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Cationic (η^1-Allyl)-palladium Complexes as Feasible Intermediates in Catalyzed Reactions

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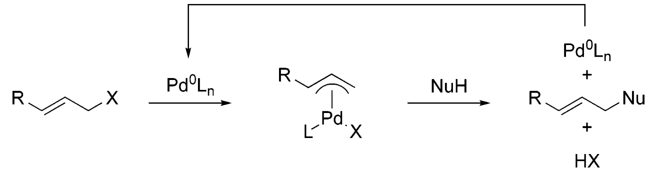
A computational study on the structure and reactivity of (η^1-allyl)-Pd complexes has been performed on model systems containing different neutral and cyclometalating ligands. A comparison of the reactivity of these compounds with the usually proposed (η^3-allyl)-Pd derivatives has been performed to investigate the feasibility of the participation of the former as intermediates in Pd-catalyzed reactions. These complexes are more stable than (η^3-allyl)-Pd derivatives with a cyclometalated PCP tridentate ligand. Intermediates, transition states, and activation and reaction energies have been calculated for several reactions of cationic and neutral complexes: (a) nucleophilic attack of NH_3 on the allyl system, (b) nucleophilic attack of the γ-allyl carbon on formaldehyde, (c) pallada-ene reactions of σ-allyl complexes with ethylene, and (d) pallada-ene type reactions of σ-allyl complexes with acetylene. Our results show that (η^1-allyl)-Pd complexes are probably not involved as intermediates in the Tsuji−Trost reactions with NH_3; that even cationic complexes would be able to react as nucleophiles with aldehydes in two different ways, and that pallada-ene type reactions of these complexes with alkenes and alkynes show more stable transition states than those corresponding to the usual mechanisms involving prior coordination of the unsaturated species followed by 1,2 migratory insertion in either σ- or π-allyl bonds.

Introduction

Allylpalladium complexes have attracted much attention due to their importance as reactive intermediates in synthetically useful catalyzed reactions.[1−3] These derivatives may undergo different reactions in the catalytic cycles, leading to the final products and regenerating the catalytically active Pd species. Computational studies have become an important tool for the study of this type of complexes.[4] Allyl ligands can react in different ways to give C−C bonds. Thus, nucleophilic attack on the terminal carbons of a η^3-allyl (or π-allyl) ligand is the key step in the palladium-catalyzed allylic substitution (Tsuji−Trost reaction, Scheme 1).[5−8] Attack of the nucleophile on the central carbon has also been documented,[9] and the reasons for this behavior have been computationally explored.[10] The regioselectivity of the reaction on terminal carbons has also been studied computationally for substrates containing nonequivalent α- and γ-carbon atoms.[11] In the case of allyl ligands substituted by alkyl or aryl groups, nucleophiles usually attack the less hindered carbon. Nevertheless, the situation is more complicated, and electronic factors depending on the ligands and the nucleophile also play an important role in both regio- and stereochemistry.[12]

Scheme 1



On the other hand, allylpalladium complexes may undergo 1,2-insertion of alkenes or alkynes, and 1,1-insertion of CO,

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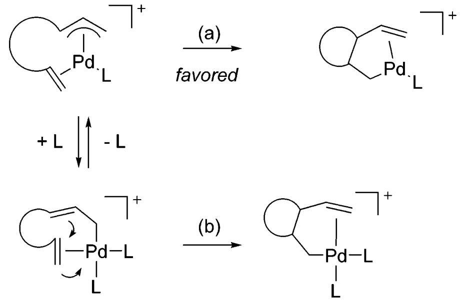
Scheme 2

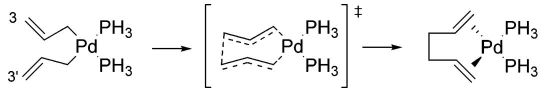


when an unsaturated carbon ligand is present in the coordination sphere.[3] Insertion of an olefin into π-allylpalladium bonds has been proposed as the key step in the Oppolzer reaction. The initially proposed metalo-ene process was shown to be strongly disfavored (Scheme 2).[13]

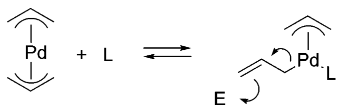
In addition, transmetalation of the allyl ligand from Pd has also been documented. Thus, transfer of allyl from Pd(II) to Zn(II) gives nucleophilic allylzinc species, which results from the umpolung of the reactivity of the starting allyl electrophiles.[14] Finally, when a second carbon ligand such an alkyl, alkenyl, alkynyl, or aryl becomes bound to Pd, a C−C reductive elimination may take place, thus affording reduced Pd(0) species, which can enter the catalytic cycle.[1,3] This is the case for allylpalladium species involved in metal-catalyzed cross-coupling reactions.[1] Reductive elimination is also possible from bis(allyl)palladium derivatives to afford 1,5-dienes as the final step in Stille[15] and Hiyama[16] cross-coupling reactions involving both an allyl-Sn or allyl-Si reagent and an allylic electrophile. The presence of ligands such as phosphines seems to play a crucial role in this step. Computational studies have allowed the proposal that the actual intermediates from which the reductive elimination takes place are bis(η^1-allyl)palladium complexes, formed by coordination of phosphines.[17] Reductive elimination taking place by C−C bond formation between the 3 and 3′ positions is far more favorable that the direct coupling between the metal-bonded carbons (Scheme 3).

On the other hand, bis(allyl)palladium complexes show nucleophilic behavior, in contrast with the electrophilic character observed for the mono(allyl) derivatives involved in the Tsuji−Trost reaction. Reaction of one of the allyl ligands with electrophiles such as aldehydes results in monoallyl derivatives, which can further react with nucleophiles, thus making bis(allyl) complexes highly valuable for synthetic purposes.[18−20] The reactive species against electrophiles have been shown to be (η^1-allyl)(η^3-allyl)palladium derivatives formed by ligand coordination to bis(η^3-allyl)palladium complexes (Scheme 4).[21] In addition, these complexes were also demonstrated to be the most stable species in the presence of phosphine ligands.[22]

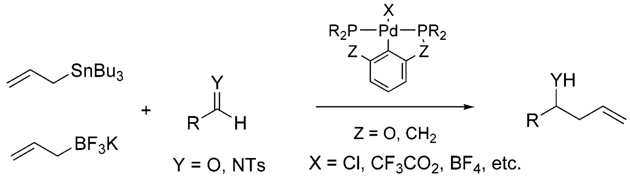
Scheme 3



Scheme 4



Scheme 5



Recently, palladated complexes derived from tricoordinate ligands have been used in the reactions of allylstannanes with aldehydes and imines (Scheme 5).[23,24] The terdentate chelating coordination forces the formation of η^1-allyl intermediates, which react with the electrophile. A low activation barrier has been calculated for the reaction of the γ-position of the η^1-allyl complex with aldehydes.[25] This type of complexes also catalyzes the formation of allylstannanes and allylboronates[23] from allylic electrophiles, since the pincer structure of the ligand prevents the formation of bis(allyl)palladium intermediates and, therefore, the homocoupling of the nucleophile.

Interconversion between (η^1-allyl)- and (η^3-allyl)palladium complexes takes place easily and constitutes a key step in the isomerization between different conformers of (η^3-allyl)palladium derivatives. This process has been studied both experimental and computationally.[26] The use of tridentate ligands has allowed isolation of (η^1-allyl)palladium derivatives.[27,28] Although π-allyl derivatives are the actual intermediates in most catalytic reactions in which allylpalladium complexes are

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involved, the ready formation of σ-allyl complexes suggests that these compounds could participate as productive intermediates in Pd-catalyzed reactions.

The intrinsic reactivity of η^1-allyl-Pd complexes must be controlled not only by hapticity but also by the electronic properties of the metallic fragment, which in turn can be modulated by appropriate choice of ligands. Herein we report our results on the computational insight into the reactivity of model (η^1-allyl)Pd complexes with different ligands. Both neutral and cationic species have been studied. We have addressed the influence of the global charge and the ligand hapticity on the activation and reaction energies of four different reactions: (a) nucleophilic attack of NH_3 on the allyl system, (b) nucleophilic attack of the γ-allyl carbon on formaldehyde, (c) pallada-ene reactions of σ-allyl complexes with ethylene, and (d) pallada-ene type reactions of σ-allyl complexes with acetylene. Finally, we have been able to assess the feasibility of the pallada-ene mechanisms as C−C bond productive steps by comparison with the usually proposed 1,2-insertion reactions of ethylene and acetylene into (σ-allyl)-Pd and (π-allyl)-Pd bonds.

Computational methods

Calculations were performed with Gaussian 03 at the DFT level.[29] The geometries of all complexes here reported were optimized using the B3LYP hybrid functional.[30] Optimizations were carried out using a basis set we refer to as B_1. It consists of the standard 6-31G(d) basis set for C, H, O, and P. The LANL2DZ basis set, which includes the relativistic effective core potential (ECP) of Hay and Wadt and employs a split-valence (double-ζ) basis set, was used for Pd.[31] For more accurate energy values, single-point calculations were performed on the optimized geometries using a larger basis set (B_2), essentially a valence triple-ζ one. Thus, the 6-311+G(2df,2p) basis set was used for C, H, N, O, and P. For Pd, the Sttutgart RSC ECP was utilized. The (8s7p6d) primitive set was contracted to [6s5p3d] and was supplemented with two f and one g polarization function ($\zeta_f = 0.6122, 2.1857$; $\zeta_g = 1.3751$).[32] Harmonic frequencies were calculated at the same level with basis set B_1, to characterize the stationary points and to determine the zero-point energies (ZPEs). Energies calculated with basis set B_1 were corrected with these ZPEs without scaling. Unless otherwise stated, the energy values in the following schemes refer to those obtained at the B3LYP/B_2//B3LYP/B_1 level. The starting approximate geometries for the transition states (TSs) were graphically located. Intrinsic reaction coordinate (IRC) studies were performed in ambiguous cases to confirm the relation of the transition states to the corresponding minima. The bonding characteristics of the different stationary points were analyzed by means of two different partition techniques, namely, the atoms-in-molecules (AIM) theory of Bader[33] and the natural bond orbital (NBO) analysis of Weinhold et al.[34] The first approach is based on a topological analysis of the electron charge density, $\rho(\mathbf{r})$ and its Laplacian $\nabla^2\rho(\mathbf{r})$. More specifically, we have located the so-called bond critical points (bcp's), i.e., points where $\rho(\mathbf{r})$ is minimum along the bond path and maximum in the other two directions. These points are associated with the positions of the chemical bonds. Then, at the bcp, $\rho(\mathbf{r})$ presents one positive curvature (λ_3) and two negative ones (λ_1, λ_2). The NBO technique permits the description of the different bonds of the system in terms of the natural hybrid orbitals centered on each atom and also provides useful information on the charge distribution of the system. Solvent effects were considered by performing single-point calculations in THF using the polarized continuum model (PCM) on the optimized structures.

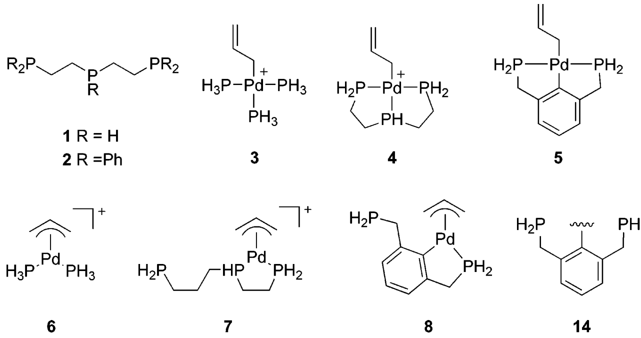

Figure 1.

Results and Discussion

1. Allylpalladium Complexes. Model complexes used for this study are depicted in Figure 1. Tridentate ligand **1** was chosen as a simplified model for triphos (**2**) and related phosphines. Comparison between the results for complexes **3** and **4** provides information about the influence of the chelate effect and the electronic character of the ligand, since the alkyl bridging moieties enhance the σ-donor ability of P atoms.[35] Neutral cyclometalated derivative **5** was used to study the different reactivity compared with cationic derivative **4**. The

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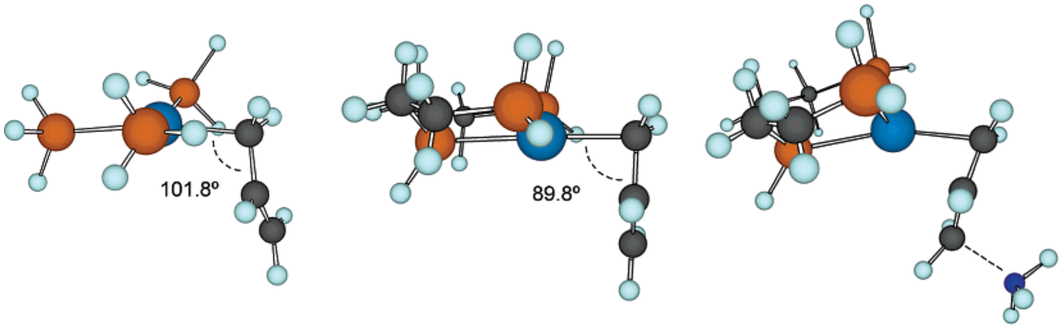
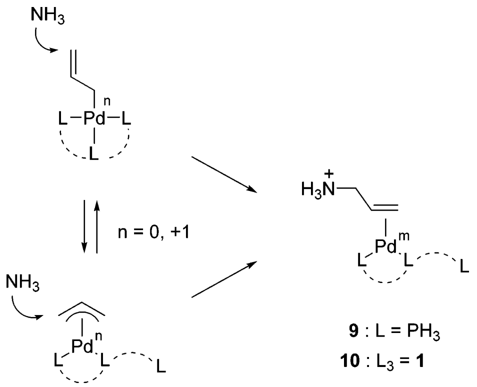


3 **4** **TS'$_{7-10}$**

Figure 2. Calculated structures for cationic η^1-allyl complexes **3** and **4** and **TS′**$_{7-10}$.

Scheme 6



reactivity of the corresponding π-allyl derivatives **6**−**8** has also been addressed.

Cationic η^1-allyl complexes **3** and **4** show small Pd−C−C angles (101.8° and 89.8°, respectively, see Figure 2), due to the interaction between the C−C π-bonding orbital of the η^1-allyl ligand with the antibonding Pd−C bond, as shown by NBO analysis. As a result, the structure resembles an incipient η^3-allyl complex.

This effect is not so important in neutral complex **5**, which shows a Pd−C−C angle of 103.0°. The donating effect of the formally anionic aryl ligand, which makes the Pd−C bond distance longer in **5** compared with **4** (2.167 vs 2.132 Å), limits the ability of the antibonding Pd−C bond to accept electron density from the double bond. η^1-Allyl derivatives **3** and **4** show lower natural charges on terminal allyl carbons (−0.36 and −0.37, respectively) compared with η^3-allyl complexes **6** and **7** (charges lie between −0.48 and −0.51), suggesting that nucleophilic attack may be more possible on the former derivatives.

2. Nucleophilic Attack of NH$_3$ on *σ*- and *π*-Allylpalladium Complexes. The reaction of π-allylpalladium derivatives with NH$_3$ has been previously studied by computational means.[11] Our aim was to explore the feasibility of the reaction on σ-allyl derivatives, which could be formed in the presence of tridentate ligands or in the presence of an excess of simple phospines. Thus, nucleophiles could attack on the γ-position of the allyl complexes to afford the corresponding Pd(0)-olefin derivative **9** and **10** (Scheme 6). Coordination of phospine to π-allyl complexes to give the σ-allyl derivatives is endothermic except for the formation of **5** (Scheme 7) and is entropically disfavored especially in the intermolecular reaction of **6**. A short lifetime for σ-allyl complexes is expected due to the low activation energies for their conversion to π-allyl derivatives.[26a]

Activation and reaction energies can be found in Table 1. The same final olefin complexes are expected regardless of the type of coordination of the allyl ligand. Although these reactions are endothermic, the formation of the olefin complexes must be followed by deprotonation of the ammonium, which makes the overall process exothermic. Reaction is faster for the PH$_3$ derivative **6** compared with complex **7**, in accord with the higher donating character of ligand **1**. In addition to the usual transition states corresponding to the attack of the nucleophile on bis(phosphine)(allyl)palladium derivatives **6** and **7** (**TS**$_{6-9}$ and **TS**$_{7-10}$), we have located two transition states showing coordination to three P atoms (**TS′**$_{6-9}$ and **TS′**$_{7-10}$, Figure 2). The geometry of these saddle points is halfway between square-planar and tetrahedral, as expected for a formal reduction from Pd(II) to Pd(0). Although this geometry resembles that of complexes **3** and **4**, in which the C−C double bond is already interacting with the metal, careful IRC studies have shown that the actual reagents are π-allyl complexes **6** and **7**. Since only two P atoms are coordinated in the reagents and products, **TS′**$_{6-9}$ and **TS′**$_{7-10}$ are the transition states for a concerted reaction of the nucleophile with concomitant phosphine coordination, followed by dissociation of P along the reaction coordinate toward the products. These transition states are less stable than **TS**$_{6-9}$ and **TS**$_{7-10}$ by 0.1 and 3.7 kcal mol^{-1}, respectively, and since their formation is less probable for entropic reasons, this pathway can be neglected. Although no other transition states have been located, the direct reaction of NH$_3$ with the γ-carbon of η^1-allyl complexes cannot be discarded. For such a process we would expect a similar transition state showing a weaker interaction between the metal and the γ-carbon, and this could be the case in solution or with γ-substituted allyl derivatives. PCM calculations in THF, which is a usual solvent for these reactions, gives similar activation energies but significantly more exothermic reactions due to the zwitterionic nature of the products.

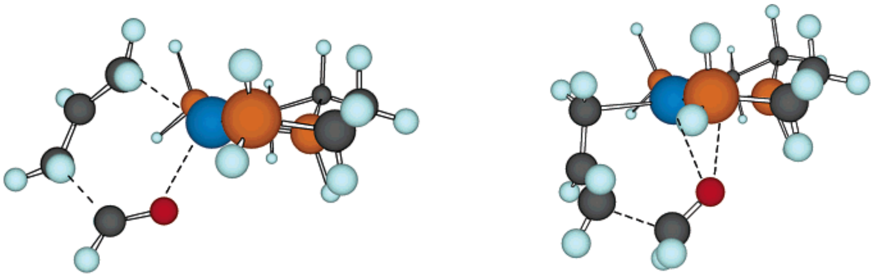
Scheme 7. Calculated Reaction Energies (B$_2$, kcal mol^{-1}) and Gibbs Free Energies (B$_1$, kcal mol^{-1}) for *η*^{1}-Allyl/*η*^{3}-Allyl Conversion

reaction	ΔE	ΔG
6 + PH$_3$ $\longrightarrow$ **3**	+ 1.6	+13.1
7 $\longrightarrow$ **4**	+ 4.2	+5.6
8 $\longrightarrow$ **5**	- 3.7	-1.4

Table 1. Calculated Activation and Reaction Energies (kcal mol^{-1}) for Nucleophilic Attack of NH$_3$ on Cationic Allyl Derivatives[a]

reagent	product	E_a[b]	ΔE[b]	$\Delta G^{\ddagger}$[b]	ΔG[b]	E_a(s)[c]	ΔE(s)[c]	E_a'[d]	$\Delta E'$[d]
6	**9**	0.8	−1.7	10.4	9.4	1.1	−10.9	7	+3.9
7	**10**	6.0	+4.9	15.7	15.2	4.7	−1.7	12.5	+10.3

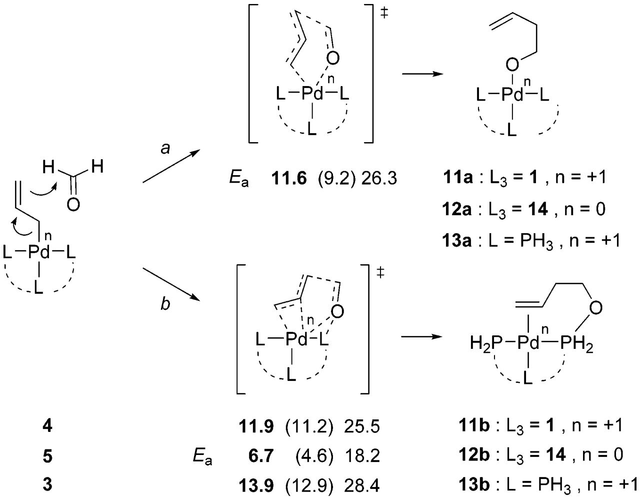
[a] E_a and ΔE are ZPE corrected. [b] Calculated with basis set B$_1$. [c] PCM in THF. [d] Calculated with basis set B$_2$.



$TS_{4\text{-}11a}$ $TS_{4\text{-}11b}$

Figure 3. Optimized structures of the two possible transition states for the reaction of **4** with HCHO.

Scheme 8. Possible Pathways for the Reaction of η^1-Allyl Complexes with HCHO[a]



[a] Activation energies calculated at B3LYP/B_2//B3LYP/B_1 (kcal mol^{-1}) are in boldface. Values in parentheses correspond to PCM calculations in THF. $\Delta G^{\ddagger}$ are in normal face.

As expected, metallacyclic derivatives **5** and **8** do not seem to easily react with nucleophiles. We were not able to locate stationary points for the reaction of ammonia with orthometalation complex **5** or **8**. The presence of the strongly donating aryl ligand favors NH_3 dissociation during the optimization to a transition state or to the putative final olefin complex.

3. Reaction of Allylpalladium Complexes with Formaldehyde. The reaction of cyclometalated complexes containing pincer ligands has been thoroughly studied by Szabó in the context of the allylation of aldehydes and imines catalyzed by this type of complexes. DFT calculations suggest that the aldehyde reacts with the γ-carbon of the allyl ligand through a concerted six-member transition state to afford an alkoxide complex (Scheme 8, pathway *a*), which further reacts with electrophiles in the reaction medium to afford the final product.[25] Our aim was to study the influence of neutral ligands in η^3-allyl derivatives in order to see if reaction of cationic complexes with electrophiles is also possible.

Interestingly, we have located two different transition states for the reaction of **4** with HCHO (Figure 3). One of them (**TS$_{4-11a}$**) is similar to the one mentioned above (Scheme 8, pathway *a*), showing a six-membered ring and a distorted bipyramidal coordination around Pd, with the incipient Pd−O bond in the equatorial plane, and very similar Pd−O and Pd−C distances (2.32 and 2.36 Å, respectively). **TS$_{4-11a}$** lies 11.6 kcal mol^{-1} above the reagents and leads to Pd alkoxide **11a** exothermically (−9.5 kcal mol^{-1}). On the other hand, a different pathway through **TS$_{4-11b}$** leads to a η^2-alkene complex **11b**, in which the oxygen atom is bonded to one of the phosphorus (Scheme 8, pathway *b*). In this transition state there is no distortion from its square planarity, and the oxygen atom lies halfway between Pd and P (Figure 3).

This novel process is less exothermic (−6.3 kcal mol^{-1}) and shows an activation energy of 11.9 kcal mol^{-1}. Although this reaction pathway could imply the decomposition of the catalyst, its feasibility would depend on the substituents on P. This process could not be operating in the case of real phosphines, since they would have different steric and electronic properties, and this behavior could be an artifact due to the model ligands. In addition, the oxygen could be trapped by electrophiles in the reaction medium before becoming bound to P. The activation energies (Scheme 8) parallel the expected nucleophilicity according to the donating character of the ligands (natural charges being −0.36, −0.37, and −0.48 for the nucleophilic carbons of **3**, **4**, and **5**, respectively). The formation of **12b** is exothermic (−3.5 kcal mol^{-1}).[36] On the other hand, we have not been able to locate the bipyramidal transition states leading to alkoxides **12a** and **13a** from complexes **5** and **3**. This can be ascribed to the high reactivity of formaldehyde, which probably reacts without barrier. The relatively low activation energies for exothermic evolution of complexes **3** and **4** suggest that cationic η^1-allyl derivatives, which could be formed in the presence of an excess of phosphine, may react with aldehydes and that this type of reaction would not be exclusive for the more reactive neutral complexes derived from pincer ligands.[37] Activation barriers are of course higher considering Gibbs free energy, due to the associative character of the process. The increase is similar for cationic complexes and for neutral **5**, for which the reaction is well established. Finally, the presence of solvent would accelerate the reaction (Scheme 8).

4. Pallada-ene Reactions of σ-Allylpalladium Complexes. Reactions of allylpalladium complexes with alkenes and alkynes are key steps in powerful synthetic methods such as the Oppolzer reaction. Some years ago, the mechanism of the 1,2-insertion of alkene into allylpalladium complexes was experimental and computationally studied.[38] DFT calculations suggested a direct insertion of the olefin in a π-allylpalladium derivative as the key C−C bond forming step in this reaction. The previously proposed pallada-ene reaction mechanism involving a π-allylpalladium and a coordinated alkene was shown to be strongly disfavored (see Scheme 2).[39]

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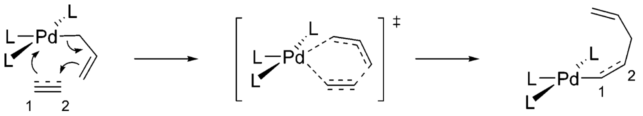
(36) We did not locate a minimum corresponding to structure **13b**. Activation of one of the P−H bonds to give a Pd hydride with a coordinated phosphide oxide is observed.

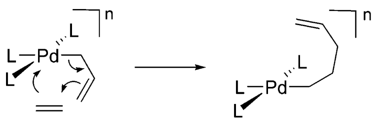
(37) According to our previous calculations on similar systems at the same level (refs 17 and 39), this activation energy value can be easily surmounted.

(38) Gómez-Bengoa, E.; Cuerva, J. M.; Echavarren, A. M.; Martorell, G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 767−769.

Scheme 9



Scheme 10



3 : L = PH_3, n = +1 **15** : L = PH_3, n = +1
4 : L_3 = **1**, n = +1 **16** : L_3 = **1**, n = +1
5 : L_3 = **14**, n = 0 **17** : L_3 = **14**, n = 0

Table 2. Calculated Activation and Reaction Energies (kcal mol^{-1}) for the Pallada-ene Reaction of σ-Allylpalladium Complexes with Ethylene[a]

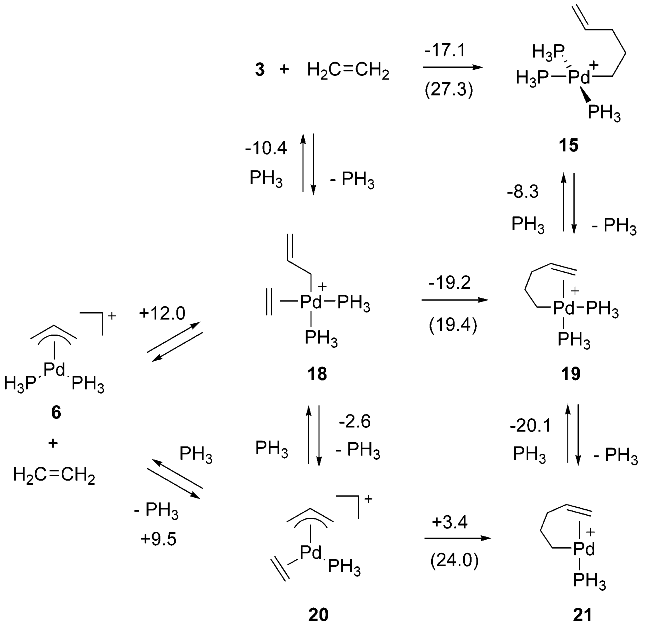
reagent	product	E_a[b]	ΔE[b]	E_a(s)[c]	ΔE(s)[c]	E_a'[d]	$\Delta E'$[d]
3	**15**	23.7	−18.1	24.4	−20.7	27.3	−17.1
4	**16**	27.8	−14.7	28.3	−17.4	30.3	−14.4
5	**17**	30.9	−14.5	30.8	−16.3	32.9	−13.0

[a] E_a and ΔE are ZPE corrected. [b] Calculated with basis set B_1. [c] PCM in THF. [d] Calculated with basis set B_2.

Considering the mechanism of the reaction of σ-allylpalladium complexes with aldehydes shown above, we reasoned that an analogous process could take place by intermolecular reaction of the same complexes with alkenes or alkynes. Thus we studied the feasibility of pallada-ene concerted reactions of σ-allyl complexes, containing a neutral or formally anionic tridentate ligand, with noncoordinated unsaturated species (Scheme 9).

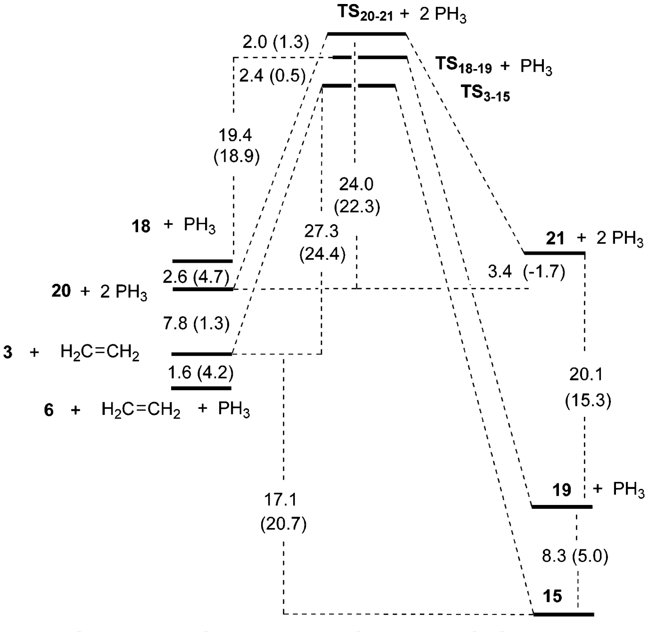
This process does not involve coordinated alkenes or alkynes, thus being mechanistically different from pathway *b* shown in Scheme 2. The unsaturated compound approaches the metal complex along a plane perpendicular to the coordination one. Thus, reactions of σ-allyl complexes **3**−**5** with ethylene give alkyl derivatives **15**−**17** through concerted transition states (Scheme 10).[40] Activation and reaction energies can be found in Table 2. In this case, calculated entropy and Gibbs energy values for these intermolecular model reactions (which can be found in the Supporting Information) are meaningless because Oppolzer reaction takes place intramolecularly.

Scheme 11. Possible Pathways for the Reaction of Allylpalladium Complexes with Ethylene[a]



[a] The reaction energies (kcal mol^{-1}) correspond to the process in the sense indicated by the closest arrow. The values in parentheses correspond to activation energies.

Scheme 12. Energy Diagram for the Reactions of Allylpalladium Complexes with Ethylene (kcal mol^{-1})[a]



[a] Values in parentheses correspond to PCM calculations in THF.

The process is exothermic and shows similar reaction energies in all cases, although activation barriers are higher than those observed for the nucleophilic and electrophilic attacks mentioned above. Reaction of cyclometalated **5** shows the highest activation energy (30.9 kcal mol^{-1}), whereas **3** is the most reactive model and evolves through a barrier of 27.3 kcal mol^{-1}. Since this value is slightly higher than that previously calculated for the direct insertion of ethylene in π-allyl derivatives (Scheme 2, pathway *a*),[39] our results suggest that both cationic σ- and π-allyl complexes might be involved in Oppolzer reactions. For that reason, we have calculated the profiles for the three possible reactions involving an allyl complex and ethylene (Scheme 11): (i) the intermolecular pallada-ene reaction, (ii) 1,2-insertion of ethylene into a (σ-allyl)-Pd bond, and (iii) the above-mentioned direct insertion of ethylene in a π-allylpalladium complex previously studied (Scheme 2, pathway *a*). Results are summarized in Schemes 11 and 12.

The starting complexes involved in the possible reactions are in equilibrium through low-barrier associative ligand exchange processes. Calculations show that the most stable situation is the mixture of **6**, ethylene, and PH_3 and that coordination of PH_3 to afford the σ-allyl derivative **3** is more favorable than the formation of the ethylene π-allyl complex **20**. Formation of ethylene σ-allyl complex **18** is disfavored. Thus, the major productive complex in the equilibrium should be **3**. Moreover, the transition state for the pallada-ene reaction from **3** to **15**

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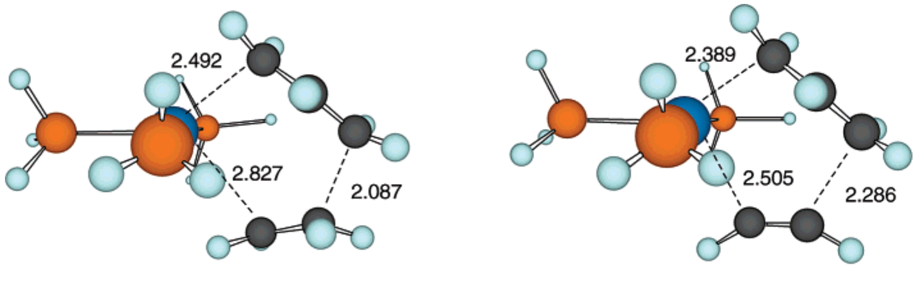
[39] Cárdenas, D. J.; Alcamí, M.; Cossío, F.; Méndez, M.; Echavarren, A. M. *Chem. Eur. J.* **2003**, *9*, 96−105.

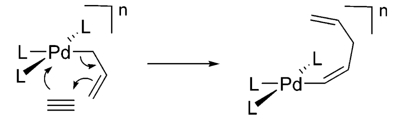
[40] A related process could be involved in Pd-catalyzed [3+2] intramolecular cycloadditions of alkenylidenecyclopropanes: (a) Gulías, M.; García, R.; Delgado, A.; Castedo, L.; Mascareñas, J. L. *J. Am. Chem. Soc.* **2006**, *128*, 384−385. (b) Suzuki, T.; Fujimoto, H. *Inorg. Chem.* **2000**, *39*, 1113−1119.



TS$_{3\text{-}15}$ **TS$_{3\text{-}22}$**

Figure 4.

Scheme 13



3 : L = PH$_3$, n = +1 **22** : L = PH$_3$, n = +1

4 : L$_3$ = **1**, n = +1 **23** : L$_3$ = **1**, n = +1

5 : L$_3$ = **14**, n = 0 **24** : L$_3$ = **14**, n = 0

shows the lowest energy compared with the other transition states involved in the possible C−C bond formation reactions, as triphosphine complex **15** is the most stable reaction product (Scheme 12).

These results support that σ-allylpalladium complexes may be involved in the reactions with alkenes. The energy differences between the transition states are not very high, and several mechanisms could be in competition. In solution, activation energies become lower, especially for the pallada-ene mechanism, due to the lesser stabilization of the reagents (Scheme 12). Transition states for the mechanisms become closer in energy. Experimental studies showed that bidentate phosphines are not good ligands for the Oppolzer reactions, and it was reasoned that chelate effects would preclude coordination of the alkene.[39] In the pallada-ene mechanism there is no need for alkene coordination for the reaction to take place, and the activation energy is much lower than that previously calculated for pathway *b* in Scheme 2 (32.2 kcal mol^{-1} with basis set B$_1$; compare with 23.7 kcal mol^{-1} at the same level for insertion in **20**). Moreover, the unfavorable entropy change due to the external attack of the alkene would not be so important in the usually reported intramolecular cycloadditions, in which both the allyl fragment and the alkene are linked to each other in the reaction substrates.

Similar results were obtained for the reaction of σ-allylpalladium derivatives with acetylene as a model for alkynes (Scheme 13). Reactions are more exothermic in this case, as expected for the cleavage of the higher energy alkynes, and activation energies are a bit lower. Again the most reactive derivative is complex **3**, and the energy gap with the other transition states increases. The slower reactions found for **4** and **5** show very similar barriers (Table 3).

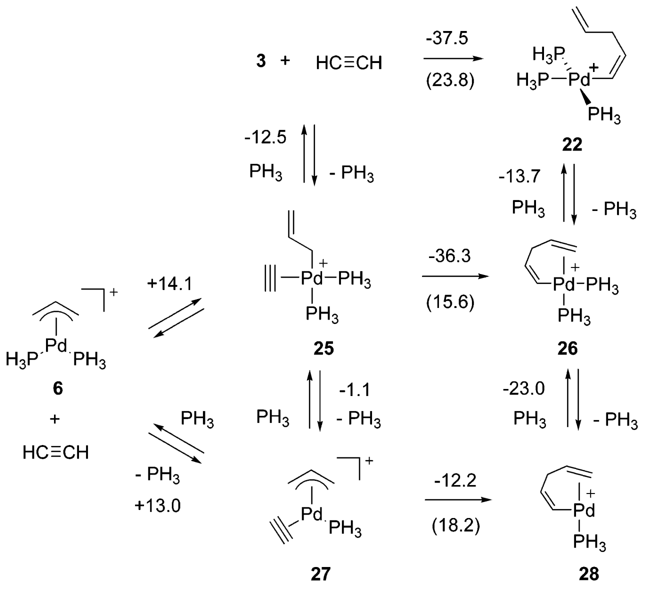
The optimized structures of the transition states for the pallada-ene processes **TS$_{3-15}$** and **TS$_{3-22}$** are shown in Figure 4. These saddle points present some differences. Thus, the formation of the new C−C bond between the carbon ligands and the development of the new double bond are more advanced in **TS$_{3-15}$**, whereas a long distance is observed for the new Pd−CH$_2$ σ-bond (2.827 Å). Electron density in the bond critical point is 0.025 (compare with 0.098 for the Pd−C bond in **3**). In contrast, **TS$_{3-22}$** shows a significantly shorter Pd−CH bond (2.505 Å, electron density 0.045) and a longer C−C distance for the forming σ-bond (2.286 Å). AIM analysis of both structures shows ring critical points in accord with the concerted process suggested by the observed bond critical points between Pd and carbons of both ligands and between the atoms involved in the C−C bond formation.

Table 3. Calculated Activation and Reaction Energies (kcal mol^{-1}) for the Intermolecular Reaction of σ-Allylpalladium Complexes with Acetylene[a]

reagent	product	E_a[b]	ΔE[b]	E_a(s)[c]	ΔE(s)[c]	E_a'[d]	$\Delta E'$[d]
3	**22**	20.9	−37.6	21.7	−39.9	23.8	−37.5
4	**23**	24.5	−32.4	24.3	−35.3	25.9	−33.0
5	**24**	24.6	−35.4	24.8	−37.7	26.1	−34.7

[a] E_a and ΔE are ZPE corrected. [b] Calculated with basis set B$_1$. [c] PCM in THF. [d] Calculated with basis set B$_2$.

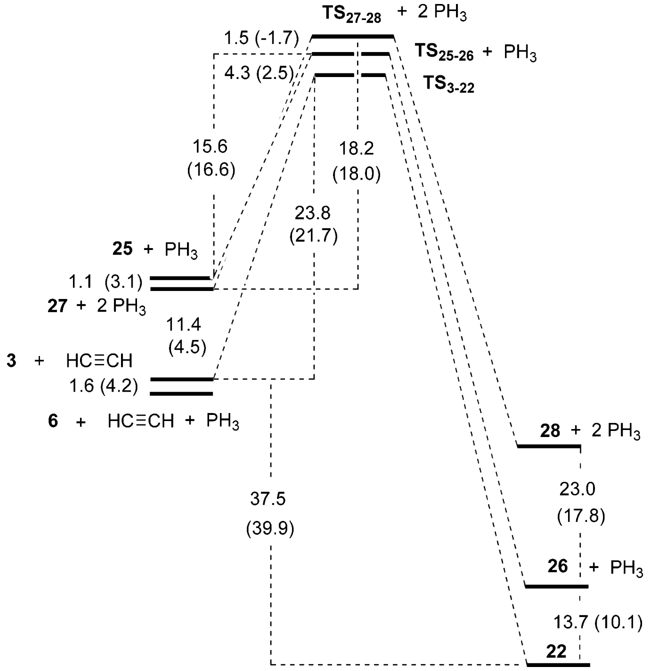
Scheme 14. Possible Pathways for the Reaction of Allylpalladium Complexes with Acetylene[a]



[a] The reaction energies (kcal mol^{-1}) correspond to the process in the sense indicated by the closest arrow. Values in parentheses correspond to activation energies.

Comparison among the three possible mechanisms outlined shows the preference for the intermolecular reaction of acetylene with σ-allyl triphosphine derivatives rather than 1,2-insertion reactions, regardless of the hapticity of the allyl ligand (Schemes 14 and 15). Given the energy differences between the transition states, the involvement of σ-allylpalladium complexes is more probable in reactions with alkynes. Again, entropy plays against this mechanism, which would be more probable in intramolecular reactions, as it is observed experimentally. Solvation has

Scheme 15. Energy Diagram for the Reactions of Allylpalladium Complexes with Acetylene (kcal mol^{-1})[a]



[a] Values in parentheses correspond to PCM calculations in THF.

the same effect as in the case of the reaction of alkenes, although in this case the less favorable process is 1,2-insertion from complex **25**.

Conclusions

We have explored the feasibility of the formation of σ-allylpalladium complexes in the presence of tridentate ligands and have studied their reactivity as electrophiles and nucleophiles and their ability to participate in pallada-ene reactions. The following conclusions can be derived from our computational study:

(a) π-Allylpalladium complexes of neutral phosphines are more stable than σ-allyl derivatives. Cyclometalated pincer ligands make σ-allylpalladium complexes the most stable species.

(b) Nucleophilic attack of NH_3 on allylpalladium complexes containing neutral phosphines is a feasible process showing relatively low activation energies. We have been able to locate transition states with three coordinated P atoms, which resemble attack on the γ-carbon in a σ-allyl complex. Nevertheless, IRC studies show that such transition states are connected with bis(phosphine)(π-allyl)Pd complexes. Concerted coordination of another phosphine along the reaction coordinate does not accelerate the process.

(c) Cationic σ-allylpalladium complexes of simple phosphines may act as nucleophiles, reacting with aldehydes with relatively low activation energies. Neutral complexes containing pincer ligands, for which this reaction is well established, are of course more reactive. In addition to the previously proposed mechanism, we have found a competitive pathway involving the formation of a η^2-alkene complex instead on a Pd alkoxide.

(d) σ-Allylpalladium complexes cannot be discarded as the actual intermediates in reactions with alkenes and alkynes. Intermolecular pallada-ene type reactions show the lowest energy transition states and give rise directly to the most stable species, compared with the usually proposed 1,2-insertion reactions of either σ- or π-complexes. Thus, the pallada-ene mechanism cannot be discarded for the key step of the Oppolzer reaction. Cationic derivatives containing neutral phosphines, which are the usual intermediates in Oppolzer and other Pd-catalyzed processes, are more reactive than neutral complexes containing cyclometalated ligands.

Therefore, our results suggest that the reactivity of new σ-allylpalladium complexes deserves experimental studies concerning their participation and possible regio- and stereochemical implications in the outcome of syntheticallly useful palladium-catalyzed reactions of allyl electrophiles.

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Supporting Information Available: Atomic coordinates and energy values for all stationary points. This material is available free of charge via the Internet at http://pubs.acs.org.

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