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Schemes_Figures_Mol_Phys.zip tables.zip	

A Theoretical Investigation on the Oxidation States of Palladium Complexes and their Role in Carbonylation Reaction

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Two different yet related topics are discussed: (i) the reduction of palladium (II) in $\text{Pd}(\text{OAc})_2$ complexes reacting with phenyl phosphines and leading to $\text{Pd}(0)$ phosphines complexes and (ii) the carbonylation reaction of allyl chlorides catalyzed by these $\text{Pd}(0)$ species. The results show that the overall reduction is an exothermic process that can be accomplished along two different reaction paths: one of them is clearly favoured. Similarly, three different channels have been determined for the carbonylation reaction that primarily differ for the timing and the way with which the reacting species bind the metal. In the first path (σ -path), the allyl fragment interacts very weakly with the metal, whereas, successively the CO molecule strongly binds it and reacts with the allyl. A second channel (π - η^3 pathway) is characterized by a π - η^3 interaction between the allyl fragment and the palladium, to which the CO molecule binds, before the two units react affording the product. In both cases, two consecutive migrations of the chlorine "assist" the course of the reaction. In a third case (η^2 pathway) the allyl fragment initially enters the palladium coordination sphere, then the CO molecule simultaneously binds it and the phosphorous atom of one phosphine ligand. The first two paths are favoured.

Keywords: carbonylation, DFT, palladium, reaction mechanism, catalysis

1. Introduction

Mixtures of $\text{Pd}(\text{II})$ compounds, especially $\text{Pd}(\text{OAc})_2$ and tertiary phosphines are widely used in many catalytic reactions. Well known examples of this usage are Suzuki [1], Heck [2], Tsuji-Trost [3] and cross-coupling [4] reactions. In spite of the synthetic importance of these processes and the large amount of experimental and theoretical work available in literature, several issues still remain unclear. One

certainly concerns the palladium oxidation state of the active catalytic complexes. Experimental and theoretical works either proposing Pd(II) complexes as active catalytic species or supporting the opposite idea (i.e. Pd(0) intermediates as true catalysts) can be found. Even if several experimental evidences support the hypothesis of a Pd(II) catalytic species [5-10], it is quite likely that both species can act as a catalyst [5-8], depending on the reaction conditions and the nature of the pre-catalyst complex. This hypothesis is enforced by the fact that Pd complexes can easily undergo redox transformations in both directions. Another interesting point, which certainly does not contribute to clarify the problem, is that an excess of phosphines enhances the catalytic rate. This promoting effect is assumed to be caused by the stabilization of the catalytic species. Since phosphines can form complexes either with Pd(0) or Pd(II), this evidence adds further uncertainty to the matter.

Furthermore, the mechanism of the possible conversion between the two oxidation states is not obvious. Kinetic studies carried out by Amatore [11] and co-workers for Pd(OAc)₂/PPh₃ mixtures show that the rate-limiting step is an intramolecular process that affords a Pd(0) species, which is unstable in the absence of a ligand excess. This species is characterized by two different ¹³P NMR signals and reacts with iodobenzene. These authors have carried out additive oxidation of iodobenzene [12] to Pd(0) complexes together with cyclic voltammetry experiments (that allow to ascertain the amount of Pd(0) species) to establish the oxidation state (i.e. Pd(0)) of the intermediates. When the reaction takes place in an excess of phosphines, it is possible to stabilize the Pd(0) species (that shows only one broad ¹³P NMR signal). The authors propose the formation of anionic Pd(0) catalytic active species [Pd(PPh₃)_n(OAc)₂]²⁻ (n = 2, 3) and also suggest the following reaction mechanism for the reduction of Pd(OAc)₂ by PPh₃:

The existence and stability of Pd(0) anionic intermediates, i.e. $\text{Pd}^0(\text{PPh}_3)_n(\text{OAc})^-$ ($n = 2, 3$) has been demonstrated either experimentally [14] or by means of theoretical calculations [15]. The role of water molecules in the reduction process has been investigated by Ozawa and collaborators [16]. They found that water molecules are necessary to produce Pd(0) species in the reaction of $\text{Pd}(\text{AcO})_2$ with three equivalents of BINAP. In addition, labelling experiments using ^{18}O suggest that the oxygen atom of the phosphine oxide comes from the acetate ligands.

The first purpose of the present paper is to clarify some of the above-mentioned aspects. In particular we intend to shed light on the real nature of Pd(0) and Pd(II) complexes which form when Pd(II) compounds bearing oxygenated ligands (such as $\text{Pd}(\text{OAc})_2$) and tertiary phosphines are combined, as occurring in many reactions catalyzed by this metal. Furthermore we aim to understand how these complexes form from the starting reagents.

In addition to these aspects, the mechanism of carbonylation reactions of allyl halides catalyzed by Pd(0) complexes is investigated. We have chosen this reaction because of its importance in both academic and industrial environment: carbonyl group certainly represents one of the most versatile functional groups in organic synthesis. Transition metal-based carbonylation chemistry has been central to an extraordinary progress in catalysis during the last half century after the pioneering work by Roelen [17] on ethene hydroformylation catalyzed by cobalt tetracarbonyl

1
2
3 hydride HCo(CO)_4 . The well-known Reppe carbonylation, for instance, is the result of
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5 an extensive research program in carbonylation chemistry carried out by Reppe and
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7 co-workers [18]. However, in all cases, high temperature (in the range 50° - 150°), high
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9 CO pressure, expensive autoclave equipment and large quantities of dangerous
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11 volatile and unstable catalysts such as HCo(CO)_4 and Fe(CO)_5 are required.
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15 The severe conditions needed in Roelen and Reppe carbonylation processes
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17 remained approximately the same for more than twenty years. Nevertheless, during
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19 the last three decades, the work of many researchers, in particular Wilkinson, Heck
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21 and Tsuji [19], led to the development of new stable and effective catalysts based on
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23 rhodium and palladium. As a result, new carbonylation procedures under mild
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25 conditions (low temperature and pressure) are now available. To carry out many of
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27 these reactions, very small amounts of stable catalyst precursors such as $\text{Pd(PH}_3\text{)Cl}_2$
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29 and $\text{RhCl(CO)}_4\text{(PPh}_3\text{)}_2$ are necessary [20]. A special case is represented by the
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31 carbonylation of allyl halides. For this reaction several papers proposing different
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33 transition metal complexes as catalysts, have appeared [21-36]. Nickel tetracarbonyl
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35 Ni(CO)_4 [22, 31, 37] was proposed for the first time by Chiusoli [22,31]. However,
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37 even if this reaction can be carried out at room temperature and under atmospheric or
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39 low CO pressures (2-3 atm.) [33], a large amount of nickel tetra-carbonyl is required.
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41 Since the direct manipulation of Ni(CO)_4 is not easy because of its high toxicity, this
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43 species has been extensively replaced by palladium complexes. As a consequence,
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45 during the last three decades, several different reaction conditions and techniques
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47 have been proposed to improve the palladium-catalyzed carbonylation of allylic
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49 systems [38-50, 71-73].
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58 Recently we have reported a theoretical investigation of the mechanism of
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60 palladium-catalyzed carbonylation of allylic systems to afford β,γ -unsaturated acyl

derivatives [51-53]. A model-system consisting of the $\text{Pd}(\text{PH}_3)\text{Cl}_2$ complex (emulating the real catalyst $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ with the metal in its +2 oxidation state), a CO molecule and allyl chloride was used [53]. This study demonstrated the existence of two different reaction pathways leading to the β,γ -unsaturated acyl chloride. In one case (η^2 pathway) the carbonylation proceeds via the formation of α -allyl palladium intermediates. In the other case the process involves a direct attack of the CO molecule onto the metal (σ pathway). Along the η^2 pathway the process is characterized by a rather complex mechanism: the CO unit does not insert directly into a Pd-C bond, but interacts simultaneously with one of the two Cl ligands and the closest carbon atom of the allyl double-bond. This affords a cyclic structure including the acyl chloride group. The highest transition state along this path is $43.9 \text{ kcal mol}^{-1}$ above reactants. A lower transition state ($33.4 \text{ kcal mol}^{-1}$ above reactants) characterizes the σ pathway: this reaction channel is definitely favoured with respect to that involving η^2 -complexes.

In the present study we examine in details the reaction mechanism of allyl chloride carbonylation catalyzed by Pd(0) species that form according to the mechanism above reported. This study should outline in details the mechanistic changes with respect to the Pd(II)-based carbonylation of a similar system and permits the understanding of the effect of the oxidation state change [53]. Pd(0) species are considered in many cases to be the active catalytic species [13, 63-70], so a systematic study comparing both oxidation states will be very insightful. It is worth to mention that here a more realistic model-system including triphenylphosphine ligands instead of simple PH_3 units (as done in previous papers) is considered. This should provide much more reliable information on the mechanism of this reaction.

2. Computational Procedures

All DFT computations have been performed with the Gaussian 03 [54] series of programs using the non-local hybrid Becke's three-parameter exchange functional [55] denoted as B3LYP in the Gaussian formalism and a locally dense basis set (LDBS) approach [56]. According to the LDBS approach, the system has been partitioned into two different regions, which were assigned basis sets of different accuracy. One region contains the atoms which play the most important role in the reaction: the metal, the allyl moiety, the acetate fragments, the CO molecule and the phosphorous atoms. For the atoms belonging to this region we have used the DZVP basis, which is a Local Spin Density (LSD)-optimized basis set of double-zeta quality [57]. For the other region, comprised of all the remaining atoms (the phenyl rings), the 3-21G* basis set [54] has been employed. When not otherwise specified, the reported energy values and/or geometrical parameters have been obtained with this basis denoted as DZVP/3-21G*.

To check the reliability of this approach we have carried out additional computations (with full geometry optimization) using the DZVP basis set on all atoms and we have compared the results to those obtained at the DZVP/3-21G* level. In these computations we have considered some of the key critical points located on the PES. We have found that the more accurate representation provides results (energetics and geometrical parameters) very similar to the DZVP/3-21G* basis. Thus, we can state with confidence that the 3-21G* basis satisfactorily emulates the DZVP representation. These data are reported in details in the Supporting Information material.

We have performed frequency computations to determine the nature of the various critical points. In most cases, the shape of the transition vector provided by the frequency computations clearly indicates which intermediates a given transition state is connected to. However a series of IRC computations has been carried out starting from the most important transition states. The relative graphics and figures are available in the Supporting Information section. Furthermore, to roughly evaluate the solvent effects, single-point calculations have been carried out on the gas-phase optimized structures with the Polarized Continuous Model method (PCM based on the integral equation formalism model) [58] available in Gaussian 03: a dielectric

constant of 7.58 emulating the tetrahydrofuran (THF) solvent has been used. An additional set of single-point computations with a more accurate basis set has been carried out on the most important critical points. The system has been again divided into different regions which were assigned basis sets of different accuracy. In particular the energy-adjusted pseudo-potential basis set proposed by Preuss and co-workers (denoted as sdd pseudopotentials in the Gaussian 03 formalism) [59] has been employed for palladium, the TZVP basis set [60] for the allyl moiety, the acetate fragments, the CO molecule and the phosphorous atoms and the DZVP basis set for the phenyl rings. This level of accuracy is denoted in the following as sdd/TZVP/DZVP level. The results of these calculations are discussed in a specific section.

3. Results and Discussion

3.A. Palladium Oxidation-Reduction in Phosphine-Palladium Complexes: a Mechanistic Hypothesis.

We have investigated the conversion and reduction mechanism of $\text{Pd}(\text{OAc})_2$ to $\text{Pd}(0)$ complexes. The model-system consists of one $\text{Pd}(\text{OAc})_2$ molecule (palladium in the +2 oxidation state) and five tri-phenylphosphine (PPh_3) molecules which come into play at different stages of the process. All energy values discussed in this section are relative to these non-interacting species, which represent the asymptotic limit (AL).

The consecutive addition of two triphenylphosphine units to the starting $\text{Pd}(\text{OAc})_2$ complex occurs in the first stage of the reaction. Although $\text{Pd}(\text{OAc})_2$ in its crystal structure is actually a trimer, we believe that the monomer is a good model for the calculations, since we can expect that the monomeric complex $\text{Pd}(\text{OAc})_2(\text{PPh}_3)_2$ will be formed via an analogous mechanism from the trimer. The corresponding energy profile is shown in Figure 1. A schematic representation of the structure of the various critical points is given in Scheme 1 and selected bond lengths are collected in Table 1. It is interesting to outline that, each time a new phosphine ligand is added to the system, shallow minima characterized by weak interactions precede the actual

formation of phosphorous-metal bonds. These interactions (mainly H-bonds between the palladium ligands and the incoming phenyl rings) significantly weaken in a solvent phase because of electrostatic effects (the PCM values are reported in round parenthesis). For completeness, all these points will be discussed. Another important structural feature of the species that form upon addition of PPh_3 molecules, is the well-known palladium propensity to reach a tetra-planar coordination. When the four ligands are not remarkably cumbersome and this configuration becomes possible, a strong energy gain is observed.

In the starting $\text{Pd}(\text{OAc})_2$ complex (**M0**) the two acetate fragments chelate the metal and saturate the four coordination sites of palladium, thus leading to an approximately square planar structure. The preliminary complex **M1** forms without overcoming any energy barrier upon addition of one phosphine ligand with a stabilization ΔE of $4.7 \text{ kcal mol}^{-1}$. Weak interactions involving one aromatic ring, the metal and one acetate ligand can be detected in **M1**. As mentioned above, this stabilization is significantly reduced when solvent effects are considered ($\Delta E = -0.6 \text{ kcal mol}^{-1}$). A further approach of PPh_3 to the metal involves a transition state (**TS1**, energy barrier of $0.9 \text{ kcal mol}^{-1}$), which remains lower than **M0**. Thus, the binding of PPh_3 to palladium is a rather easy process that causes the almost complete breaking of one Pd-O bond, as observed in the resulting intermediate **M2**. The new Pd-P1 bond ($2.304 \text{ \AA}$) is determined by the interaction between the phosphorus lone pair and the empty metal d orbitals. It replaces the weaker Pd-O1 bond ($\text{Pd-O1} = 3.008 \text{ \AA}$) and results in a significant stabilization of the new complex **M2**, which is $29.5 \text{ kcal mol}^{-1}$ lower than **M0** ($28.3 \text{ kcal mol}^{-1}$ in the presence of solvent effects). A further contribution to the overall stabilization is probably due to a strain decrease of the palladium-acetate oxygen structure and the corresponding strengthening of the Pd-O2

bond. In particular, the replacement of one oxygen with a phosphorous atom allows a more regular and stable square planar coordination of the metal.

(Table 1 here)

(Figure 1 here)

The energy profile for the addition of a second phosphine ligand is almost identical to that previously discussed. A slight stabilization accompanies the formation of a new preliminary complex **M3** (4.3 kcal mol⁻¹ lower than **M2** and 33.8 kcal mol⁻¹ lower than **M0**). The weak interactions that stabilize this intermediate (again weak H-bonds) are totally lost in condensed phase, where **M3** is 26.7 kcal mol⁻¹ below **M0** and hence 1.6 kcal mol⁻¹ higher than **M2**. Even if this marked destabilization of **M3** is partly due to the frozen geometry (only PCM single point calculations have been carried out), these results suggest that the intermediate **M3** does not probably exist in condensed phase or that it is in equilibrium with **M2**.

(Scheme 1 here)

The definitive binding of the second phosphine to palladium is a crucial point of the process. As a matter of fact, the resulting complex Pd(OAc)₂(PPh₃)₂ can exist in two different configurations (*cis* and *trans*) and each of them originates a unique reaction pathway (denoted here as *cis* and *trans* channel) leading to palladium reduction.

We first discuss the *trans*-channel. The corresponding energy profile is depicted in Figure 2. The various structures located along the reaction path are

schematically represented in Scheme 2 and 3, and the most important geometrical parameters are reported in Table 2 and 3. From **M3**, the transition state **TS2** leads to the formation of the *trans* complex **M4**. In **TS2** the length of the new forming phosphorus-palladium bond (P2-Pd) is 3.040 Å (i.e. almost identical to the value found in **TS1**) whereas the breaking oxygen-palladium bond Pd-O3 is still rather short: 2.377 Å. The corresponding activation barrier ($E(\text{TS2}) - E(\text{M3})$) is 4.5 kcal mol⁻¹ and does not change significantly in the presence of solvent effects (4.1 kcal mol⁻¹). It is reasonable to believe that a steric hindrance around palladium makes this barrier higher than that associated to **TS1**. The *trans* complex **M4** (Pd(OAc)₂(PPh₃)₂) exists in a typical planar tetra-coordinated configuration and is characterized by a strong energy stabilization: 17.3 kcal mol⁻¹ with respect to **M3** and 51.1 kcal mol⁻¹ below the AL (this value becomes 45.2 kcal mol⁻¹ in the presence of solvent). In **M4**, the oxidation state of palladium is still unchanged i.e. +2.

(Table 2 here)

(Table 3 here)

(Figure 2 here)

A barrierless rotation around Pd-O2 connects **M4** to the intermediate **M5** where the oxygen atom O1 is now facing the phosphorus atom P1 (O1-P1 = 2.884 Å). In spite of the new O1-P1 interaction, this structure is slightly higher in energy than **M4** (2.5 and 3.4 kcal mol⁻¹ in gas-phase and solvent, respectively). This is probably due to the unfavourable steric interactions among the phosphine phenyl rings, which must stay closer to accommodate the acetate fragment after rotation. The structural arrangement of **M5** anticipates the next crucial step i.e. the palladium reduction that

requires the transfer of the two acetate fragments to the phosphorus atom P1 (that becomes oxidized). This process occurs in two steps and involves a third phosphine, which enters the palladium coordination sphere. In the first step (transition state **TS3**) one oxygen atom of each acetate forms two almost complete bonds with the phosphorus atom P1 ($P1-O1 = 1.861 \text{ \AA}$ and $P1-O3 = 1.904 \text{ \AA}$). Simultaneously the bond between the palladium and the second oxygen atom of each acetate significantly elongates. The lengths of these two palladium-oxygen bonds underline the asynchronous character of the acetate migration, $Pd-O4 (2.438 \text{ \AA})$ being shorter than $Pd-O2 (2.539 \text{ \AA})$. A simultaneous removal of the phosphorus from the palladium is observed ($P1-Pd = 2.478 \text{ \AA}$). To balance the consequent loss of electron density on the metal orbitals, one of the phenyl group moves closer to the palladium, thus donating a certain amount of charge from the ring π system (in particular, two carbon atoms of the benzene ring become rather close to the metal, the corresponding carbon-palladium distances being 2.402 and $2.686 \text{ \AA}$). Thus, this transition state describes a situation where ligands and electron density are exchanged between the phosphorus (P1) and the palladium atoms, which are involved in a oxidation and reduction process, respectively. Also, the phosphorus atom (P1) is becoming penta-coordinated, because the low energy d-orbitals make possible the interaction with the oxygen atoms of the migrating acetate. Even though penta-coordinated phosphorus complexes may be quite unusual, they have been characterized experimentally [61]. **TS3** is $25.5 \text{ kcal mol}^{-1}$ above the previous intermediate (**M5**) and $22.7 \text{ kcal mol}^{-1}$ below the AL (in the presence of solvent these values become 33.9 and $7.9 \text{ kcal mol}^{-1}$, respectively). **TS3** leads to **M6**, which is $35.8 \text{ kcal mol}^{-1}$ below **M0**, in which both acetates have completed the migration to phosphorus, even if in one case a weak interaction with palladium is still observed ($Pd-O2 = 3.743 \text{ \AA}$). The π system of one phenyl ring of the

leaving phosphine strongly interacts with the metal. The aromatic ring is simultaneously bonded to P1 and behaves as a metal ligand, allowing a significant charge transfer to the palladium and determining a strong stabilization of the system, as it has been observed in this kind of processes [13].

(Scheme 2 here)

(Scheme 3 here)

The redox process is completed with the transition state **TS4** (second step) that corresponds to the definitive detachment of the phosphorus atom (bearing five ligands) from palladium. The phosphorous ligands include now the original three phenyl rings (one is still partly bonded to Pd) and the two acetates fragments. The separation of the five-coordinated phosphorous is helped by the approach of a new phosphine ligand to the metal ($P3-Pd = 3.544 \text{ \AA}$), which has now a unsaturated coordination sphere. The resulting intermediate **M7** ($41.8 \text{ kcal mol}^{-1}$ below the starting reactants in gas phase and $36.2 \text{ kcal mol}^{-1}$ in solvent) is formed by the $Pd(PPh_3)_2$ and $PPh_3(OAc)_2$ complexes. The two acetates that coordinate the palladium in the starting species have been replaced by two phosphines. Thus, the metal has been reduced and the resulting oxidation state is now zero, while the phosphorus oxidation state has increased to five. The diagram of Figure 2 shows that the final species **M7** is higher in energy than **M4**. This is mainly a consequence of the “holes” in the coordination sphere of palladium which can accept two more phosphine ligands, thus restoring the optimum tetra-coordination state.

We must stress an additional aspect concerning the redox process. Since **TS4** is almost degenerate to **M6**, it is more cautious to consider this transition state as a

computational shortcoming (which could easily disappear when changing the computational level) and the redox transformation a very asynchronous concerted process occurring in two phases. Furthermore, it is important to note that the redox transformation appears to be the rate-determining step of the whole process. This would be in agreement with the results of experimental kinetic studies [11] for mixtures $\text{Pd}(\text{OAc})_2/\text{PPh}_3$ that show that the rate-limiting step of the reaction is an intra-molecular endothermic process affording a $\text{Pd}(0)$ species. On the other hand, it is important to mention that the presence of a third ligand does not imply that the reaction is first order in phosphine, since it remains always at a non bonding distance from the palladium atom, and it is not involved in the bond breaking and forming process (**TS3**). Indeed, the interaction between the metallic centre and such a PPh_3 is very weak and could be suppressed for instance if the solvent was considered explicitly, so the proposed mechanism is still zero order in PPh_3 , as it was determined experimentally.

The binding of two additional phosphines to $\text{Pd}(\text{PPh}_3)_2$ again involves the preliminary formation of weakly bound intermediates corresponding to shallow minima on the potential surface. One phosphine ligand weakly interacts with $\text{Pd}(\text{PPh}_3)_2$ and affords **M8** without overcoming any activation barrier. **M8** is 45.8 kcal mol⁻¹ below the asymptotic limit (35.8 kcal mol⁻¹ at the PCM level). The energy barrier ($E(\text{TS5}) - E(\text{M8})$) for the definitive phosphine binding leading to **M9** is very low, being only 0.23 kcal mol⁻¹ (0.92 kcal mol⁻¹ when solvent effects are included). **M9** is a planar tri-coordinated palladium complex $\text{Pd}(\text{PPh}_3)_3$ which lies 55.6 kcal mol⁻¹ below reactants (45.0 kcal mol⁻¹ in the presence of solvent). The addition of a further phosphine follows the same pattern. **M10** is the preliminary weakly bound complex, (60.1 kcal mol⁻¹ more stable than reactants; 43.2 kcal mol⁻¹ at the PCM level) and

TS6 is the transition state leading to the formation of the final tetra-coordinated complex **M11**, which adopts a tetrahedral structure, typical of d^{10} metals like Pd(0) that also minimizes the repulsion between the cumbersome PPh_3 ligands. This steric hindrance is responsible for the small stabilization associated with the entering of the forth phosphine in the metal coordination sphere: **M11** lies $62.4 \text{ kcal mol}^{-1}$ below the reactants, and only 2.3 lower than **M10** (these values become 44.4 and $1.2 \text{ kcal mol}^{-1}$, respectively, in the presence of solvent). Selected bond lengths for the intermediate complexes (**M8**, **M9**, **M10** and **M11**) and the corresponding transition structures (**TS5** and **TS6**) are collected in Table 4. In summary, the role of the additional phosphines is mostly to stabilize the resulting Pd(0) species. This result agrees with the fact that in the absence of one excess of ligand the products decompose rapidly.

(Table 4 here)

As above mentioned, a second reaction path (denoted as *cis*-channel) originates from **M3**. The energy profile is reported in Figure 2 and a schematic representation of the structures located on the initial part of this path is given in Scheme 4. The corresponding geometry parameters are collected in Table 5. A transition state **TS7** leads from **M3** to a $(Pd(OAc)_2(PPh_3)_2)$ *cis* complex **M12**, by overcoming an energy barrier ($E(\text{TS7}) - E(\text{M3})$) of $10.3 \text{ kcal mol}^{-1}$ ($7.4 \text{ kcal mol}^{-1}$ in solvent). This barrier is $5.8 \text{ kcal mol}^{-1}$ larger than that associated with transition state **TS2** leading to the *trans* complex and **M12** is $7.0 \text{ kcal mol}^{-1}$ higher in energy than the corresponding *trans*-complex **M4**. This difference is certainly caused by the steric repulsion between the two adjacent phosphine ligands. The key step for Pd oxidation, i.e. transfer of the two acetate ligands from the metal to the phosphine phosphorous atom, involves the transition state **TS8** where the migration of the two acetate

fragments follows a mechanism slightly different with respect to that previously discussed for the *trans* complex. An additional, third phosphine ligand (not bound to palladium) is immediately involved, entering the system at this stage. The corresponding phosphorus atom P3 interacts with the two acetates. In particular the oxygen (O2) of one acetate is bridging the Pd and P3 atoms: the P3-O2 interaction is already rather strong (2.130 Å) and the Pd-O2 bond remains significant (Pd-O2 = 2.649 Å). Even the second oxygen of the same acetate (O1) considerably interacts with the phosphorus (P3-O1 = 2.572 Å). The second acetate fragment remains closer to the metal (Pd-O3) = 2.252 Å) and its interaction with the approaching phosphine is much weaker (P3-O2 = 2.941 Å). In summary, the incoming phosphine “captures” the two acetates helping their expulsion from the coordination sphere of the metal that retains the electrons of the Pd-OAc bonds, thus reducing its oxidation state. However, **TS8** is characterized by a rather high energy barrier (41.8 kcal mol⁻¹ in gas phase and 52.2 kcal mol⁻¹ in solvent) and lies 20.3 kcal mol⁻¹ (19.7 kcal mol⁻¹ at the PCM level) above the highest transition state located along the *trans* pathway. Thus, the *cis* channel cannot effectively compete with the *trans* one and for this reason we do not discuss further.

(Table 5 here)

(Scheme 4 here)

(Figure 3 here)

The phosphorous species that forms after **TS4** (PPh₃(OAc)₂) easily converts into the corresponding phosphine oxide, which is detected experimentally at the end of the reaction, by reaction with one water molecule. The intermediates and transition states along this path are represented in Scheme 5, while the energy profile is

displayed in Figure 3. From now on, we refer to the separated reagents of this process ($\text{PPh}_3(\text{OAc})_2$ and one water molecule) as **M13**. The interaction between these two species leads to the barrierless formation of a complex (**M14**) characterized by a hydrogen bond between H1 and O2 that keeps the two molecules together and lowers the energy of the system by $7.4 \text{ kcal mol}^{-1}$ with respect to the isolated reactants. As expected this energy stabilization is smaller when the solvent effects are introduced in a PCM calculation and becomes $2.9 \text{ kcal mol}^{-1}$. In the next step (**TS9**), the water molecule closely approaches the phosphorus atom causing a significant series of chemical transformations, which directly lead to the product. In **TS9**, the water molecule is strongly interacting with the phosphorus: the O5-P1 distance is $1.918 \text{ \AA}$. Simultaneously, each of the two water hydrogen atoms is hopping to one acetate oxygen, namely the one which is not bonded to the phosphorus atom. This double transfer is not synchronous: H1 is almost equally shared between O2 and O5 ($\text{H1-O2} = 1.172 \text{ \AA}$ and $\text{H1-O5} = 1.244 \text{ \AA}$), while H2 is only weakly interacting with O4 ($\text{H2-O4} = 1.968 \text{ \AA}$). The behaviour of the two acetates on the phosphorus is analogous: the P1-O1 bond has evidently elongated ($\text{P1-O1} = 2.131 \text{ \AA}$) so that an acetic acid molecule is almost formed and being expelled from the phosphorus coordination shell. On the contrary, the corresponding P1-O3 bond, because of the weakening of the trans effect associated to Pd-O1, is shorter than in **M14** ($1.750 \text{ \AA}$): the acetate is still bonded to the phosphorus, which is octahedrally coordinated. The **TS9** transition state lies $9.3 \text{ kcal mol}^{-1}$ above the isolated reactants ($\text{PPh}_3(\text{OAc})_2 + \text{H}_2\text{O}$) and the relative activation energy with respect to the previous intermediate (**M14**) is $16.7 \text{ kcal mol}^{-1}$. The energy barrier rises to $21.5 \text{ kcal mol}^{-1}$ at the PCM level, because the stabilizing hydrogen bond network loses strength and importance when the solvent effects are considered. On the other hand, since the precursor **M7** lies already 41.8

kcal mol⁻¹ below the asymptotic limit (36.2 kcal mol⁻¹ when the solvent is considered), it is reasonable to assume that the system will have energy enough to overcome the barrier easily. In spite of the above-mentioned asynchronicity, an IRC calculation demonstrated that **TS9** is directly connected to the final product of this process: **M15**. This species corresponds to the phosphine oxide Ph₃P=O (where the phosphorous has still the formal oxidation state +5) interacting with two acetic acid molecules. The phosphine oxide features a tetrahedral geometry and the two hydrogen bonds which keep this complex close to the acetic acid molecules are almost identical: H1-O5 = 1.728 Å and H2-O5 = 1.735 Å. **M15** lies largely below the initial reactants: 47.1 kcal mol⁻¹ (37.8 kcal mol⁻¹ at the PCM level). In conclusion, the formation of the phosphine oxide is strongly exothermic and characterized by an energy barrier quite small: hence the process seems to be rather easy.

(Table 6 here)

(Scheme 5 here)

3.B. Allyl Chloride Carbonylation Catalyzed by Pd(0) Complexes

In this section, we discuss the carbonylation reaction of allyl chloride catalyzed by Pd(0) complexes that easily form when Pd(OAc)₂ species are used in the presence of an excess of phosphines. To this purpose we use a model-system consisting of Pd(PPh₃)₄, a CO molecule and the allyl chloride molecule. These three non-interacting chemical species represent now the asymptotic limit (AL).

(Figure 4 here)

3.B.1. The σ -Pathway.

This pathway (σ -pathway) originates from a direct, weak and initial interaction of the chlorine atom with the metal and leads to the formation of allyl-palladium σ complexes. The corresponding reaction profile is shown in Figure 4 and a schematic representation of the various structures located along it is given in Scheme 6. Selected bond lengths for the critical points are reported in Table 7. Palladium complexes such as $\text{Pd}(\text{PPh}_3)_4$ are characterized by a high steric hindrance, which makes difficult the entering of an additional group in the metal coordination sphere. To avoid the formation of penta-coordinated transient species (bipyramidal configuration) with strong steric repulsions, the replacement of one ligand by a new group must occur in two steps. Thus, in the present case, the expulsion of one phosphine from $\text{Pd}(\text{PPh}_3)_4$ anticipates the binding of a chloroallyl molecule, as a new ligand. This stage (expulsion of PPh_3) is the same as the reverse of the final step (**M9** $\rightarrow$ **M11**) of the process described in the previous section and will not be discussed again. In the resulting trigonal complex $\text{Pd}(\text{PPh}_3)_3$ there is now enough room to allow the allyl unit to approach the metal. This affords a preliminary intermediate, **M16**, where a very weak interaction involving the chlorine atom (Cl-Pd distance = 4.697 Å) binds the allyl molecule to the metal. In **M16**, which is 3.0 kcal mol⁻¹ above the AL (1.6 kcal mol⁻¹ below when solvent effects are included), the metal retains its planar trigonal configuration. When a CO molecule approaches the complex, a more stable complex (**M17** 8.1 kcal mol⁻¹ below the AL) forms, through a shallow transition state **TS10**: the new bond (Pd-C4 = 2.015 Å) is quite strong despite the crowded coordination sphere. Actually the important step of the reaction is the next one when the CO molecule establishes a simultaneous interaction with the palladium and the allyl group (transition state **TS11**). In **TS11** the carbon atom C4 of the CO unit forms two new bonds: one with palladium and one with the C1 allyl carbon. The formation of the C1-

C4 bond (1.912 Å) causes important structural changes in the allyl moiety: while the C2-C3 bond increases its double bond character (C2-C3 = 1.399 Å), C1-C2 is turning into a single bond (C1-C2 = 1.419 Å). As a consequence the chlorine atom migrates from C3 (allyl system) to palladium: the C3-Cl and Pd-Cl bond lengths are 2.392 and 4.654 Å, respectively. This structural rearrangement also leads to a significant weakening of the Pd-P3 bond (2.626 Å): for electronic and, above all, steric reasons, the palladium cannot bear so many ligands. The remarkable migrating and bridging attitude of chlorine and halogens in general has already been observed in several systems of this kind and it has been demonstrated to represent a crucial step in the carbonylation reaction [62,52,53]. An approximate tetrahedral structure of palladium characterizes **TS11**. Once again, the presence of five groups and the steric hindrance of the cumbersome phenyl rings prevents palladium to adopt the more typical planar tetra-coordination. This transition state is 24.9 kcal mol⁻¹ above the asymptotic limit (15.0 kcal mol⁻¹ at the PCM level) and the corresponding barrier (E(**TS11**) – E(**M17**)) is 33.0 kcal mol⁻¹ (26.8 kcal mol⁻¹ in solvent). It is important to point out that in this step, which is rate-determining for this pathway, the Pd formal oxidation state is changing from 0 to +2.

(Scheme 6 here)

(Table 7 here)

The resulting intermediate (**M18**) is rather stable being 13.2 kcal mol⁻¹ below the asymptotic limit. The palladium has reached a square planar tetra-coordination and is surrounded by one chlorine atom, the ally carbonyl chain and two phosphines. The third phosphine has been almost definitely expelled (the Pd-P3 bond length is 4.291 Å) and the Pd oxidation state is now unquestionably +2. In the subsequent step

(transition state **TS12**), we observe a back migration of the chlorine atom from the palladium to the carbonyl atom C4; the Pd-carbon bond breaks (Pd-C4 = 2.384 Å) and a phosphine enters again the palladium coordination sphere (Pd-P3 bond length = 2.698 Å). Hence, the palladium oxidation state changes again: from +2 to 0. It is interesting to highlight the role of the chlorine atom which “assists” the carbonylation process. Its double migration forward and backward the metal allows to complete the carbonyl insertion and to undergo the internal rearrangement of the allyl moiety necessary to afford the final product i.e. the acylchloride and the Pd(PPh₃)₃ complex (6.4 kcal mol⁻¹ below reactants). An additional phosphine ligand can approach the metal, give back the regenerated catalyst Pd(PPh₃)₄ (lying 13.4 kcal mol⁻¹ below the AL), thus closing the catalytic cycle.

3.B.2. The $\pi\eta^3$ -allyl-palladium complexes pathway

As previously shown, after the initial displacement of a phosphine, in Pd(PPh₃)₃, the metal can accept a chloro-allyl group as new ligand. However, this time, the resulting complex, **M19** (see Scheme 7), features a $\pi\eta^2$ metal coordination through the C1-C2 double bond that gives rise to an actual binding between Cl-CH₂-CH=CH₂ and the palladium. **M19** is a tetrahedral intermediate where the typical donation/back donation pattern can be observed: electron density is donated from the C1=C2 π bonding orbital to the empty metal d-orbitals and back-donated from the filled d-orbitals to the C1=C2 π^* anti-bonding orbital. The slight elongation of the C=C bond (C1-C2 = 1.373 Å) is a clear indication of this situation. **M19** is rather unstable and lies 7.9 kcal mol⁻¹ above reactants: (Pd(PPh₃)₄ + chloro-allyl + CO). It is also higher in energy than Pd(PPh₃)₃ + chloroallyl + CO + PPh₃: therefore, the binding of the allyl fragment to Pd(PPh₃)₃ destabilizes the system, probably for steric reasons that

prevent stronger interaction between the ligands and the metal. The incapability of the palladium to adopt the typical and preferred square-planar coordination reflects this quite unstable setting. As a matter of fact, the displacement of one phosphine from **M19** can very easily take place through the next transition state, **TS13**, which is associated to an energy barrier of 0.2 kcal mol⁻¹ only. This leads to a complex, **M20**, in which the palladium is coordinated by three ligands only and which is 3.3 kcal mol⁻¹ more stable than the three-phosphine complex **M19** (and 4.6 kcal mol⁻¹ above the AL). At the PCM level, this complex is, on the contrary, a little bit more stable than the AL: 1.5 kcal mol⁻¹. As observed several times in the present study, the loss of a phosphine from crowded tetra-coordinated palladium complexes is easy and may lead to a negative energy variation as consequence of the strengthening of the remaining metal-ligands interactions. In **M20**, the C1-C2 double bond is a little longer (1.396 Å) indicating that the allyl-palladium bond has become stronger. Also the two phosphines on the palladium move closer and strengthen their bond with the metal. Furthermore, a very loose interaction between the palladium and the expelled phosphine can still be detected (Pd-P3 = 4.877 Å).

(Table 8)

In the next transition state (**TS14**), the chlorine atom shows once again its great migrating attitude, passing from the allyl group (namely the C3 carbon atom) to the palladium. Also in this case, it is interesting to highlight the long distance between the halogen atom and the metal (Cl-C3 = 3.298 Å): it is evident that these two centres do not need to closely approach each other for their interaction to be effective. The analysis of the eigenvector associated to the negative eigenvalue of the Hessian matrix indicates that also the approaching of C3 to the palladium is actually taking place.

TS14 is located 22.2 kcal mol⁻¹ above the reactants (Pd(PPh₃)₄ + chloroallyl + CO) and its intrinsic activation energy (E(**TS14**) – E(**M20**)) is 17.6 kcal mol⁻¹ (12.5 at the PCM level). The Pd formal oxidation state is passing from 0 to +2. It is important to underline that this critical point, that results to be the highest along the reaction channel that is being discussed, is slightly lower in energy than **TS11**, the highest transition state located on the σ -pathway described in the previous section: by 2.7 kcal mol⁻¹ (2.8 kcal mol⁻¹ at the PCM level). Another significant result is that an analogous transition state describing the migration of the chlorine atom, in which three (and not two) phosphines are bonded to the palladium (i.e. proceeding directly from **M19**) lies 5.4 kcal mol⁻¹ above **TS14**, so that the pathway featuring two phosphines on the metal is favoured. As above-anticipated, the migration of the chlorine onto the palladium has the consequence of yielding a $\pi \eta^3$ type interaction between the allyl fragment and the metal centre (**M21**) in which all the three carbon atoms are practically at the same distance from the palladium: C1-Pd = 2.247 Å, C2-Pd = 2.251 Å and C3-Pd = 2.268 Å. In this configuration, being still bonded to two phosphines, the palladium electronic shell is saturated (just like it was surrounded by the usual four ligands). For this reason, the chlorine atom remains partially detached from the metal (as noted above, chlorine-palladium interactions can be effectual even at large distances): the Cl-Pd distance is 2.968 Å, about 0.5 Å longer than an ordinary chlorine-palladium bond. Also the slight separation of the third “spectator” phosphine that is now basically not interacting with the metal (Pd-P3 = 5.124 Å) has certainly the same motivation. All these transformations do not lead to any significant energy variation though: **M21** has the same energy as **M20**. The subsequent step (**TS15**) is, once more, an easy removal of a phosphine that allows to make room around the palladium coordination sphere for the incoming new ligand. Even in this case, the process is

favoured by the strengthening of the interaction between the palladium and the groups, which remain bonded to it. As a matter of fact in **TS15**, while one phosphine moves away ($\text{Pd-P2} = 2.905 \text{ \AA}$), the allyl moiety and especially the chlorine atom (which stayed farther in **M21**) approach the metal ($\text{Pd-Cl} = 2.576 \text{ \AA}$). In this case, the energy activation is higher than for **TS13**: $5.8 \text{ kcal mol}^{-1}$ ($7.7 \text{ kcal mol}^{-1}$ at the PCM level) because, in this case, not only the breaking of the palladium-phosphorous is taking place, but also a motion of the chlorine atom, which moves to a *trans* position with respect to the allyl fragment. Hence in the next complex, **M22**, the palladium is surrounded by a chlorine atom, the ally fragment (again in a $\pi\text{-}\eta^3$ fashion) and a single phosphine. The expelled phosphine still retains a partial, weak interaction with the metal ($\text{P2-Pd} = 4.540 \text{ \AA}$), while, as anticipated above, the chlorine is now $0.53 \text{ \AA}$ closer to it with respect to **M21** ($\text{Pd-Cl} = 2.440 \text{ \AA}$). Also in this case, the loss of a phosphine causes only a small energy change, **M22** being $0.8 \text{ kcal mol}^{-1}$ above **M21** and $5.4 \text{ kcal mol}^{-1}$ above the reactants.

(Table 9 here)

The next stage involves the entering of the CO molecule into the palladium coordination sphere (**TS16**). The approach of the new ligand, which is forming the new C4-Pd bond ($2.244 \text{ \AA}$), causes a change of the way through which the allyl unit interacts with the metal: one carbon atom moves away from the palladium ($\text{Pd-C1} = 2.253 \text{ \AA}$), while another metal-carbon bond ($\text{Pd-C3} = 2.247 \text{ \AA}$) is becoming a single σ -bond. In other words the allyl chain remains connected to the palladium through C3 only. Also the chlorine atom and the phosphine are slightly moving far from the metal, as consequence of the incoming of the CO molecule. Although the addition of

the new ligand is not sterically hindered, the activation energy associated to the process is neither negligible nor very high: $9.1 \text{ kcal mol}^{-1}$: especially the formation of the new C4-Pd bond requires a certain degree of electronic re-organization on the metal.

(Table 10)

(Figure 5 here)

(Scheme 7 here)

In the next intermediate, **M23**, the palladium has reached its typical and stable square planar tetra-coordination, which, until this point was impossible for the presence of two (or more) cumbersome triphenylphosphines in the metal coordination sphere. The other important feature of this structure is the presence, among the metal ligands, of the two groups between which the new C-C will form (i.e. the allyl group and the CO molecule). In particular, the distance between the two carbon atoms, C3 and C4, which will establish the bond, is $2.813 \text{ \AA}$. A weak, but not negligible interaction is active between one “spectator” phosphine and the metal ($\text{P2-Pd} = 3.977 \text{ \AA}$). Several attempts of bonding this phosphine to the palladium failed: however, since the steric hindrance is allowing it, a slight interaction is present and surely contributes to stabilize this complex, which is $4.7 \text{ kcal mol}^{-1}$ above the AL. It is interesting to note that, all the intermediates located until now along this pathway lie more or less at the same energy level, regardless of the nature of the metal ligands (allyl, chlorine, phosphine or CO molecule), except for **M19** where three cumbersome triphenylphosphines are bonded to the palladium). In **M23**, the palladium oxidation number is still +2.

(Scheme 8 here)

Before proceeding along this reaction channel, it is necessary to point out that before the CO comes into play, from **M21** the system can evolve to **M23** in a different way (a schematic representation of the structures of this alternative part of the reaction pathway is given in Scheme 8). The diffuse nature of the $\pi\text{-}\eta^3$ bonding in **M21** allows an easy conversion to an α -allyl-palladium complex in which the allyl is attached to the metal through a single σ carbon-metal bond (C3-Pd). In this case, this transformation takes place before and not simultaneously with the CO approach, like it happens in **TS16**. In the transition state **TS17** the Pd-C1 bond is clearly elongating (Pd-C1 = 2.890 Å), C1-C2 is assuming a double bond character (C1-C2 = 1.365 Å) and the chlorine atom is approaching the palladium (Pd-Cl = 2.616 Å), which is being taken off part of the charge density previously donated from the allyl unit. Since only a rearrangement of the allyl-palladium bonding is taking place, the energy barrier associated to **TS17** is quite modest: 3.2 kcal mol⁻¹. As anticipated, the complex that forms, **M24**, is characterized by a σ carbon-palladium bond and by a square-planar coordination. However, **M24** is less stable than both **M21** and **M22** (it is located 6.7 kcal mol⁻¹ above the AL). This is a sign of a slight bigger strength of the $\pi\text{-}\eta^3$ interaction over a σ -bond and of the weakness of the palladium-triphenylphosphine bond when the system is crowded and electronically saturated. The next transition state **TS18** involves the approach of the CO molecule to the palladium and the simultaneous expulsion of one phosphine: this leads the system to the above-described **M23** complex. Even in this case the forming Pd-C4 bond is almost formed (Pd-C4 = 2.292 Å) and **TS18** is only 0.6 kcal mol⁻¹ below **TS16** (but 1.8 kcal mol⁻¹

above at the PCM level), that is the corresponding transition state for the Pd-C4 bond formation from the $\pi\text{-}\eta^3$ **M22** complex. In **TS18** no electronic rearrangement is needed for the allyl-palladium interaction and also a phosphorous-palladium bond is being broken (Pd-P2 = 3.173 Å). **TS18** has an activation energy of 7.2 kcal mol⁻¹ (this point is 13.9 kcal mol⁻¹ above the reagents) confirming that the forming of the palladium-CO bond requires a certain amount of energy. An energy analysis of the two alternative paths proceeding from **M21** to **M23** allows us to conclude that both are possible and competitive; the differences between them are actually slight and rely basically on the timing by which the ligands are added and removed from the palladium before reaching the **M23** intermediate (see also Figure 5).

(Scheme 9 here)

The transition state **TS19** following **M23** (see Scheme 9) is the critical point, which describes the other crucial transformation of the process: the formation of the C3-C4 bond. The two atoms are part of the allyl chain and the CO molecule, which are in *cis* position around the metal, so that their approach is not difficult (C3-C4 = 2.053 Å). The transition state is characterized by a three-centered structure: apart from the C3-C4 approach, simultaneously, the C4 bond is moving closer to the palladium (Pd-C4 = 1.903 Å), whereas C3 is moving away from it (2.404 Å) so that only the former will remain bonded to metal. The energy barrier related to this process is 15.8 kcal mol⁻¹ (13.3 kcal mol⁻¹ at the PCM level) and furthermore **TS19** lies 1.7 kcal mol⁻¹ (0.6 kcal mol⁻¹ at the PCM level) lower than **TS14**, the highest point located on this reaction pathway. The structure of **TS19** is emblematic of how the metal performs its catalytic, assisting role, by acting as a “dock” to which two groups can attach to,

before connecting to each other. Even in this case, an equivalent transition state, in which one more phosphine is on the metal, has been located: this structure is 4.1 kcal mol⁻¹ less stable than **TS19**. Once again, even if bonded to the metal, an additional phosphine does not afford an energy stabilization. After the discussed C-C bond formation, the system evolves to an intermediate, **M25**, in which the palladium is bearing three ligands only: one phosphine, one chlorine atom and the allyl carbonyl chain. The CO unit has inserted into the carbon-palladium bond and now the metal is linked to a 4-carbon chain. In spite of the unsaturated metal coordination sphere, this complex is more stable than all the other structures determined so far, because of the formation of a new carbon-carbon bond (**M25** lies 0.4 kcal mol⁻¹ below the AL and 5.1 lower than the previous intermediate). At this point, there is space for an easy approach of a triphenylphosphine to the unsaturated palladium (**TS20**, activation energy= 0.4 kcal mol⁻¹) that brings the system to the already discussed **M18**. The subsequent steps are obviously those already described in the section 3.B.1 and terminates the catalytic cycle. It is worth mentioning that a transition state for an approach of the chloroallyl unit to the palladium in the initial Pd(PPh₃)₃ complex that would eventually lead directly to its oxidation has been found. This transition state would lead to **M24** (see Scheme 8), after the concerted breaking of the allylic carbon-chlorine bond and the formation of the relative carbon-palladium and chlorine-palladium bonds. Additionally, one phosphine leaves the metal. Although this transition state exists, it is located very high in energy compared to any other points discussed so far: 39.6 kcal mol⁻¹. It is evident that there is a high cost of energy for the system when a single carbon atom is involved in the breaking of a bond and the simultaneous forming of an interaction with the palladium. In all the cases of carbon-metal σ -bond formation described above, the carbon atom was previously involved in

a π -interaction (η^2 or η^3) with the palladium that makes smooth and quite easy the establishment of the subsequent bond.

(Table 11)

3.B.3. Formation of $\pi \eta^2$ -allyl-palladium complexes: an alternative way to carbonylation?

The investigation of the potential surface has shown the existence of a third carbonylation pathway involving the formation of $\pi \eta^2$ complexes between the allyl moiety and the metal (η^2 pathway). From the above-discussed **M19** tetrahedral intermediate, the CO molecule can enter the metal coordination sphere (transition state **TS21**, see Scheme 10) and simultaneously interacts with the allyl chain (C1-C4 = 1.766 Å) and one of the three phosphine units (C4-P1 = 2.434 Å). As a consequence of these interactions the C1C2 double bond becomes much longer (C1-C2 = 1.425 Å) and the Pd-C2 forming is almost complete. A cyclic structure can be recognized involving the following five atoms: C2, Pd, P1, C4 and C1 that forms completely in the following intermediate **M26**. However **TS21** is 45.1 kcal mol⁻¹ above the starting reagents and 22.9 kcal mol⁻¹ higher than **TS14** (these values become 12.3 and 30.4 kcal mol⁻¹ when solvent effects are taken into account). **M26** is also very high in energy being 35.1 kcal mol⁻¹ less stable than the reagents. Thus, the η^2 pathway cannot compete with the $\pi\text{-}\eta^3$ (and not even with the σ pathway) and will not be discussed further.

(Scheme 10)

3.C. Extended Basis Set (sdd/TZVP/DZVP) Results

In this section, we discuss the results obtained at the extended sdd/TZVP/DZVP level for the following critical points: (a) **M3, TS2, M4, M5, TS3, M12** and **TS8** for the conversion and reduction mechanism of $\text{Pd}(\text{OAc})_2$ to $\text{Pd}(0)$ complexes (Figure 1 and Figure 2); (b) **M17** and **TS11** for the carbonylation along the σ -pathway (Figure 4); (c) **M20, TS14, TS16, TS18, M22, M23, M24** and **TS19** for the carbonylation occurring along the $\pi \eta^3$ -pathway (Figure 5); (d) **TS21** i.e. the transition state for the carbonylation along the $\pi \eta^3$ -channel. The energy values obtained at the sdd/TZVP/DZVP level are reported in square brackets in Figure 1, 2, 4 and 5.

The most important aspects evidenced by these computations (compared to the DZVP/3-21G* energetics) can be summarized as follows:

(i) The $\text{Pd}(\text{II}) \rightarrow \text{Pd}(0)$ reduction remains an easy process and the general pattern of the energy profile does not change appreciably. The *trans* pathway is still favored over the *cis* one being **TS8** 15.9 kcal mol⁻¹ higher in energy than **TS3**. Also the corresponding intrinsic energy barrier is higher for the *cis* pathway (55.2 kcal mol⁻¹) than for the *trans* pathway (43.3 kcal mol⁻¹). The energy difference between **TS3** and **TS8** and the starting reagents becomes larger at the sdd/TZVP/DZVP level: thus both critical points are now (more realistically) above the AL

(ii) The mechanistic pattern describing the possible reaction channels for the carbonylation of allyl chloride catalyzed by $\text{Pd}(\text{PPh}_3)_4$ does not change significantly. The values of the intrinsic energy barriers for the most important transition states of the $\pi\text{-}\eta^3$ pathway (**TS14, TS16, TS18** and **TS19**) are very similar to those obtained with the DZVP/3-21G* basis set. The most significant difference has been found for the **M22** $\rightarrow$ **TS16** energy barrier, which is now 3.7 kcal mol⁻¹ lower. Therefore, the

system is likely to evolve from **M21** to **M23** along the **TS16** channel instead of the **TS18** channel (these points were almost degenerate at the DZVP/3-21G* level). Furthermore the $\pi\text{-}\eta^3$ pathway is more favored with respect to the σ -pathway: the highest transition state found along the former pathway (**TS14**) lies now 10 kcal mol⁻¹ lower than the highest transition state on the latter (**TS11**).

(iii) The transition state **TS21** for the rate-determining step of the third possible carbonylation pathway (η^2 -pathway), lies 45.2 kcal mol⁻¹ above the AL and 37.2 kcal mol⁻¹ higher than **TS14**. Thus, even according to the extended basis set computations, this channel to carbonylation cannot compete with the two above discussed $\pi\text{-}\eta^3$ and σ reaction pathways.

4. Conclusions

Our results can be summarized as follows:

1) The reduction process of Pd(II) to Pd(0) requires an excess of phosphines that react easily (low barriers and high exothermicity) with the starting reagent Pd(OAc)₂.

2) The consecutive interaction of two phosphines with Pd(OAc)₂ leads to the tetra-coordinated *trans*-Pd(OAc)₂(PPh₃)₂ species (**M4**) where the metal is still in the +2 oxidation state. The actual reduction goes first through an intra-molecular rearrangement where the two acetate fragments move toward the phosphorus atom of one phosphine ligand bound to the metal. Then, an additional phosphine enters the system leading to the formation of Pd(PPh₃)₂ and PPh₃(OAc)₂. In the final stage, the involvement of two more phosphines affords the final product Pd(PPh₃)₄ where the oxidation state of the metal is zero. We would like to point out that our computations, because of the approximations that feature our model-system, do not completely rule

out the conclusions reached by Amatore and Jutland [11] who suggest the involvement of ionic species. [74]

3) An alternative path leading to reduction involves the tetra-coordinated *cis*-Pd(OAc)₂(PPh₃)₂ complex exists, but it is highly disfavoured since it requires the overcoming of larger energy barriers.

4) The existence of three pathways leading to the carbonylation of allyl chloride catalyzed by Pd(0) species such as Pd(PPh₃)₄ has been demonstrated. In the σ -pathway, the first significant coordination to the palladium complex is that of CO. Then, the allyl is involved in the formation of a cyclic transition structure, where the CO molecule interacts at the same time with the allyl chain and the metal. Simultaneously the chlorine atom migrates to the palladium. This transition state (**TS11**, 24.9 kcal mol⁻¹ above the reactants) corresponds to the rate-determining step of the process. The catalytic cycle terminates after a second migration of the chlorine atom and a final addition of a phosphine to the palladium complex. This regenerates the initial catalyst Pd(PPh₃)₄. This mechanism is very similar to that determined in a previous work for the same reaction catalyzed by Pd(II) species (PdCl₂(PR₃)₂) [53].

The second pathway (π - η^3 -pathway) features the formation of η^3 complexes that follows the initial coordination of the allyl substrate in a π η^3 fashion. This step, which corresponds to the rate determining step of the process (**TS14**, 22.2 kcal mol⁻¹ above the reactants), is associated with the chlorine migration to the metal that oxidizes to Pd(II). In a subsequent step the CO molecule also binds to palladium before insertion into the palladium-allyl bond. A second migration of the chlorine atom terminates the catalytic cycle and determines the release of the product. A final addition of a phosphine to the palladium complex leads to the regenerated catalyst Pd(PPh₃)₄. Since the transition states for the rate-determining steps of these two

reaction channels are very close in energy, both reaction paths are likely and can compete.

Finally, a third pathway (η^2 -pathway) involves the CO attack on a $\pi \eta^2$ allyl-palladium complexes, which anticipates the chlorine migration. However, in this case, the transition state of the rate-determining step (TS21) is much higher in energy than the above-mentioned transition states, so that this reaction path cannot compete with the two above described.

5) Our computations clearly indicate that, when using catalysts such as $\text{Pd}(\text{OAc})_2$ with an excess of phosphines, the real catalyst is a $\text{Pd}(0)$ species.

6) During the carbonylation the Pd formal oxidation state changes from 0 to +2 and then to 0 again.

7) The inclusion of solvent effects, computed with the PCM approach, does not significantly affect the mechanistic scenario obtained from gas-phase computations

8) The chlorine atom plays a determinant role in this kind of processes, thanks to its significant migrating attitude and capacity of interacting with the metal even at long distances.

9) The cumbersome phosphines influence the course of the reaction and the stability of the various complexes: in several cases, the metal prefers to expel a phosphine in order to reduce the steric hindrance in the coordination sphere and hence allowing stronger bonds with the remaining ligands.

10) The computations at the extended sdd/TZVP/DZVP level do not significantly affect the mechanistic picture provided by the DZVP/3-21G* basis set. The intrinsic energy barriers computed for the key steps of the various reaction paths

and the relative stability of the most important transition states change only slightly,
thus confirming the conclusions reached at the less accurate level.

Acknowledgments

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Table 1. Selected bond lengths (Å) for the critical points **M0**, **M1**, **TS1**, **M2** and **M3**.

Table 2. Selected bond lengths (Å) for the critical points **TS2**, **M4** and **M5**

Table 3. Selected bond lengths (Å) for the critical points **TS3**, **M6**, **TS4** and **M7**

Table 4. Selected bond lengths (Å) for the critical points **M8**, **TS5**, **M9**, **M10**, **TS6** and **M11**.

Table 5. Selected bond lengths (Å) for the critical points **TS7**, **M12** and **TS8**.

Table 6. Selected bond lengths (Å) for the critical points **M13**, **M14**, **TS9** and **M15**.

Table 7. Selected bond lengths (Å) for the critical points **M16**, **TS10**, **M17**, **TS11**, **M18** and **TS12**.

Table 8. Selected bond lengths (Å) for the critical points **M19**, **TS13**, **M20**.

Table 9. Selected bond lengths (Å) for the critical points **TS14**, **M21**, **TS15** and **M22**.

Table 10. Selected bond lengths (Å) for the critical points **TS16**, **M23**, **TS17**, **M24** and **TS18**

Table 11. Selected bond lengths (Å) for the critical points **TS19**, **M25** and **TS20**

Figure 1. Energy profile of the addition of two tri-phenylphosphine units to the starting $\text{Pd}(\text{OAc})_2$ complex. Energy values are in kcal mol^{-1} . PCM values in round brackets and sdd/TZVP/DZVP values in square brackets. The position of the x axis (energy of asymptotic limit) has been set according to the DZVP/3-21G^* values.

Figure 2. Energy profile of the *trans*- and *cis*-channel (dashed line) for the palladium reduction process. Energy values are in kcal mol^{-1} . PCM values in round brackets and sdd/TZVP/DZVP values in square brackets. The position of the x axis (energy of asymptotic limit) has been set according to the DZVP/3-21G^* values.

Figure 3. Energy profile of the σ -pathway for the carbonylation reaction of allyl chloride catalyzed by $\text{Pd}(0)$ complexes. Energy values are in kcal mol^{-1} . PCM values in round brackets.

Figure 4. Energy profile of the σ -pathway for the carbonylation reaction of allyl chloride catalyzed by $\text{Pd}(0)$ complexes. Energy values are in kcal mol^{-1} . PCM values in round brackets and sdd/TZVP/DZVP values in square brackets. The position of the x axis (energy of asymptotic limit) has been set according to the DZVP/3-21G^* values.

Figure 5. Energy profile of the $\pi \eta^3$ -pathway for the carbonylation reaction of allyl chloride catalyzed by $\text{Pd}(0)$ complexes. In dashed line (and italic for lettering), the second possible pathway connecting **M21** to **M23**. Energy values are in kcal mol^{-1} . PCM values in round brackets and sdd/TZVP/DZVP values in square brackets. The

position of the x axis (energy of asymptotic limit) has been set according to the DZVP/3-21G* values.

Scheme 1. Representation of the structure of the critical points localized on the profile of the addition of two tri-phenylphosphine units to the starting Pd(OAc)₂ complex

Scheme 2. Representation of the structures located along *trans*-channel (first part) for the palladium reduction process

Scheme 3. Representation of the structures located along *trans*-channel (second part) for the palladium reduction process

Scheme 4. Representation of the structures located along the first part of the *cis*-channel for the palladium reduction process

Scheme 5. Representation of the structure of the critical points located in the path for the formation of the phosphine oxide

Scheme 6. Representation of the structure of the critical points located along the σ -pathway for the carbonylation reaction of allyl chloride catalyzed by Pd(0) complexes

Scheme 7. Structures of the critical points located along the first part of the $\pi \eta^3$ -pathway for the carbonylation reaction of allyl chloride catalyzed by Pd(0) complexes

Scheme 8. Representation of the structure of the critical points located along an alternative channel for passing from **M21** to **M25** along the $\pi \eta^3$ -pathway for the carbonylation reaction of allyl chloride catalyzed by Pd(0) complexes

Scheme 9. Representation of the structure of the critical points located along the second part of the $\pi \eta^3$ -pathway for the carbonylation reaction of allyl chloride catalyzed by Pd(0) complexes

Scheme 10. Representation of the structures of the critical points located on the η^2 pathway

- [1] N. Miyaura, A. Suzuki, Chem. Rev. **95**, 2457 (1995).
- [2] R. F. Heck, Org. React. **27**, 345 (1982).
- [3] B. M. Trost, D. L. Van Vranken, Chem. Rev. **96**, 395 (1996).
- [4] E. I. Negishi, Acc. Chem. Res. **15** 340 (1982). M. Kalek, J. Stawinski, Organometallics **26**, 5840 (2007).
- [5] G. Kiss, Chem. Rev. **101**, 3435 (2001): refs. 13k, q, s, 14b, 20f and 49 therein.
- [6] J. F. Knifton, J. Am. Oil. Chem. Soc. **55**, 496 (1978).
- [7] D. M. Fenton, J. Org. Chem. **38** 3192 (1973).
- [8] K. Bittler, N. Kutepow, D. Neubauer, H. Reis, Angew. Chem. Int. Ed. Engl. **7**, 329 (1968).
- [9] E. I. Negishi, A.O. King, N.J. Okukado, Org. Chem. **42**, 1821 (1977). J. F. Fauvarque, A. Jutand, Bull. Soc. Chim. Fr. 765 (1976).
- [10] C. Amatore, M. Azzabi, A.J. Jutand, Organomet. Chem. **363**, C41 (1989).
- [11] C. Amatore, A. Jutand, M.A. M'Barki, Organometallics **11**, 3009 (1992). C. Amatore, E. Carré, A. Jutand, M.A. M'Barki, Organometallics **14**, 1818 (1995). C. Amatore, A. Jutand, J. Organomet. Chem. **576**, 254 (1999).
- [12] C. Amatore, M. Azzabi, A. Jutand, J. Am. Chem. Soc **113**, 8375 (1991). J.K. Kochi, Organometallic Mechanisms and Catalysis, Academic Press: New York 1978, Part I, Chapter 7. C. Amatore, M. Azzabi, A. Jutand, J. Am. Chem. Soc. **113**, 1670 (1991). C. Amatore, A. Jutand, F. Khalil, M.A. M'Barki, L. Mottier, Organometallics **12**, (1993) 3168. A.L. Casado, P. Espinet, J. Am. Chem. Soc. **120**, 8978 (1998). A.L. Casado, P. Espinet, Organometallics **17**, 954 (1998). P. Espinet, A. M. Echavarren, Angew.

- Chem., Int. Ed. **43**, 4704 (2004). F. M. Bickelhaupt, T. Ziegler, P.v.R. Schleyer, *Organometallics* **14**, 2288 (1995). A. Diefenbach, F.M. Bickelhaupt, *J. Chem. Phys.* **115**, 4030 (2001). K. Albert, P. Gisdakis, N. Rösch, *Organometallics* **17**, 1608 (1998). M. Jakt, L. Johannissen, H.S. Rzepa, D.A. Widdowson, A. Wilhelm, *J. Chem. Soc., Perkin Trans.* **2**, 576 (2002). A. Sundermann, O. Uzan, J. M. L. Martin, *Chem. Eur. J.* **7**, 1703 (2001). M.H. Senn, T. Ziegler, *Organometallics* **23**, 2980 (2004). L.J. Goosen, D. Koley, H. Hermann, W. Thiel, *Chem. Commun.* 2141 (2004).
- [13] S. Kozuch, C. Amatore, A. Jutand, S. Shaik, *Organometallics* **24**, 2319 (2005).
- [14] C. Amatore, E. Carré, A. Jutand, M.A. M'Barki, G. Meyer, *Organometallics* **14**, 5605 (1995). C. Amatore, A. Jutand, *Acc. Chem. Res.* **33**, 314 (2000).
- [15] S. Kozuch, S. Shaik, C. Amatore, A. Jutand, *Chem. Eur. J.* **10**, 3072 (2004).
- [16] F. Ozawa, A. Kubo, T. Hayashi, *Chem. Lett.* 2177 (1992).
- [17] W.A. Hermann, *J. Organomet. Chem.* **383**, 21 (1990).
- [18] G. Kiss, *Chem. Rev.* **101**, 3435 (2001).
- [19] J. A. Osborn, J. F. Young, G. Wilkinson, *J. Chem. Soc., Chem. Commun.* 17 (1965). R.F. Heck, *Palladium Reagents in Organic Synthesis*, Academic Press, New York 1985. – J. Tsuji, *Organic Synthesis and Palladium Compounds*, Springer, Berlin 1980.
- [20] H.M. Colquhoun, D.J. Thompson, M.V. Twigg, *Carbonylation: Direct Synthesis of Carbonyl Compounds*, Plenum Press, New York, (1991).
- [21] M. Beller, B. Cornilis, C.D. Frohning, C.W. Kohlpaintner, *J. Mol. Cat.* **104**, 17 (1995).
- [22] G.P. Chiusoli, *Chim. Ind.* **41**, 503 (1959).
- [23] J. Tsuji, M. Morikawa, J. Kiji, *Tetrahedron Lett.* 1811 (1963).
- [24] F. Joo, H. Alper, *Organometallics* **4**, 1775 (1985). S-I. Murahashi, Y. Imada, Y. Taniguchi, S. Higashiura, *Tetrahedron Lett.* **29**, 4945 (1988).
- [25] A. Yamamoto, *Bull. Chem. Soc. Jpn.* **68**, 433 (1995).
- [26] H. Jiang, Y. Xu, S. Liao, D. Yu, H. Chen, X. Li, *J. Mol. Cat. A: Chemical* **130**, 79 (1998).
- [27] F. Bertoux, E. Monflier, Y. Castanet, A. Mortreux, *J. Mol. Cat. A: Chemical* **143**, 11 (1999).
- [28] R. Grigg, A. Liu, D. Shaw, S. Suganthan, D.E. Woodall, G. Yoganathan, *Tetrahedron Lett.* **41**, 7125 (2000).
- [29] M.M. Bio, L. Leighton, *Organic Letters* **2**, 2905 (2000).
- [30] S. El Houssame, L. El Firdoussi, S. Allaoud, A. Karim, Y. Castanet, A. Mortreux, *J. Mol. Cat. A: Chemical* **168**, 15 (2001).
- [31] G.P. Chiusoli, *Angew. Chem.* **72**, 74 (1960).
- [32] R.F. Heck, *J. Am. Chem. Soc.* **85** (1963) 2013.
- [33] G.P. Chiusoli, L. Cassar, *Angew. Chem. Int. Ed. Engl.* **6**, 124 (1967).
- [34] R.F. Heck, *Acc. Chem. Res.* **2**, 10 (1969).
- [35] G.P. Chiusoli, *Acc. Chem. Res.* **6**, 422 (1973).
- [36] E. J. Kuhlmann, J. J. Alexander, *Coordination Chemistry Reviews* **33**, 195 (1980).
- [37] G. Garcia-Gomez, J.M. Moreto, *J. Am. Chem. Soc.* **121**, 878 (1999).
- [38] J. R. Johnson, P.S. Tully, P.B. Mackenzie, M. Sabat, *J. Am. Chem. Soc.* **113**, 6172 (1991). B.A. Grisso, J.R. Johnson, P.B. Mackenzie, *J. Am. Chem. Soc.* **114**, 5160 (1992).
- [39] W.T. Dent, R. Long, G.H. Whitfield, *J. Chem Soc.* 1588 (1964). R. Long, G.H. Whitfield, *J. Chem Soc.* 1852 (1964).

- [40] J. Tsuji, J. Kiji, S. Imamura, M. Morikawa, *J. Am. Chem. Soc.* **86**, 4350 (1964).
J. Tsuji, *Acc. Chem. Res.* **2**, 144 (1969).
- [41] D. Mllstein, *Organometallics* **1**, 888 (1982).
- [42] J. Tsuji, K. Sato, H. Okumoto, *J. Org. Chem.* **49**, 1341 (1984).
- [43] S-I. Murahashi, Y. Imada, Y. Taniguchi, S. Higashiura, *Tetrahedron Lett.* **29**, (1988) 4945.
- [44] J. Kiji, T. Okano, Y. Higashimae, Y. Fukui, *Bull. Chem. Soc. Jpn.* **69**, 1029 (1996).
- [45] H. Jiang, Y. Xu, S. Liao, D. Yu, H. Chen, X. Li, *J. Mol. Cat.* **130**, 79 (1998).
- [46] F. Bertoux, E. Monflier, Y. Castanet, A. Montreux, *J. Mol. Cat.* **143**, 11 (1999).
- [47] S. El Houssame, L. El Firdoussi, S. Allaoud, A. Karim, Y. Castanet, A. Mortreux, *J. Mol. Cat. A: Chem.* **168**, 15 (2001).
- [48] J. G. Knight, K. Tchabanenko, *Tetrahedron* **58**, 6659 (2002).
- [49] R. Song, J. Zeng, B. Zhong, *Catalysis Lett.* **82**, 89 (2002).
- [50] T. Okano, N. Okabe, *Bull. Chem. Soc. Jpn.* **65**, 2589 (1992).
- [51] F. Bernardi, A. Bottoni, M. Nicastro, I. Rossi, J.J. Novoa, X. Prat-Resina, *Organometallics* **19**, 2170 (2000).
- [52] A. Bottoni, G.P. Miscione, G. P., J.J. Novoa, X. Prat-Resina, *J. Am. Chem. Soc.* **125**, 10412 (2003).
- [53] M.A. Carvajal, G.P. Miscione, J.J. Novoa, A. Bottoni, *Organometallics* **24**, 2086 (2005).
- [54] Gaussian 03, Revision C.02, M. J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, (2004).
- [55] A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
- [56] [a] G. A. Di Labio, D. A. Pratt, J. S. Wright, *Chem. Phys. Lett.* **297**, 181 (1998).
[b] J.S. Wright, E. R. Johnson, G.A. Di Labio, *J. Am. Chem. Soc.* **123**, 1173 (2001).
- [57] N. Godbout, D.R. Salahub, J. Andzelm, E. Wimmer, *Can. J. Chem.* **70**, 5600 (1992).
- [58] S. Miertus, E. Scrocco, J. Tomasi, *Chem. Phys.* **55**, 117 (1981). S. Miertus, J. Tomasi, *Chem. Phys.* **65**, 239 (1982).
- [59] D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta* **77**, 123 (1990)
- [60] A. Schaefer, H. Horn, and R. Ahlrichs, *J. Chem. Phys.*, **97**, 2571 (1992); A. Schaefer, C. Huber, and R. Ahlrichs, *J. Chem. Phys.*, **100**, 5829 (1994).

- [61] A. J. Blake, R.W. Cockam, E.A.V. Ebsworth, S.G.D. Henderson, J. H. Holloway, N.J. Pilkington, D. W. H. Rankin, *Phosphorus and Sulfur*, **30**, 143 (1987).
- [62] [a] M.A. Carvajal, G.P. Miscione, A. Accardi, J.J. Novoa, A. Bottoni, *Molecular Physics* **104**, 805 (2006). [b] M.A. Carvajal, G.P. Miscione, A. Accardi, J.J. Novoa, A. Bottoni, *Journal of Organometallic Chemistry* **691**, 4498 (2006). [c] F. Bernardi, G.P. Miscione, A. Bottoni, *Organometallics* **20**, 2751 (2001).
- [63] L. J. Goossen, D. Koley, H.L. Hermann, W. Thiel, *Organometallics*, **24**, 2398 (2005).
- [64] A.A.C. Braga, G. Ujaque, F. Maseras, *Organometallics*, **25**, 3647 (2006).
- [65] A. Ariafard, Z. Lin, *Organometallics*, **25**, 4030 (2006).
- [66] M. Ahlquist, P.-O. Norrby, *Organometallics*, **26**, 550 (2007).
- [67] P. Surawatanawong, M.B. Hall *Organometallics*, **27**, 6222 (2008).
- [68] R. Martin, S.L. Buchwald, *Acc. Chem. Res.* **41**, 1461 (2008).
- [69] M. Catellani, E. Motti, N. Della CA', *Acc. Chem. Res.* **41**, 1512 (2008).
- [70] G.C. Fu, *Acc. Chem. Res.* **41**, 1555 (2008).
- [71] E. Zuidema, C. Bo, P.W.N.M. van Leeuwen, *J. Am. Chem. Soc.* **129**, 3989 (2007).
- [72] X. Zhang, Z. Lu, C. Fu and S. Ma, *Org. & Biomol.Chem.* **7**, 3258 (2009).
- [73] J. Takaya, K. Sangu K, N. Iwasawa *Angew. Chem.-Int. Ed.* **48**, 7090 (2009).
- [74] In order to verify the hypothesis that the reaction follows a pathway involving ionic species [11], we have carried out PCM calculations on the two following systems: a) $\text{PPh}_3(\text{OAc})_2 + \text{Pd}(\text{PPh}_3)_2$ (**M7**) and the alternative charged system b) $\text{PPh}_3(\text{OAc})^{(+)} + \text{Pd}(\text{PPh}_3)_2(\text{OAc})^{(-)}$ which would form in the case of a ionic pathway. The solvent emulated by the PCM calculations was nitromethane ($\epsilon = 38.2$). The computational results show that system a) is $29.6 \text{ kcal mole}^{-1}$ more stable than system b). Also, we have compared, in the same medium, the relative stability of $\text{PPh}_3(\text{OAc})_2$ and $\text{PPh}_3(\text{OAc})^+ + (\text{OAc})^-$. Even in this case the neutral system turns out to be more stable (by $6.4 \text{ kcal mol}^{-1}$) than the charged one.
- The above described computational findings suggest that, at least for the present model, the mechanism proposed in our study seems to be favoured with respect to a reaction pathway involving ionic species. However, it is possible, even if unlikely if we consider the significant energy difference between system a) and system b), that the approximations of an implicit solvent model (such as PCM) affect this conclusion and that the employment of a larger model system (possibly with explicit solvent description) may lead to different results.

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trans channel

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 $E_a = 4.5$ (4.1)

TS2

M4

M5

 $E_a = 25.5$ (33.9)

TS3

M6

TS4

M7

M8

URL: <http://mc.manuscriptcentral.com/tandf/tmph>

trans channel

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M9

M11

TS6

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M13

+ H₂O

M14

TS9

M15

Molecular Physics

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Molecular Physics

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Table 1. Selected bond lengths (Å) for the critical points **M0**, **M1**, **TS1**, **M2** and **M3**.

	Pd-O1	Pd-O2	Pd-O3	Pd-O4	Pd-P1	O1-H1	Pd-P2	O1-H2
M0	2.094	2.097	2.104	2.101	/	/	/	/
M1	2.106	2.095	2.100	2.109	3.747	2.439	/	/
TS1	2.251	2.053	2.163	2.081	3.072	2.440	/	/
M2	3.088	2.042	2.239	2.119	2.304	/	/	/
M3	2.991	2.056	2.199	2.132	2.309	/	4.110	2.292

Table 2. Selected bond lengths (Å) for the critical points **TS2**, **M4** and **M5**

	Pd-O1	Pd-O2	Pd-O3	Pd-O4	Pd-P1	Pd-P2	O1-P1	O3-P1
TS2	3.048	2.109	2.377	2.125	2.296	3.040	4.087	3.927
M4	3.005	2.073	3.181	2.082	2.396	2.412	3.427	4.376
M5	3.137	2.084	3.047	2.064	2.410	2.410	2.884	3.862

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Table 3. Selected bond lengths (Å) for the critical points **TS3**, **M6**, **TS4** and **M7**

	Pd-O2	Pd-O4	O1-P1	O3-P1	Pd-P1	Pd-P2	P1-C1	Pd-C1	Pd-C2	Pd-P3
TS3	2.539	2.438	1.861	1.904	2.478	2.504	1.914	2.402	2.686	/
M6	3.743	5.134	1.857	1.863	5.134	2.355	1.820	2.310	2.397	4.743
TS4	3.520	4.529	1.861	1.863	4.530	2.361	1.824	3.226	2.446	3.544
M7	/	/	1.846	1.846	/	2.365	/	/	/	2.365

Table 4. Selected bond lengths (Å) for the critical points **M8**, **TS5**, **M9**, **M10**, **TS6** and **M11**.

	Pd-P2	Pd-P3	Pd-P4	C3-H3	Pd-P5	C4-H4
M8	2.365	2.370	4.856	2.800	/	
TS5	2.368	2.371	3.970	3.180	/	
M9	2.431	2.424	2.416	/	/	
M10	2.421	2.413	2.431	/	5.161	2.811
TS6	2.462	2.465	2.459	/	3.447	/
M11	2.550	2.543	2.550	/	2.535	

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Table 5. Selected bond lengths (Å) for the critical points **TS7**, **M12** and **TS8**.

	Pd-O1	Pd-O2	Pd-O3	Pd-O4	Pd-P1	Pd-P2	O2-P3	O1-P3	O4-P3
TS7	3.120	2.166	2.117	2.420	2.300	2.787	/	/	/
M12	2.949	2.118	2.119	2.967	2.327	2.330	/	/	/
TS8	/	2.649	2.252	3.573	2.513	2.366	2.130	2.572	2.941

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Table 6. Selected bond lengths (Å) for the critical points **M13**, **M14**, **TS9** and **M15**.

	P1-O1	P1-O3	P1-O5	H1-O2	H1-O5	H2-O4	H2-O5
M13	1.846	1.846	/	/	0.969	/	0.969
M14	1.876	1.827	/	1.900	0.980	/	0.968
TS9	2.131	1.750	1.918	1.172	1.244	1.968	0.980
M15	4.156	4.032	1.529	0.998	1.735	0.999	1.728

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Table 7. Selected bond lengths (Å) for the critical points **M16**, **TS10**, **M17**, **TS11**, **M18** and **TS12**.

	Pd-P1	Pd-P2	Pd-P3	Pd-Cl	C3-Cl	C4-Cl	Pd-C4	C1-C4
M16	2.422	2.433	2.424	4.697	1.848	/	/	/
TS10	2.430	2.453	2.438	8.422	1.842	/	3.244	/
M17	2.533	2.515	2.518	7.482	1.844	/	2.015	/
TS11	2.535	2.508	2.626	4.654	2.392	/	2.087	1.912
M18	2.618	2.408	4.291	2.485	/	2.860	2.048	1.541
TS12	2.684	2.437	2.698	2.928	/	1.998	2.384	1.530

Table 8. Selected bond lengths (Å) for the critical points **M19**, **TS13**, **M20**.

	Pd-C1	Pd-C2	Pd-P1	Pd-P2	Pd-P3	C3-Cl	C1-C2
M19	2.386	2.443	2.492	2.506	2.622	1.880	1.373
TS13	2.321	2.368	2.473	2.481	2.856	1.881	1.381
M20	2.227	2.263	2.427	2.438	4.877	1.885	1.396

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Table 9. Selected bond lengths (Å) for the critical points **TS14**, **M21**, **TS15** and **M22**.

	Pd-C1	Pd-C2	Pd-C3	Pd-P1	Pd-P2	Pd-Cl	C3-Cl	C1-C2	C2-C3
TS14	2.147	2.337	3.040	2.366	2.529	3.298	2.637	1.429	1.392
M21	2.247	2.251	2.268	2.428	2.442	2.968	/	1.411	1.406
TS15	2.222	2.240	2.266	2.395	2.905	2.576	/	1.412	1.405
M22	2.242	2.225	2.201	2.404	4.540	2.440	/	1.402	1.417

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Table 10. Selected bond lengths (Å) for the critical points **TS16, M23, TS17, M24** and **TS18**.

	Pd-C1	Pd-C3	Pd-C4	Pd-P1	Pd-P2	Pd-Cl	C4-C1	C1-C2	C2-C3
TS16	2.247	2.253	2.244	2.389	5.167	2.588	3.445	1.411	1.410
M23	/	2.164	1.958	2.504	3.977	2.416	2.813	1.349	1.471
TS17	2.890	2.137	/	2.395	2.467	2.616	/	1.365	1.450
M24	/	2.133	/	2.375	2.568	2.472	/	1.351	1.471
TS18	/	2.132	2.292	2.396	3.173	2.460	3.924	1.351	1.465

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Table 11. Selected bond lengths (Å) for the critical points **TS19**, **M25** and **TS20**

	C4-O	Pd-C3	Pd-C4	Pd-P1	Pd-P2	Pd-Cl	C4-C1	C1-C2	C2-C3
TS19	1.164	2.404	1.903	2.387	5.763	2.432	2.053	1.345	1.478
M25	1.196	/	2.004	2.375	6.238	2.393	1.536	1.338	1.509
TS20	1.196	/	1.994	2.389	3.367	2.402	1.527	1.337	1.507

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Supporting information file for the paper:

A Theoretical Investigation on the Oxidation States of Palladium Complexes and their Role in Carbonylation Reaction

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A. Full geometry optimizations with the DZVP basis set on all atoms

To check the reliability of the approach using the DZVP basis set on all atoms except the phenyl rings (on which the 3-21G* basis set has been employed), we have carried out additional computations (with full geometry optimization) using the DZVP basis set on all atoms and we have compared the results to those obtained at the DZVP/3-21G* level. The full geometry optimizations have been performed on the following critical points: **M5**, **TS3**, **M6**, **TS4**, **M11**, **TS11**, **M20**, **TS14**, corresponding to four key steps. We have found that the more accurate representation provides results (energetics and geometrical parameters) very similar to the DZVP/3-21G* basis.

We report here the schematic representation of the eight structures with the values of the most important geometry parameters obtained at the DZVP/3-21G* level and with the full DZVP basis set (values in italic and in brackets). The four activation energy barriers are also displayed: values obtained with the DZVP basis set are in italic and in brackets.

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B. IRC calculations

A series of IRC computations has been carried out starting from the most important transition state structures in order to confirm the topology connections. The transition states for which the IRC calculations have been performed are the following: **TS3** (toward reagents and products), **TS4** (toward reagents), **TS11** (toward reagents), **TS19** (toward reagents and products). In several cases, as the transition state involves the displacement of a phosphine group from the metal, the IRC calculations cannot clearly indicate a complete separation of the two groups. As a matter of fact, once the Pd-P bond has slightly elongated in the first steps of the IRC calculation, the phosphine group tends to maintain a slight interaction with the metal and not to totally separate. However, even in these cases, the vibrational analysis undoubtedly shows that the normal mode with imaginary frequency involves the breaking of the Pd-P bond.

We report here the results of the IRC calculations as (i) schematic representation of the structure of the initial transition state, the last point of the IRC and the following intermediate on the PES; (ii) graphics in which the y axis represents the energy of the various IRC points (in kcal mol⁻¹, the energy of the transition state is the reference) and the x axis the net reaction coordinate.

TS3 toward M5 (reagents)

TS3 toward M6 (products)

TS4 toward M6 (reagents)

TS11 toward **M17** (reagents)

TS19 toward **M23** (reagents)

TS19 toward M25 (products)