Umpolung of the Allylpalladium Reactivity: Mechanism and Regioselectivity of the Electrophilic Attack on Bis-Allylpalladium Complexes Formed in Palladium-Catalyzed Transformations

Kálmán J. Szabó*[a]

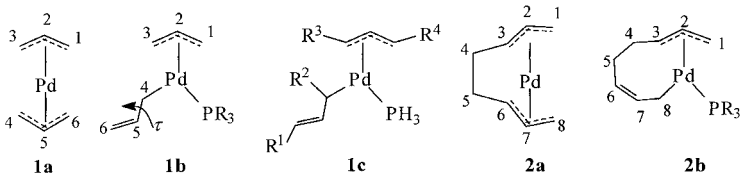
Abstract: The structure and reactivity of various bis-allylpalladium complexes occurring as catalytic intermediates in important synthetic transformations have been studied by applying density functional theory at the B3PW91(DZ + P) level. It was found that η^1,η^3 coordinated bis-allylpalladium complexes are readily formed from the corresponding η^3,η^3 complexes, especially in the presence of π-acceptor phosphine ligands. The theoretical calculations indicate $d_\sigma \rightarrow \pi^*$ type hyperconjugative interactions occurring in the η^1-coordinated allyl moiety of the η^1,η^3 coordinated complexes. These hyperconjugative interactions influence the structure of the complexes and dramatically increase the reactivity of the double bond in the η^1-moiety. The DFT results indicate a remarkably low activation barrier for the electrophilic attack on the η^1-allyl functionality. In bridged η^1,η^3 complexes, the electrophilic attack occurs with a very high regioselectivity, which can be explained on the basis of $d-\pi$ type hyperconjugative interactions.

Keywords: allylpalladium complexes · catalysts · density functional calculations · electrophilic additions · regioselectivity

Introduction

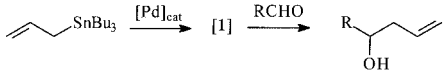
Allylpalladium chemistry has become one of the most successful areas of organometallic catalysis due to its remarkable capacity for continuous renewal. Catalytic transformations involving nucleophilic attack on (η^3-allyl)palladium intermediates have been widely applied in a number of important chemical processes[1–5] including allylic substitution and the oxidation of alkenes and conjugated dienes. However, recently, catalytic transformations proceeding through an initial *electrophilic* attack on bis-allylpalladium complexes (**1**–**2**) have attracted much attention.[6–12] Furthermore, it has been demonstrated that, under catalytic conditions, bisallylpalladium complexes can undergo an initial *electrophilic* attack on one of the allyl-moieties followed by a *nucleophilic* attack on the other one.[6, 11] Thus, bisallyl-palladium intermediates can be classified[6] as *catalytic* amphiphilic (i.e., both electrophilic and nucleophilic) species, which are exceptionally useful reagents in organic synthesis. Since catalytic transformations proceeding through bis-allylpalladium intermediates provide access to electrophilic reagents, and involve a remarkable amphiphilic reactivity, these catalytic procedures represent a new dimension for allylpalladium chemistry.

[a] Dr. K. J. Szabó
Department of Organic Chemistry, Arrhenius Laboratory
Stockholm University, 106 91 Stockholm (Sweden)
Fax: (+46) 8-15-49-08
E-mail: kalman@organ.su.se



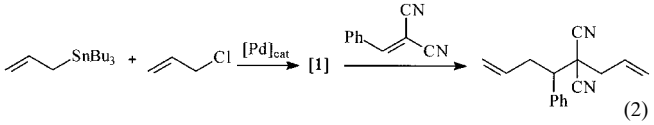
1a **1b** **1c** **2a** **2b**

Bisallyl-palladium intermermediates can be formed in a number of catalytic reactions. Yamamoto and co-workers[13] have generated bis-allylpalladium intermediate **1** from allyltributylstannane in the presence of catalytic amounts of palladium salts [Eq. 1]. The bis-allylpalladium complex formed in this reaction is readily attacked by electrophiles such as aldehydes and imines without assistance from Lewis acids.



(1)

In another reaction,[6] the bis-allylpalladium intermediate has been formed from a mixture of allyltributylstannane and allylchloride in the presence of palladium catalyst. This bis-allylpalladium intermediate is attacked by an activated olefin electrophile followed by a nucleophilic attack on the (mono-)-allylpalladium complex formed [Eq. (2)].



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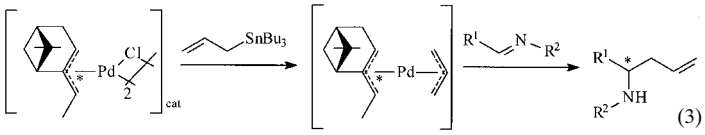
The same authors[7] describe a catalytic asymmetric allylation reaction, in which the bis-allylpalladium complex is formed from a chiral (mono-)allylpalladium complex and allyltributylstannane [Eq. (3)]. Subsequently, this complex undergoes electrophilic attack by imines affording allylamines with a high-level of enantiomeric excess. It has also been shown that, in these catalytic processes, the allylstannane reagent can be replaced by allyltrimethylsilanes.[8]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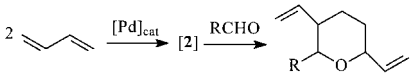
Reactive bis-allylpalladium intermediates are also formed in catalytic processes of great industrial importance, such as in dimerization and telomerization of conjugated dienes.[9–12, 14, 15] Tsuji and co-workers[1, 11] have shown that treatment of butadine with aldehydes leads to formation of 3,6-divinyltetrahydropyranes [Eq. (4)]. This reaction is supposed to proceed through bis-allylpalladium intermediate **2** by employing the amphiphilic reactivity of this complex. In an analoguous process, in the telomerization of butadiene and ammonia,[1, 14, 15] the bisallylpalladium intermediate **2** is first protonated by a weak acid or water and then attacked by ammonia as nucleophile [Eq. (5)].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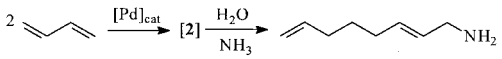
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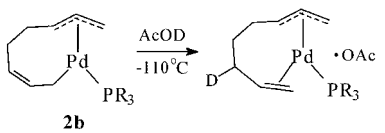
Mechanistic studies by Yamamoto and co-workers[13] have shown that (η^3-allyl)$_2$-palladium complex (**1a**) can be detected in the reaction mixture in the palladium-catalyzed reaction of allylstannanes with aldehydes [Eq. (1)]. Since phosphine ligands, such as PPh_3, are usually also present under the conditions applied, it was assumed[13] that **1a** coordinates a phosphine ligand and the actual substrate of the electrophilic attack is the η^1,η^3-allylpalladium complex (**1b**). Jolly and co-workers[16] studied the mechanism of the palladium-catalyzed dimerization of butadienes in the presence of phosphine ligands. Under the conditions applied, the (η^3,η^3-octadienyl)-palladium complex (**2a**) could not be detected, but formation of the η^1,η^3-allyl form **2b** could be observed at low temperature ($-30\,^\circ C$). The authors also studied the reactivity and regiochemistry of the electrophilic attack on **2b**.[16] It was found that complex **2b** can be protonated by a weak acid, acetic acid, at $-110\,^\circ C$. Furthermore, using AcOD, it could also be established that the protonation takes place exclusively at the C6 position [Eq. (6)].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The above mechanistic studies have revealed two important features of the electrophilic attack of **1b** and **2b**: 1) Bis-allylpalladium complexes display an extremely high affinity towards electrophiles; and 2) the electrophilic attack takes place with an unusually high regioselectivity. Feature 1) is somewhat difficult to understand in the light of the fact that (mono-)allylpalladium complexes resist protonation even in the presence of strong mineral acids.[17–20] In fact many palladium-catalyzed reactions proceeding through (η^3-allyl)-palladium intermediates are conducted in acetic acid at room temperature without protonation of the allyl moiety.[21, 22] Furthermore, standard activated alkens, such as allylsilanes, do not react with weak acids (such as AcOH), aldehydes, or imines in absence of Lewis acids at room temperature or at lower temperatures.[23] Feature 2) is also surprising since the electrophilic attack is expected at the most nucleophilic, metallated η^1-carbon (C8 position) of **2b**.

In recent years numerous theoretical studies have been published[24] on the structure[19, 20, 25–27] and reactivity[27–32] of (mono-)allylpalladium complexes. The reactivity studies were restricted to the mechanistic aspects of the *nucleophilic* attack on (mono-)allylpalladium intermediates in catalytic processes.[27–31] However, despite the considerable synthetic and mechanistic importance of bis-allylpalladium chemistry, there has been a remarkable absence of high level theoretical calculations published in this field. Bancroft, Puddephatt, and co-workers[33] assigned the molecular orbitals of **1a** from a combined photoelectron spectroscopy–Xα study. However, the ligand and substituent effects on the structure of bis-allylpalladium complexes; the origin of the remarkably high reactivity toward *electrophiles* and the electronic effects responsible for the high regioselectivity in the electrophilic attack have largely remained unstudied. The present study was undertaken to investigate these important structural and mechanistic features by discussing the following questions:

1) What is the coordination state of the allyl ligands in **1** and **2** in the presence of phosphine and other ligands occurring under the catalytic conditions?
2) How does the π-acceptor/σ-donor character of the ligands influence the stability of the η^1,η^3-allylpalladium species?
3) What is the influence of the allylic substituents on the mode of coordination of the allylic ligands?
4) What electronic effects are responsible for the remarkable reactivity of **1** and **2** toward electrophiles?
5) What is the origin of the high regioselectivity in the electrophilic attack?

In order to answer these questions, density functional theory (DFT) calculations have been carried out for bis-allylpalladium complexes **1a–g** and **2a–e**, and the reactivity of these species has been studied with acetic acid and formaldehyde electrophiles (**4–9**). These calculations also aim to provide help for the design and development of new catalytic transformations proceeding through bis-allylpalladium complexes, and therefore particular attention is paid to the synthetically important structural and reactivity features of these complexes.

Computational methods: Unless otherwise stated, the geometries were fully optimized employing a Becke-type[34]

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three-parameter density functional model B3PW91. This so-called hybrid functional includes the exact (Hartree–Fock) exchange, the gradient corrected exchange functional of Becke[34] and the more recent correlation functional of Perdew and Wang.[35] All calculations have been carried out using a double-ζ(DZ) + P basis constructed from the LANL2DZ basis[36–38] by adding one set of d-polarization functions to the heavy atoms (exponents: C 0.63, N 0.864, O 1.154, P 0.34) and one set of diffuse d-functions on palladium (exponent: 0.0628). Harmonic frequencies have been calculated at the level of optimization for all structures to characterise the calculated stationary points and to determine the zero-point energies (ZPE). Fully optimized transition state structures **4a**, **5a**, **6a**, **7a**, **8a**, and **9a** have been characterized by a single imaginary frequency, while the rest of the fully optimized structures possess only real frequencies. The charges have been calculated by the natural bond orbital (NBO) method by Weinhold and co-workers.[39] All calculations have been carried out by employing the Gaussian 98 program package.[40]

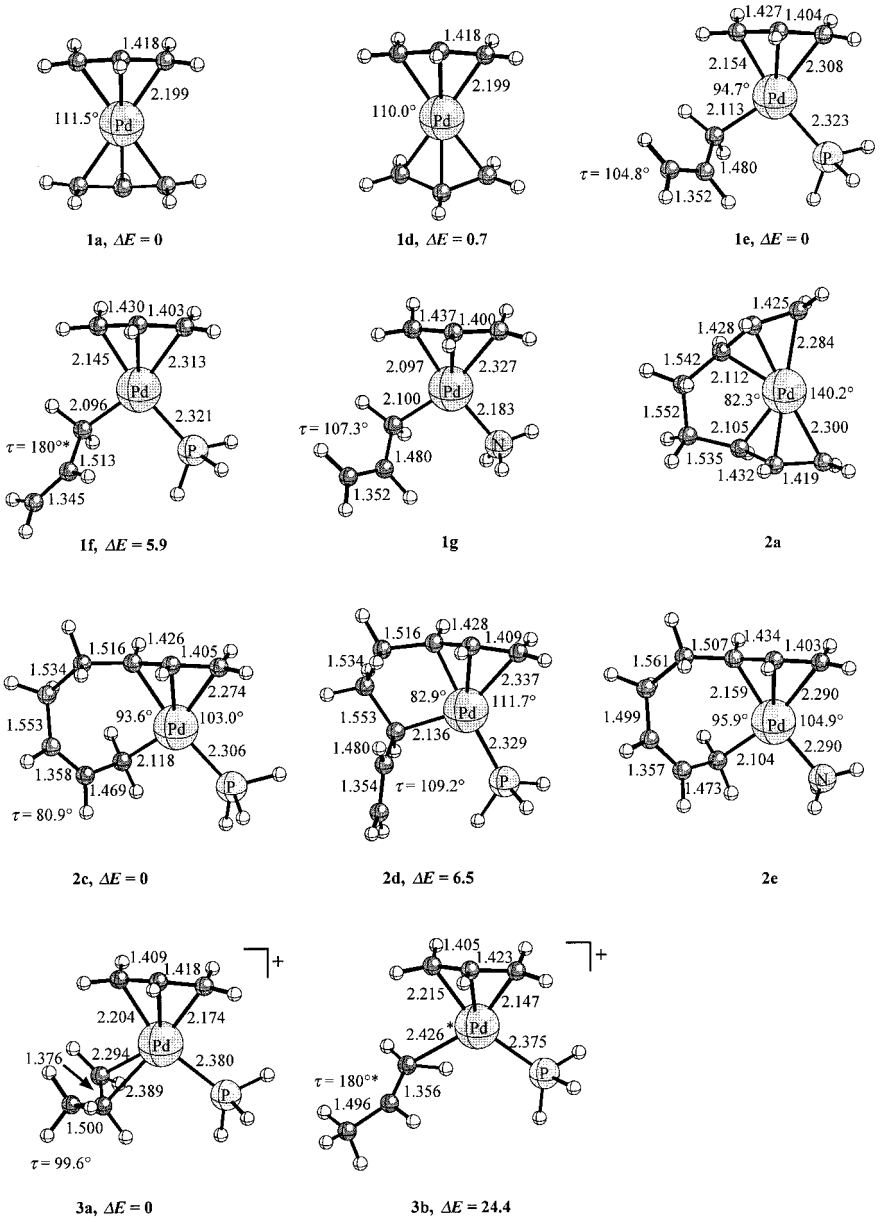

Figure 1. Selected B3PW91/LANL2DZ + P geometrical parameters of bis-allylpalladium complexes (bond lengths in Å, angles in degrees, energies in kcal mol^{-1}). Geometrical parameters restricted in the geometry optimization are denoted by *.

Results and Discussion

The B3PW91/LANL2DZ + P geometrical parameters and energies of **1**–**9** calculated in this work are given in Figures 1 and 2, the rotation potentials calculated for **1e** and **3a** are given in Figure 3 and the calculated activation energies are displayed in Figure 4.

Structure and stability of the η^3,η^3-bis-allylpalladium complexes: The parent bis (η^3-allyl)palladium complex may have two different configurations: Complex **1a** has *trans* oriented allyl ligands and possesses C_{2h} symmetry; while in complex **1d**, the allyl ligands are *cis* and the molecular symmetry is C_{2v}. The bond lengths from the terminal carbon (C_t) to palladium and to the central carbon (C_c) are identical in the *trans* and *cis* form. In both complexes the C_t-Pd-C_t angles (110–112°) deviate by about 20° from 90°, as is preferred in square-planar sixteen electron complexes.[41] The *trans*-complex **1a** is somewhat more stable (0.7 kcal mol^{-1}) than the *cis*-complex **1d**. According to NMR results,[13] the dominating species in the solution of bis(η^3-allyl)palladium complexes is the *trans*-form **1a**, however the *cis*-form **1d** can also be detected, because of the small energy difference.

Only a single *cis*-oriented form could be obtained for the (η^3,η^3-octadienyl)palladium complex (**2a**). This complex possesses C_1 symmetry, due to twisting of the ethylene bridge joining the two η^3-coordinated allyl moieties. A comparison of the structures of **2a** and **1d** reveals a tremendous angle strain imposed by the ethylene bridge in **2a**. The C1-Pd-C8 angle is 140.2°, deviating by 50° from the 90°-angle favored in square-planar complexes. The sizeable angle strain is also reflected by the unusually long Pd–C1(C8) bond lengths (2.28–2.30 Å). On the other hand, the relatively short Pd–C3(C6) bond

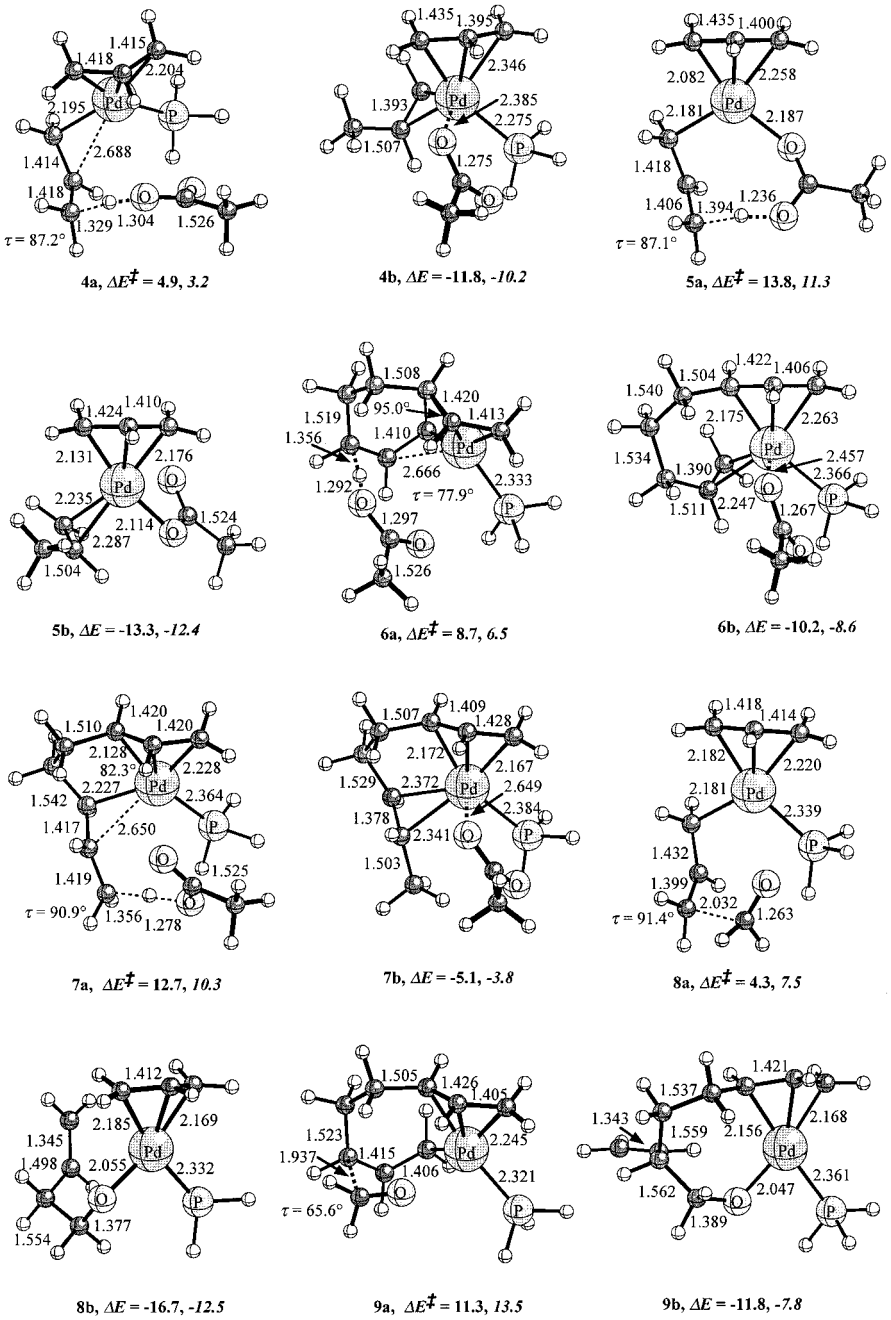

Figure 2. Selected B3PW91/LANL2DZ+P geometrical parameters for TS structures and products of the electrophilic attack by acetic acid and formaldehyde on bis-allylpalladium complexes **1** and **2** (bond lengths in Å, angles in degrees, energies in kcal mol^{-1}). The zero-point vibration corrected energies are given in an italic type face.

lengths (2.10–2.11 Å) can be explained by a favorable C3-Pd-C6 angle (82.3°).

Structure and stability of the η^1,η^3-bis-allylpalladium complex (1e): Phosphine ligands frequently occur in the reaction conditions of catalytic transformations proceeding through bis-allylpalladium complexes. These ligands may react with η^3,η^3 complexes, such as **1a**, leading to the η^3,η^1-bis-allylpalladium species, which are the presumed substrates of the electrophilic attack.[13, 16] Therefore, the study of the structure and properties of η^1,η^3 complexes, such as **1e**, is a prerequisite for understanding the reactivity of bis-allylpalladium complexes. In the present theoretical studies, the trialkyl- (R = Me, Bu, *i*Pr) and triarylphosphine (R = Ph) ligands employed under catalytic conditions[6, 9–11, 13, 16] are approximated by a phosphine (PH_3) ligand. The strong π-acceptor character of the phosphine ligand, is very similar to the electronic effects of the experimentally used phosphine derivatives.[42]

Coordination of a PH_3 ligand to **1a** (Table 1) is a highly exothermic reaction ($\Delta E_{comp} = -19.2$ kcal mol^{-1}). In the species formed, **1e**, one of the allyl-moieties is coordinated in an η^1-fashion, which relieves the C3-Pd-C4 angle strain. As one goes from **1a** to **1e**, the C3-Pd-C4 angle decreases by 17°, approaching the favored ligand-metal-ligand angle of 90°. The η^1-allyl ligand exerts a large *trans* influence on the Pd–C1 bond (2.308 Å), which is longer by 0.15 Å than the Pd–C3 bond (2.154 Å). Although the C5–C6 bond has a distinct double bond character, it is somewhat longer (1.35 Å) than a typical C=C double bond (1.33–1.34 Å); this suggests conjugative interactions with the Pd–C4 bond. Furthermore, the torsional angle τ (104.8°, measured as Pd-C4-C5-C6) in **1e** allows conjugative interactions between the π-type orbitals of the C5–C6 bond and the σ-type orbital of the Pd–C4 bond (see below).

In order to analyze the nature of the electronic interactions between the C=C double bond and the Pd–C4 bond in the η^1-coordinated allyl moiety, a rotation potential as a function of τ was calculated for **1e** (Figure 3). The rotation potential shows a minimum at 105°, corresponding to the fully optimized form **1e**, and a maximum at 180° for **1f**. A decrease in the electronic interactions on changing τ from 104° to 180° is clearly reflected by two factors: 1) the thermodynamic destabilization of the complex by 6 kcal mol^{-1}; 2) a contraction of the Pd–C4 and C5–C6 bonds, and an elongation of the C4–C5 bond in **1f**.

Structure and stability of bridged η^1,η^3-bis-allylpalladium complexes: Coordination of a PH_3 ligand to **2a** may result in two different η^1,η^3-complexes. The formation of **2c** is highly

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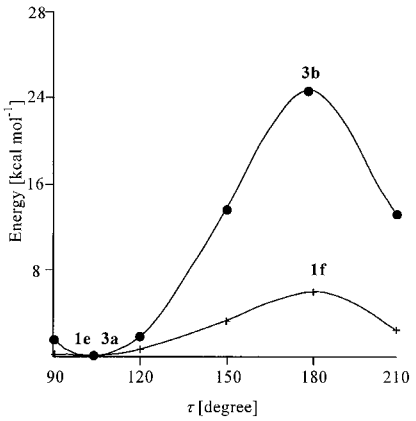


Figure 3. Rotation potentials of **1e** and **3a**. Energy values are obtained by freezing the Pd-C4-C5-C6 dihedral angle (τ) at different values and reoptimizing all the other geometrical parameters at the B3PW91/LANL2DZ + P level.

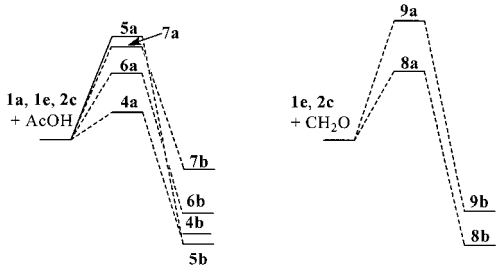


Figure 4. Comparison of the activation energies [kcal mol^{-1}] obtained for the reactions of bis-allylpalladium complexes **1** and **2** with acetic acid and formaldehyde.

Table 1. Complexation energies calculated for η^3,η^3-complexes **1a** and **1b**.

η^3,η^3 Complex	Ligand	η^1,η^3 Complex	ΔE_{comp}[a]
1a	PH_3	**1e**	– 19.2
1a	NH_3	**1g**	– 8.0
2a	PH_3	**2c**	– 44.1
2a	PH_3	**2d**	– 37.6
2a	NH_3	**2e**	– 32.2

[a] $\Delta E_{comp} = E(\eta^1,\eta^3) - [E(\eta^3,\eta^3) + E(\text{ligand})]$, in kcal mol^{-1}.

exothermic with an energy of -44.1 kcal mol^{-1} (Table 1). Interestingly this complexation energy is almost the same as the complexation energy of the PH_3 ligand to a "naked" (η^3-allyl)palladium complex (approximately -40 kcal mol^{-1}).[25] Complex **2d** is also formed in an exothermic process, however, the stabilization energy is lower than for **2c**.

In **2c** C3···C8 close a seven-membered ring with palladium, which efficiently relieves the large angle strain of **2a**. As one goes from **2a** to **2c**, both C-Pd-C coordination angles approach the favored angle of 90°: One of them increases from 82 to 93° and the other decreases from 140 to 103°. On the other hand, a five-membered ring is formed in **2d**; this implies that considerable angle strain remains in the molecule: one of the C-Pd-C angles remains practically unchanged (83°) and the other one is only decreased to 112°. The larger angle strain in **2d** than in **2c** leads to thermodynamic destabilization. In addition, in **2d** an alkylated internal carbon (C6) is coordinated to palladium, which further destabilizes the complex (see above). These destabilizing factors explains the observation that under experimental conditions[16] only the seven-membered complex **2b** corresponding to **2c**, has been found, while analogues of the five-membered ring form **2d** has never been detected. The C6-C7-C8-Pd torsion angle of **2c** (corresponding to τ in **1e**) is 80.9°, which also allows electronic interactions to occure between C6–C7 and C8–Pd.

Ligand effects on the stability of the η^1,η^3 complexes: Although, most frequently, π-acceptor phosphine ligands are applied in catalytic reactions proceeding through bis-allylpalladium intermediates, the influence of ligands with a pronounced σ-donor character also has some interesting mechanistic implications. Previous theoretical studies have shown[25] that the complexation energy of the purely σ-donor NH_3 and π-acceptor PH_3 ligands to the "naked" (η^3-allyl)-palladium complex is approximately the same (about -40 kcal mol^{-1} per ligand). However, coordination of NH_3 to η^3,η^3-allylpalladium complexes (**1a**) and (**2a**) is a much less exothermic process than coordination of PH_3 to these species (Table 1). These results clearly indicate that the η^1,η^3-bis-allylpalladium complexes can be generated more easily from the corresponding η^3,η^3-form by coordination of π-acceptor ligands, such as phosphines, than by coordination of σ-donor ligands, such as amines. The geometry and conformation (τ) of the η^1-coordinated allyl ligand in the amino **1g** and **2e** and corresponding phosphine complexes **1e** and **2c** are similar; this indicates the presence of similar electronic interactions between the Pd–C bond and the C=C double bond.

Substituent effects on the stability of the η^1,η^3-complexes: The effects of the allylic substituents depend on the coordination state (η^1 or η^3) of the allyl moiety. This effect becomes very important when the η^1,η^3-complexes are formed from unsymmetrically substituted η^3,η^3-precursors under catalytic conditions. Methyl substitution of the allylic terminal carbons (Table 2) in **1e** leads to the most stable form, when the substituent is adjacent to the double bond in the η^1-allyl moiety ($R^1 = Me$). When the methyl substituent is attached to one of the terminal carbons of the η^3-allyl moiety, the relative energy is somewhat higher (1 kcal mol^{-1}). However, methyl substitution of the metallated carbon in **1c** ($R^2 = Me$) leads to a considerable destabilization of the complex (4.5 kcal mol^{-1}); this indicates that formation of this complex is less probable than the formation of other isomers from a monomethyl substituted η^3,η^3-complex. When both allylic terminal positions are methylated, the η^3-disubstituted allyl complex (**1c**, $R^3 = R^4 = Me$) is more stable than the isomeric η^1-disubstituted species (**1c**, $R^1 = R^2 = Me$, Table 2).

In addition to the ring strain (see below), the alkyl substitution also contributes to the destabilization of the cyclic complex **2d**. In this complex, an internal carbon (C6) is coordinated to palladium closing a strained five-membered ring. On the other hand, in the other cyclic isomer **2c**, an unsubstituted terminal carbon is coordinated to palladium resulting a seven-membered ring providing a more stable complex.

Table 2. Relative energy [kcal mol^{-1}] of the methyl substituted complexes **1c**.

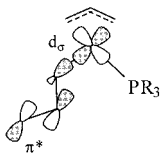
R^1	R^2	R^3	R^4	ΔE
		mono-substitution		
Me	H	H	H	0.0
H	Me	H	H	4.5
H	H	Me	H	0.9
H	H	H	Me	1.0
		di-substitution		
Me	Me	H	H	2.7
H	H	Me	Me	0.0

Effects of terminal protonation of the η^1-allyl moiety: Protonation at C6 in **1e** leads to a strong direct coordination of C5 to palladium **3a** and an increase of the double bond character of C4–C5 (1.376 Å). Accordingly, the C6 protonated η^1-allyl moiety in **3a** can be best described as a propene molecule coordinated to palladium in an η^2-fashion. The τ value (99.6°) in **3a** is similar to the corresponding value in the unprotonated complex **1e** (104.8°).

The rotation potential of **3a** as a function of τ is given in Figure 3. The maximum of the rotation potential is encountered at 180° for **3b**,[43] similar to the corresponding potential obtained for **1e**. However, the relative energy of **3b** is 24 kcal mol^{-1} above the energy of the fully optimized structure **3a**. Since the interaction between C5 and palladium is hindered in **3b**, the stabilization energy in **3a** due to the coordination of C5 to palladium can be estimated to be 24 kcal mol^{-1}. These results has important implications for the reactivity of C6 in **1e**. An electrophilic attack, such as protonation, generates an unfilled p_π-orbital at the adjacent carbon (C5), which is involved in a stabilizing interaction with palladium.

Notably the isomeric form, protonated at the central carbon (C5) of **1e**, does not represent a minimum on the potential energy surface. This species undergoes a spontaneous proton shift affording **3a**. This can be explained by the fact that the C5-protonated form does not benefit from the C5–Pd interaction stabilizing **3a**.

Interactions of the π-type orbitals of the η^1-allyl moiety with palladium: The above studies revealed that the π-type MOs of the η^1-allyl moiety in **1e** are involved in significant electronic interactions with the d orbitals of palladium. The rotation potential calculated as a function of τ indicates that the electronic interactions are strongest when the Pd-C4-C5-C6 angle is about 100°, and weakest when this angle is 180°. In **1e**, the electronic interactions involve elongation of the Pd–C4 and C5–C6 bonds and contraction of the C4–C5 bond (c.f. **1e** and **1f**). These stereoelectronic and geometrical features can easily be explained on the basis of $d_\sigma \rightarrow \pi^*$-type hyperconjugative interactions. When τ approaches 90°, the d_σ(C4–Pd) orbital and the π*(C5–C6) MO are properly aligned for a side-by-side π-type overlap. This overlap increases the C4–C5 bonding, which leads to shortening of the C4–C5 bond. On the other hand, electron density is transferred from the filled d_σ to the antibonding π* MO, which leads to weakening and elongation of the C4–Pd and C5–C6 bonds. The hyperconjugative interactions can be shut off upon rotation to the **1f** form ($\tau = 180°$), in which the d_σ(C4–Pd) and π*(C5–C6) MOs are orthogonal. The electron density transfer to the π*(C5–C6) MO is also reflected by the electronic charges of **1f** and **1e**. As one goes from **1f** to the conjugated form **1e**, the group charge on the double bond (CH_2=CH) is increased from −0.048 to −0.086 e.



The electronic interactions in the protonated form **3a** are also related to the hyperconjugative interactions in **1e**. For example, the conformational requirements (τ) of the interactions in **1e** and **3a** are the same. However, the protonation in **3a** leads to very strong interactions between C5 and palladium, involving rehybridization of C4. As a consequence, the interaction between C4–C5 and palladium corresponds to a standard η^2-type olefin–palladium bonding.[41, 44, 45] Since the protonation is the simplest electrophilic attack, one can expect that the structure and stability of the transition state in the electrophilic attack are determined by electronic effects intermediate to the d–π interactions present in **1e** and **3a**. Since the stereoelectronic requirements of these interactions are the same, it can be expected that the preferred conformation of the allyl moiety attacked is encountered when τ is approximately 90°.

Reactions of the bis-allylpalladium complexes with electrophiles: Investigation of the reactivity of bis-allylpalladium complexes toward electrophiles has involved calculation of the transition state (TS) structures and activation energies for the reaction of several above discussed complexes with acetic acid and formaldehyde (Figure 2). Acetic acid is a simple electrophilic reagent, and its reaction with **2b** is experimentally well documented.[16] Formaldehyde is considered as a model substrate for the aromatic and aliphatic aldehydes and ketones frequently used as reactants in the catalytic processes.[8, 11, 13]

Reaction of acyclic bis-allylpalladium complexes with acetic acid: In the TS structure (**4a**) obtained for the electrophilic attack of acetic acid on **1e**, the acetate is *syn* to palladium. This geometry also involves electrostatic interactions between the acetate ion and the metal atom, which stabilize the TS structure. The τ angle is 87° ensuring the stereoelectronic requirements of the d–π type hyperconjugative interactions. These interactions are apparently more intensive than in the parent **1e** complex, as shown by the elongation of Pd–C4 (2.195 Å) and C5–C6 (1.418 Å) and shortening of C4–C5 (1.414 Å). A partial η^2 coordination is indicated by the relatively short Pd–C5 distance (2.688 Å). The activation barrier of the reaction is unusually low (3.2 kcal mol^{-1}), which can be explained by the above discussed stabilizing factors: electrostatic OAc–Pd interaction, and d–π type hyperconjugative interactions. In the reaction product (**4b**), C4–C5 is η^2-coordinated to palladium and the structure of the complex is very similar to that of **3a**. The acetate ion is weakly coordinated to the fifth coordination place of palladium. However, the long Pd–O distance (2.385 Å) indicates that this coordination is much weaker than the usual in plane

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coordination of an acetate, where the typical Pd–O distance is about 2.11 Å.[46]

The TS structure for the reaction of the η^3,η^3-complex **1a** and acetic acid was also localized (**5a**). Interestingly, in **5a**, the conformation and geometry of the allyl moiety attacked is about the same as in **4a**, indicating that the electrophilic attack at the η^3-coordinated allyl proceeds through the initial formation of the η^1-allyl moiety. The free coordination site generated by the $\eta^3 \rightarrow \eta^1$ transformation is occupied by the acetate ion. The activation barrier (Figure 4) of the electrophilic attack on **1a** is much higher (11 kcal mol^{-1}) than that of the corresponding reaction involving the η^1,η^3-complex **1e** (3 kcal mol^{-1}). As has been shown above (Table 1), coordination of σ-donor ligands, stabilizes the η^1,η^3 complexes much less than coordination of π-acceptor ligands, which probably accounts for the high activation energy calculated for the reaction involving **5a**.

Reaction of 2c with acetic acid: The η^1-allyl moiety of **2c** can be attacked both at the C6 position and at the metallated carbon (C8), leading to two different regioisomers. The C6 attack proceeds through TS structure **6a** with a low activation barrier of 6.5 kcal mol^{-1}. On the other hand, the C8 attack involving **7a** as a TS requires a considerably higher activation barrier of 10.3 kcal mol^{-1}. In both TSs, the conformation and geometry of the η^1-allyl moiety is similar to that discussed for the acyclic complex **4a**; this indicates that the driving force of the reaction is the maximalization of the d–π type hyperconjugative interactions. In **6a** C7 is able to coordinate to palladium without significant changes of the C3···C8–Pd seven-membered ring structure. However, in the TS structure of the C8 attack (**7a**) the d–π interactions bias a five-membered ring involving C3···C6–Pd atoms. The five-membered ring in **7a** is more strained than the seven-membered ring formed in the C6 attack (**6a**), which increases the activation barrier. In addition, the metallated carbon (C6) of the η^1-moiety in **7a** bears an alkyl substituent, which is also destabilizing (see below).

The seven-membered ring structure is fully developed in the product of the C6 attack (**6b**) and a five-membered ring structure can be found in the product of the C8 attack (**7b**). The five-membered ring structure **7b** is less stable by 4.8 kcal mol^{-1} than its isomer **6b**. This energy difference is similar to the stability difference of 6.5 kcal mol^{-1} calculated for the unprotonated five- and seven-membered species **2c** and **2d** (Figure 1). Clearly, the seven-membered ring structure is most stable in both the parent compound (**2c**) and the TS structure (**6a**), which significantly contributes to the high regioselectivity of the electrophilic attack.

The above results on the facile and regioselective protonation of **2c** with acetic acid are in good agreement with the findings of Jolly and co-workers.[16] According to these authors, analogues of **2c** are protonated at the C6 position even at very low temperature [Eq. (6)]. Furthermore, low temperature NMR studies[16] indicate that in the product of protonation, the acetate ion coordinates to the fifth coordination position of palladium, while the terminal double bond and the phosphine ligand lie in the coordination plane of palladium. All these structural features are also clearly displayed in product **6b**.

Reactions with formaldehyde: The electrophilic attack of formaldehyde on **1e** and **2c** involves TS structures **8a** and **9a**, respectively. The key conformation (τ) and geometry features of the η^1-allyl moiety in these TS structures are the same as in the corresponding TS structures of the protonation reaction (**4a** and **6a**). Furthermore, although the activation barriers are higher (7.5 and 13.5 kcal mol^{-1}) than in the protonation, these activation energies are still low considering the weak electrophilicity of CH_2O toward alkenes.

The relatively low activation energies are in accordance with the experimental findings that catalytic reactions involving attack by aldehydes and ketones on bis-allylpalladium complexes [Eq. (1) and (4)] occur at room temperature without participation of Lewis acids.[8, 13] The fact that the C6 position of **2c** can be attacked with a low activation energy through TS structure **9a**, incorporating a seven-membered ring unit, explains the observation of Tsuji and co-workers[11] that, in telomerization of butadiene with aldehydes [Eq. (4)], only six-membered ring (3,6-divinyltetrahydropyrane) is formed instead of an eight-membered ring, which would be expected in case of a C8 attack.

In the products of the formaldehyde attack (**8b** and **9b**), the resulting alkoxide group moves in the coordination plane of palladium, displacing the alkene moiety. Under catalytic conditions, this alkoxide group may undergo nucleophilic attack at C3 providing 3,6-divinyltetrahydropyranes [Eq. (4)].

Relevance of this study in the chemistry of bis-allylpalladium complexes

Structure and stability of the bis-allylpalladium complexes: The two η^3-coordinated allyl moieties impose considerable ring strain on **1a** and in particular on **2a**. This ring strain can be relieved by coordinating a spectator ligand involving the change of the coordination state of one of the allyl moieties. In ethylene bridged η^1,η^3 complexes, the seven-membered form (**2c**) is more stable than the isomeric five-membered ring form. Spectator ligands with a π-acceptor character, such as phosphine, stabilize the η^1,η^3 complexes more than σ-donor ligands, such as ammonia (Table 1). The effects of alkyl substituents on the stability of the η^1,η^3 complexes depend on the coordination state of the substituted allyl moiety. Alkyl substituents at the metallated terminal carbon (C4 in **1b**) destabilize the complex.

The double bond in the η^1,η^3 complexes is involved in $d_\sigma \rightarrow \pi^*$ type hyperconjugative interactions with palladium. These interactions influence the structure and stability of the complexes. The structural effects involve: elongation of the Pd–C4 and C5–C6 bonds and shortening of the C4–C5 bond as well as a distinct conformation for the η^1-allyl moiety ($\tau \approx 100^\circ$). The hyperconjugative interactions thermodynamically stabilize the complexes up to 6 kcal mol^{-1}. Protonation of the terminal position of the η^1-allyl moiety (C6 in **1b**) leads to coordination of the C5 carbon to palladium resulting in an η^2-coordinated species, such as **3a**.

Reactivity of the bis-allylpalladium complexes: Electrophiles, such as weak acids and aldehydes, attack the η^1 moiety of the bis-allylpalladium complexes with a remarkably low activation energy. The electrophilic attack is facilitated by three important factors: the highly exothermic $\eta^3 \rightarrow \eta^1$ conversion of one of the allyl moieties, especially in the presence of π-acceptor phosphine ligands, the presence of intensive $d_\sigma \rightarrow \pi^*$ type hyperconjugative interactions in the η^1-allyl moiety, and interactions between the electrophile and palladium in the TS of the electrophilic attack. In absence of π-acceptor phosphine ligands the electrophilic attack proceeds trough the initial formation of an η^1,η^3 complex, in which the free coordination site is occupied by a counter ion (**5a**) or a solvent molecule. The TS geometry in this attack is very similar to the TS structure of the phosphine assisted reaction (c.f. **4a** and **5a**), however the activation energy is considerably lower, when a π-acceptor phosphine ligand is coordinated to palladium (Figure 4).

In contrast to bis-allylpalladium complexes, common catalytic (mono-)allylpalladium intermediates do not react with electrophiles. This can be ascribed to two important differences: in (mono-)allylpalladium complexes the $\eta^3 \rightarrow \eta^1$ conversion is endothermic even in the presence of π-acceptor phosphine ligands;[32] and in the absence of a strong π–donor ligand (such as the η^3-allyl ligand in **1e** or **2c**) the $d_\sigma \rightarrow \pi^*$ hyperconjugative electron donation in the η^1-moiety of a (mono-)allylpalladium complex is less effective than this type of hyperconjugation exerted in an η^1,η^3-bis-allylpalladium species.

The bridged complex (**2c**) is attacked exclusively at the C6 position in a process proceeding through the TS structure **6a** incorporating a C3···C8–Pd seven-membered ring. Attack at the C8 position has a higher activation energy since the corresponding TS (**7a**) has a strained five-membered ring structure. Considering the stability of the isomeric bridged complexes (**2c** and **2d**) and the topological preference of the TS structures, an exceptionally high C6 regioselectivity can be predicted for the electrophilic attack on bridged η^1,η^3-bis-allylpalladium complexes.

Conclusion

This theoretical study describes the structure and reactivity of two main types of bis-allylpalladium complexes (**1b** and **2b**) that are catalytic intermediates in important synthetic transformations [Eq. (1) to (5)]. The structure and reactivity of the complexes is strongly influenced by $d_\sigma \rightarrow \pi^*$ type hyperconjugative interactions occurring in the η^1-coordinated allyl moiety in **1b** and **2b**. These hyperconjugative interactions remarkably increase the reactivity of the double bond in the η^1-moiety and enhance the regioselectivity of the electrophilic attack.

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