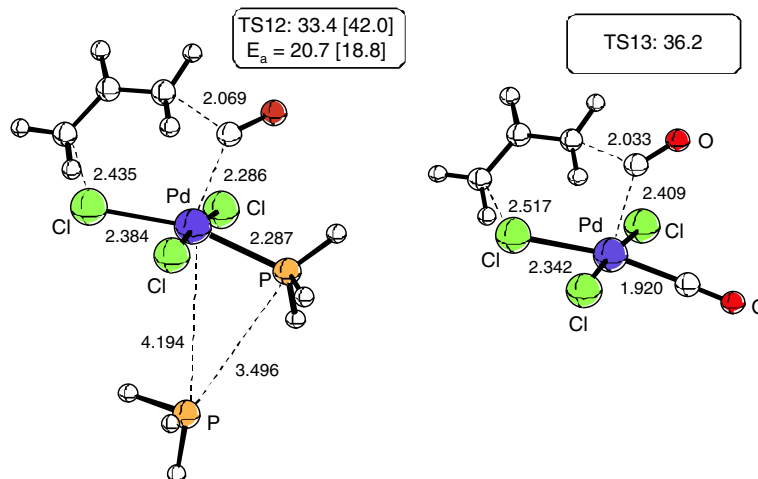

Fig. 7. Schematic representation of the structures of the two transition states TS12 and TS13 obtained with the sdd/6-31G* basis. The energies (kcal mol^{-1}) are relative to reactants (*trans*-Cl$_2$Pd(PH$_3$)$_2$ + allyl chloride). Bond lengths are in Å and angles in °.

much smaller i.e., 33.4 kcal mol^{-1}. Thus, also for the palladium-catalyzed carbonylation of allyl halides, the most likely reaction path involves a direct attack of the halogen atom on the metal.

It is interesting to point out that also in this case a connection between the two reaction channels (η^2 and η^1) exists on the potential surface. A transition state corresponding to the "gate" between the two regions of the surface allows the passage from the intermediate M5 (η^2 complex) to the intermediate M9 (intermediate with the bridging chlorine) by overcoming a barrier of 13.3 kcal mol^{-1}. Since this transition state is only 20.1 kcal mol^{-1} above the asymptotic limit, an alternative way to carbonylation could involve η^2 complexes, as suggested by the experiment. More precisely, the alternative reaction path could be as follows: (1) formation of the η^2 intermediate M5; (2) transformation from M5 to M7; (3) final carbonylation step.

We have also investigated the possibility that Cl$_2$Pd(CO)PH$_3$ and Cl$_2$Pd(CO)$_2$ act as catalytic species. These complexes can originate when CO attacks the Cl$_2$Pd(PH$_3$)$_2$ complex. Since Cl$_2$Pd(CO)PH$_3$ and Cl$_2$Pd(CO)$_2$ are 1.5 and 5.8 kcal mol^{-1} higher than the starting Cl$_2$Pd(PH$_3$)$_2$, respectively, the equilibrium Cl$_2$Pd(PH$_3$)$_2$ + 2CO = Cl$_2$Pd(CO)PH$_3$ + CO + PH$_3$ = Cl$_2$Pd(CO)$_2$ + 2PH$_3$ is shifted to the left and only a small amount of Cl$_2$Pd(CO)PH$_3$ and Cl$_2$Pd(CO)$_2$ will be present at low CO pressure. However, the number of Cl$_2$Pd(CO)PH$_3$ and Cl$_2$Pd(CO)$_2$ molecules can significantly increase if high CO pressures are used. Thus, we have investigated the existence of reaction channels to carbonylation originating from Cl$_2$Pd(CO)PH$_3$ and Cl$_2$Pd(CO)$_2$ as "active" catalytic species.

While in the case of Cl$_2$Pd(CO)PH$_3$ we have found that the reaction with the substrate almost immediately leads to the same reaction channels previously discussed for Cl$_2$Pd(PH$_3$)$_2$, for Cl$_2$Pd(CO)$_2$ we have obtained an interesting and somewhat unexpected mechanistic picture. Again, two different reaction paths are possible: one involving the formation of η^2 intermediates and one characterized by the direct attack of the substrate chlorine on the metal. Analysis of the rate determining steps along the two paths shows that the direct attack is again favored. The corresponding transition state TS13 (see Fig. 7) is very similar to TS12. Again the approaching CO simultaneously interacts with the metal and the terminal substrate CH$_2$ group. More interesting, TS13 is 36.2 kcal mol^{-1} higher than reactants and, thus, only 2.8 kcal mol^{-1} above TS12. These results suggest that, in the presence of high CO pressure, this way to carbonylation, where Cl$_2$Pd(CO)$_2$ is the active catalyst, could become important.

The inclusion of solvent effects (CH$_2$Cl$_2$ is again the emulated solvent) does not affect the mechanistic scenario, as found for the nickel catalyzed reaction. For instance, the barrier for the transformation M5 → TS7 → M6 only slightly decreases: from 37.1 (gas phase) to 36.2 kcal mol^{-1}.

Similarly, the barrier for the transformation M9 → TS12 → M10 varies from 20.7 (gas phase) to 18.8 kcal mol^{-1}. More important, TS7 is still much higher in energy than TS12 (8.1 kcal mol^{-1} is the difference after solvation) and, consequently, the direct attack of the halogen remains the favored path.

5. Conclusions

In this short review, we have described the most important results of recent computational studies on the carbonylation of allyl halides catalyzed by nickel and palladium complexes. The most important points can be summarized as follows:

(i) In both cases (nickel and palladium catalysis), we have demonstrated the existence of two different reaction pathways leading to the carbonylation product, i.e., β,γ-unsaturated,acyl halides. In one case the reaction proceeds via the formation of η^2 and/or η^3 allyl–metal intermediates (attack of the allyl π system on the metal). In the other case the process involves the direct attack of the halogen on the nickel and palladium atoms and the formation of η^1 intermediates.

(ii) While in the case of nickel the existence of both η^2 and η^3 allyl–metal complexes has been demonstrated, for the palladium only η^2 intermediates have been found.

(iii) The pathway where the substrate halogen attacks the metal is always the most likely carbonylation mechanism. In both cases (nickel and palladium) the transition state of the rate-determining step along this path is significantly higher in energy than the corresponding transition state along the path involving η^2 and/or η^3 intermediates.

(iv) A common and interesting feature of the nickel and palladium catalyzed processes is the existence of a "gate" on the potential surface connecting the two different reaction pathways. This topological gate allows an easy transformation from the η^2 (palladium) or η^3 (nickel) complexes to the η^1 intermediates. Thus, an alternative and competitive way to carbonylation is represented by: (A) formation of η^2 and/or η^3 intermediates; (B) transformation to η^1 intermediates; and (C) carbonylation. The possibility of this alternative path can explain the experimental evidence that points to a π allyl–metal complex as the likely intermediate of these catalyzed carbonylation reactions.

(v) An interesting point is the fact that the activation barriers computed for the nickel-catalyzed carbonylation are significantly lower than those obtained for the palladium-catalyzed process. This is in agreement with the evidence that, while mild conditions are required in the former case, significantly stronger conditions (high temperature and pressure) must often be used in the latter.

(vi) The inclusion of solvent effects in the computations does neither remarkably change the activation barriers nor affect the mechanistic picture provided by the simple gas-phase model.

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