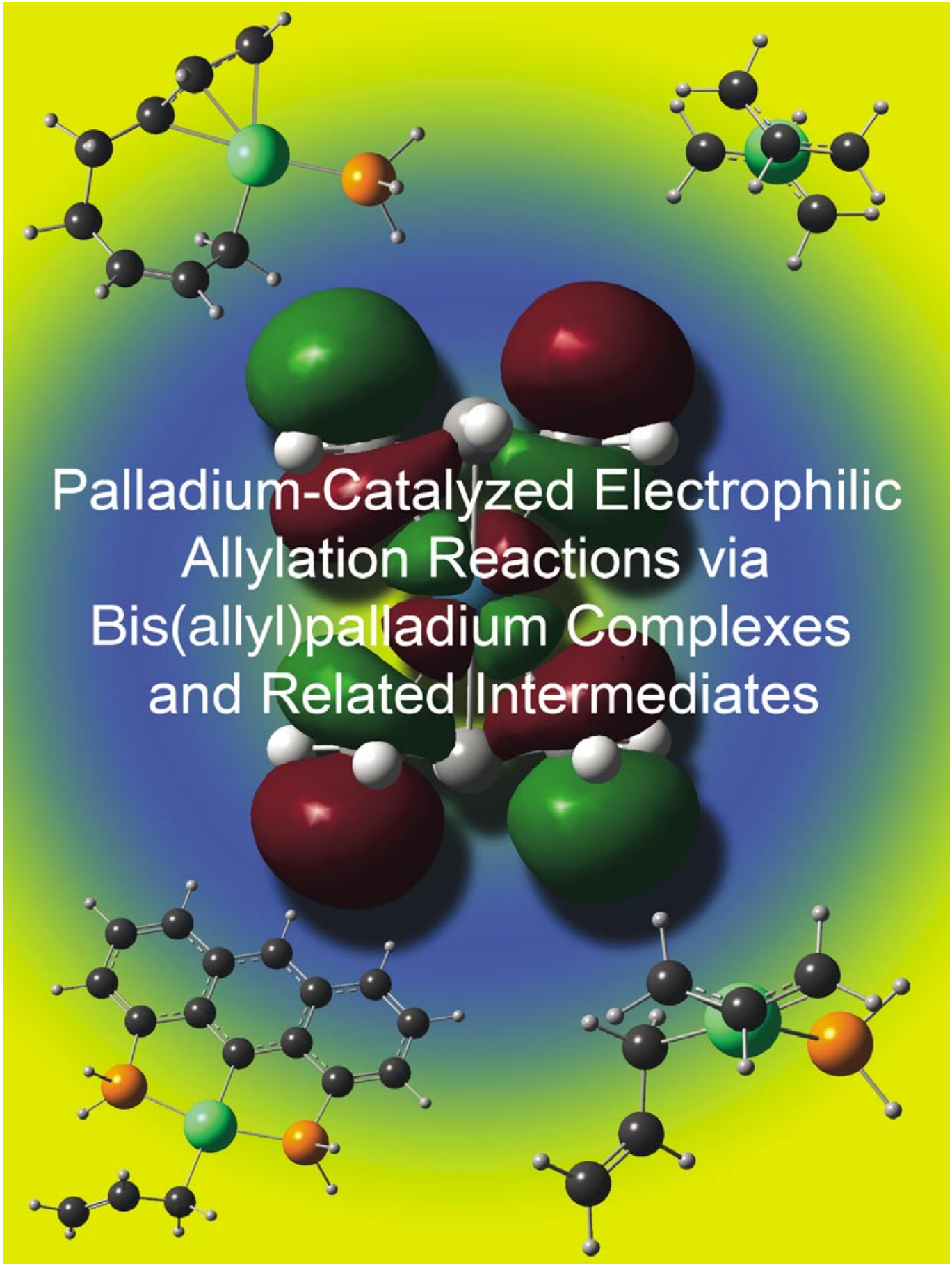

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Palladium-Catalyzed Electrophilic Allylation Reactions via Bis(allyl)palladium Complexes and Related Intermediates

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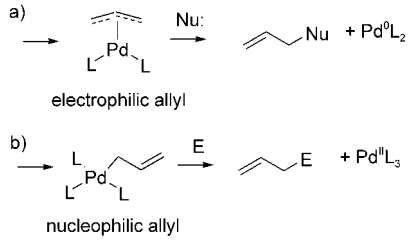
Abstract: The synthetic scope of the allyl–palladium chemistry can be extended to involve electrophilic reagents. The greatest challange in these reactions is the catalytic generation of an allyl–palladium intermediate incorporating a nucleophilic allyl moiety. A vast majority of the published reactions that involve palladium-catalyzed allylation of electrophiles proceed via bis(allyl)-palladium intermediates. The η^1-moiety of the bis(allyl)-palladium intermediates reacts with electrophiles, including aldehydes, imines, or Michael acceptors. Recently, catalytic electrophilic allylations via mono-allylpalladium complexes were also presented by employment of so-called "pincer complex" catalysts.

Keywords: allylation · density functional calculations · electrophilic substitution · homogeneous catalysis · palladium

Introduction

Transformations catalyzed by allyl–palladium complexes represent one of the most important areas of homogenous catalysis.[1–3] A synthetically attractive feature of this type of chemistry is the possibility of controlling the chemo-, regio-, and stereoselectivity of the carbon–carbon bond formation reaction between the employed reagent and the allyl moiety of the complex. The catalytic cycle of these transformations can be divided into two major parts. The first part is the generation of the allyl–palladium intermediate, in which the palladium is in oxidation state +2. This can be achieved through many reactions by using appropriate palladium sources and functionalized allylic precursors. In most reactions so-called "spectator ligands" are also employed. These ligands do not participate directly in the transformation of the allyl moiety; nevertheless they have a decisive role in the determination of the reactivity of the allyl–palladium intermediate. The second part of the reaction is the coupling of the allyl moiety with an appropriate reagent. In the most commonly used reactions, the allyl moiety has an electrophilic character, and therefore it reacts with nucleophiles (Scheme 1a). Typical nucleophiles are malonates and congeners; however, a great variety of other conventional nucleophiles also work well.[1,2] The nucleophilic attack also leads to reduction of palladium(II) to palladium(0) necessitating a subsequent oxidation step to maintain the catalytic cycle.



Scheme 1. The most important processes in palladium-catalyzed allylation: generation of the allyl–palladium intermediate and reaction with a) nucleophilic reagent or b) electrophilic reagent.

Possibilities to extend the synthetic scope of the allyl–palladium chemistry to electrophilic reagents, such as aldehydes, imines, and Michel acceptors have been the subject of a great deal of interest in mechanistic and in synthetic organic chemistry.[4–18] The greatest challenge in these processes is to generate an allyl–palladium intermediate with a nucleophilic allyl moiety (Scheme 1b). The electrophilic attack on the allyl–palladium species does not change the oxidation state of palladium, thus this process leads to the allylated electrophile and a palladium(II) species. Apparently, the mechanistic features of the nucleophilic attack on allyl–palladium complexes (Scheme 1a) and the electrophlic attack on analogue species are fundamentally different.

The subject of the present concept paper is to review the synthetic and mechanistic aspects of the employment of electrophilic reagents in allyl–palladium chemistry. Therefore, this study involves rationalization of the nucleophilic

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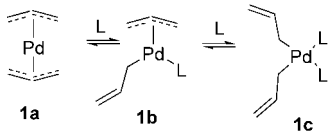
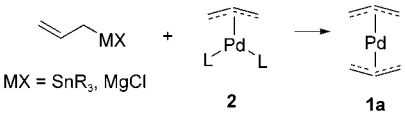
reactivity of the appropriate allyl–palladium complexes, possibilities to generate these complexes, and the synthetic utility of the palladium-catalyzed transformations providing allylated electrophiles (Scheme 1b). On the other hand, palladium-catalyzed allylation reactions involving nucleophilic reagents (Scheme 1a) have been extensively reviewed,[1,3,19–23] and, therefore, these reactions are not included in this paper.

Bis(allyl)palladium Complexes

A vast majority of the published reactions involving palladium-catalyzed allylation of electrophiles proceed via bis(allyl)palladium intermediates. These complexes incorporate two allyl moieties that can bind with different hapticity to palladium (Scheme 2). The different complexes may interconvert by ligand coordination. Bis(allyl)palladium complexes can easily be generated by reaction of mono-allylpalladium complexes and allylmetal species, such as Grignard reagents (Scheme 3).[4,24–26]



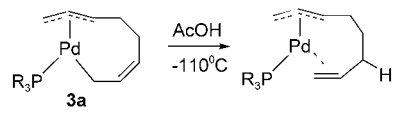
Scheme 2. Bis(allyl)palladium complexes with different hapticity. **1a**: η^3,η^3-bisallypalladium complex (also called bis-π-allylpalladium complex); **1b**: η^1,η^3-bis(allyl)palladium complex; **1c**: η^1,η^1-bis(allyl)palladium complex.



Scheme 3. Generation of bis(allyl)palladium complexes from allyl–metal species and mono-allylpalladium complexes.

Although, complex **1** and its alkyl-substituted analogues have been isolated and characterized by NMR spectroscopy and X-ray diffraction,[4,24–29] these complexes are usually less stable than their mono-allylpalladium analogues. It was shown that bis(allyl)palladium complexes readily react with electrophiles. Jolly and co-workers[30] have shown that the bridged η^3,η^3-bis(allyl)palladium complex **3a** can be protonated by acetic acid even at low temperature (Scheme 4). Furthermore, Yamamoto and co-workers demonstrated that complex **1** reacts readily with aldehyde electrophiles.[4]

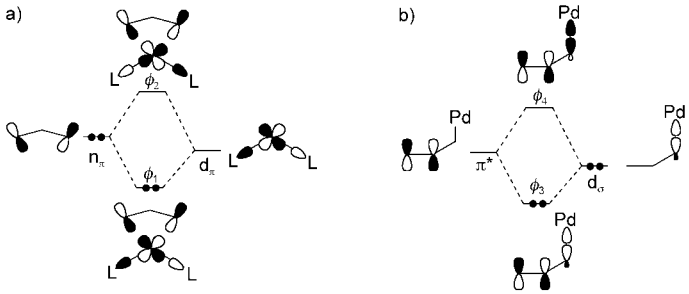
A particularly interesting mechanistic question concerns the orthogonal reactivity of the allyl moiety in bis(allyl)palladium (**1**) and mono-allylpalladium (**2**) complexes.



Scheme 4. Facile protonation of **3** with a weak acid.

Reactivity of the Allyl Moiety in Mono- and Bis(allyl)palladium Complexes

The major differences in the reactivity of mono- and bis(allyl)palladium complexes arise from the different hapticity of the allyl–palladium bonding. The basic reactivity of the (η^3-allyl)palladium complexes can be described by a simplified molecular orbital (MO) diagram constructed from the allylic n_π orbital and the metallic d_π fragment orbitals (Scheme 5a).[31] This interaction leads to the carbon–metal



Scheme 5. Qualitative MO diagram to describe the most important frontal orbital interactions in a) an (η^3-allyl)palladium complex and b) in an (η^1-allyl)palladium complex.

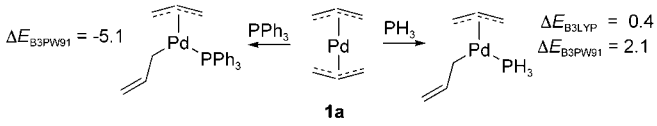
bonding orbital ϕ_1 and the unoccupied MO ϕ_2. The antibonding ϕ_2 MO is energetically accessible for nucleophiles and gives the allyl moiety an electrophilic character. The MO relevant for the reactivity of the η^1-allyl complexes can be derived from the π* MO of the double bond and the d_σ MO of the palladium–carbon σ-bond.[12] This d_σ–π* interaction is a classical hyperconjugation interaction, introducing π* character into the ϕ_3 MO. The intensity of the hyperconjugative interactions can be enhanced by increasing the electron density on palladium.

As it is appears in Scheme 5, the nature of the allyl–metal interactions is fundamentally different in (η^3-allyl)palladium and (η^1-allyl)palladium complexes. In (η^3-allyl)palladium complexes, the allyl system donates electrons to the PdL_2 fragment (Scheme 5a), and, therefore, π-acceptor ligands (L), such as phosphanes, activate the allyl moiety towards a nucleophilic attack. On the other hand, in (η^1-allyl)palladium complexes the palladium atom donates electrons to the allyl moiety (Scheme 5b). Accordingly, the allyl moiety can be activated toward electrophilic reagents by employment of electron-donor ligands on palladium.

Density Functional Theory (DFT) Studies Involving Bis(allyl)palladium Complexes

Both experimental[29,30] and theoretical studies[12,17,32] show that η^1,η^3-bis(allyl)palladium complexes easily form from the η^3,η^3 forms in the presence of ligands coordinating to palladium. These ligands can be spectator ligands, such as various phosphanes, or the electrophilic substrates, such as

aldehydes and imines. Density functional calculations indicate that the coordination of phosphanes to **1a** and its derivatives is a slightly exothermic or a slightly endothermic process depending on the coordinating species (Scheme 6).



1a

Scheme 6. DFT-calculated complexation energies of **1a** with PPh_3 and PH_3 (using B3LYP[32] and B3PW91[33] functionals). The energies are given in kcal mol^{-1}.

The hyperconjugative interactions in the η^1-moiety (Scheme 5b) of the η^1,η^3-bis(allyl)palladium complexes lead to characteristic structural features. Density functional calculations (at the B3PW91/LANL2DZ level of theory) for complex **4a** (Figure 1) revealed[12] that the Pd-C1-C2-C3 torsional angle (τ) is 104.8°; this allows an optimal overlap between the π^* and d_σ MOs in the η^1-allyl moiety (Scheme 5b). Although, the C2–C3 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), suggesting conjugative interactions with the Pd–C1 bond. In order to analyze the nature of the electronic interactions between the C2–C3 double bond and the Pd–C1 bond in the η^1-coordinated allyl moiety, the geometrical parameters for complex **4b** were also calculated. Complex **4b** was derived from **4a** by restricting the τ torsional angle at 180°, in order to shut down the hyperconjugative interactions between the π^* and d_σ MOs in the η^1-allyl moiety. A decrease in the electronic interactions on changing τ from 104° (**4a**) to 180° (**4b**) is clearly reflected by two factors: 1) the thermodynamic destabilization of the complex by 6 kcal mol^{-1}; and 2) a contraction of the Pd–C1 and C2–C3 bonds, and an elongation of the C1–C2 bond in **4b**.

DFT studies also revealed[12,17] that the electrophilic attack by aldehyde electrophiles occurs with a low activation barrier (8–15 kcal mol^{-1}) at the C3 position of the η^1-allyl moiety (e.g., **4**). The driving force of this reaction is the increased hyperconjugation between the developing carbocation center at C2 and the Pd–C1 bond. This interaction is clearly reflected by the bond lengths of the η^1-allyl moiety in the TS structure **4b**. As one goes from **4a** to TS structure **4b** the C1–C2 bond is shortened indicating an increased hyperconjugative interaction.

The mechanism of the electrophilic attack on the allyl moiety of bis(allyl)palladium complexes triggering hyperconjugative interactions between a developing carbocation and an electron-rich carbon–metal bond apparently resembles the corresponding reactions involving main-group allyl–metal reagents (such as allylsilanes and -stannanes) or Grignard reagents. However there are some important differences as well: 1) reactions proceeding through bis(allyl)-palladium complexes requires only catalytic amounts (typically 5 mol %) of palladium; and 2) in bis(allyl)palladium complexes the electronic and steric effects of the spectator ligands (including the η^3-allyl moiety) can be employed to tune the reactivity and the selectivity of the electrophilic attack.

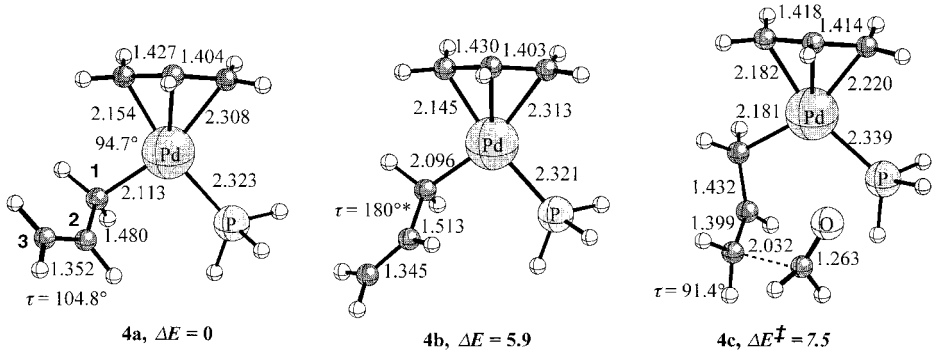
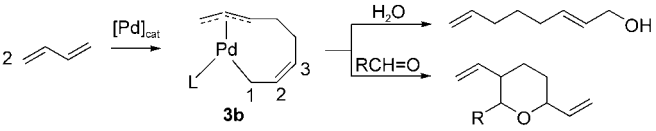


Figure 1. DFT structure of η^1,η^3-bisallylpalladium complexes **4a**,**b** and TS **4c**. The dihedral angle τ is defined as Pd-C1-C2-C3 The τ angle is frozen at 180° in **4b** (denoted by *). The energies are given in kcal mol^{-1}, the bond lengths are given in Å, and the angles are given in degrees.

Telomerization of Conjugated Dienes

Telomerization of butadiene is one of the earliest published catalytic reactions involving bis(allyl)palladium intermediates.[1–3,34,35] The first step of this reaction is the dimerization of the diene, such as butadiene (Scheme 7), to give a bridged bis(allyl)palladium complex (**3b**). This complex reacts with many protic reagents including water, alcohols, carboxylic acids, and amines. Butadiene telomerization with water is the first step in the commercial production of *n*-octanol, which is one of the most important industrial applications of allyl–palladium chemistry.[36] Aldehyde or imine reagents can also be employed in the telomerization reactions to give divinyl-substituted heterocyclic products. The first step in these reactions is an electrophilic attack at the C3 carbon atom of the η^1-allyl moiety. The facile stiochimetric protonation of complex **3** with acetic acid (Scheme 4) indicates that this reaction easily occurs under catalytic conditions.[12,30] Furthermore, attack at the C3 carbon atom leads to an optimal hyperconjugative stabi-



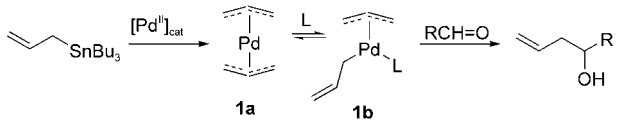
Scheme 7. Examples for telomerization of butadiene via bis(allyl)palladium complex **3b**.

lization of the TS structure (c.f. Figure 1) of the process.[12] The electrophilic attack affords an η^3-(mono-allyl)palladium intermediate, which can undergo a subsequent nucleophilic attack. The anionic nucleophile may be generated by deprotonation of the employed protic reagent, or by formation of an enolate ion resulted in the electrophilic attack.

The palladium-catalyzed telomerization of conjugated dienes with alcohols, phenols, and aldehydes continues to attract considerable attention in both academic and industrial research. The most important current development of this reaction involves the increase of the reactivity and stability of the catalyst in order to increase the so-called turnover frequency (TOF) and turnover number (TON) of the catalyst. With an appropriate choice of the spectator ligand L, a high yield can be achieved by using 0.001–0.00033 mol% palladium catalyst under moderate reaction conditions.[37] Another important issue concerns the regioselectivity of the nucleophilic attack, which can also be influenced by ligand effects.[37–39]

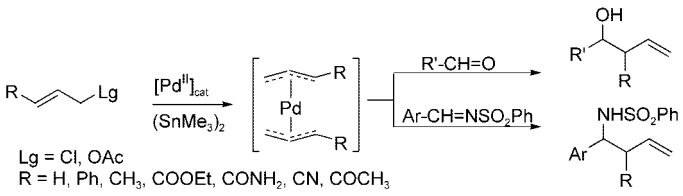
Catalytic Generation of Bis(allyl)palladium Complexes from Allyl Stannanes

Yamamoto and co-workers[4,5] have shown that bis(allyl)palladium complexes can be generated under catalytic conditions from allyltributylstannane derivatives and palladium(II) salts. The bis(allyl)palladium complex formed in this reaction readily reacts with aldehyde and imine electrophiles (Scheme 8). Introduction of allylstannanes to generate bis(allyl)palladium complexes under catalytic conditions was an important innovation, which considerably increased the diversity of the allylic precursors employed in the reaction.



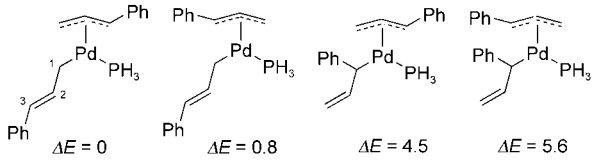
Scheme 8. Example for catalytic generation of bis(allyl)palladium complexes **1a–b** followed by reaction with an aldehyde electrophile.

The synthetic scope of the electophilic substitution reaction can be extended by in situ generation of the allylstannane precursor of the reaction. This can be achieved by employing readily available allyl chloride and allyl acetate precursors in the presence of hexamethylditin (Scheme 9).[15–17] The first step of this reaction is the palladium-catalyzed formation of the transient allylstannane, which subsequently form the bis(allyl)palladium complex and reacts with the electrophile. By this dicatalytic, one-pot reaction various allyl-substituted homoallylalcohol and -amine products can be obtained.



Scheme 9. Electrophilic substitution of in situ generated functionalized allyl stannanes.

The palladium-catalyzed electrophilic allylation reactions with functionalized allylic substrates usually provide the branched allylic isomer.[4,15–17] Selective formation of this allylic isomer is in sharp contrast to the regioselectivity observed for palladium-catalyzed nucleophilic substitutions, which usually gives the linear allylic isomer.[2,20] The regioselectivity of the electrophilic attack can be explained by the influence of the substituent effects on the stability of the η^1-allyl moiety of the bis(allyl)palladium intermediate.[15–17] DFT studies clearly show that the terminally substituted η^1-allyl complexes are more stable when the alkyl or aryl substituents are attached at the C3 carbon atom of the allyl moiety (Scheme 10). Since the electrophilic attack also occurs at the C3 position of the η^1-allyl moiety, the catalytic reaction affords the branched allylic isomer.[15–17] The diastereoselectivity of the catalytic reaction is dependent on the actual substrates and on the reaction conditions. A high *anti*-diastereoselectivity can be achieved by employment of bulky substituents, such as R = Ar, COOEt (Scheme 10).[17]

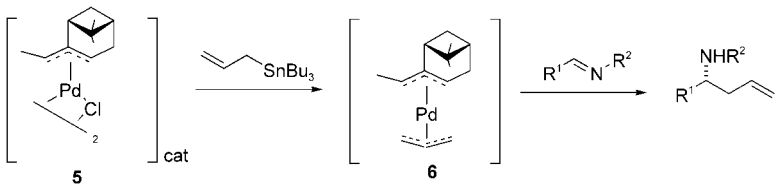


Scheme 10. Stability of the isomeric disubstituted bis(allyl)palladium complexes. The energy values are in kcal mol^{-1}.

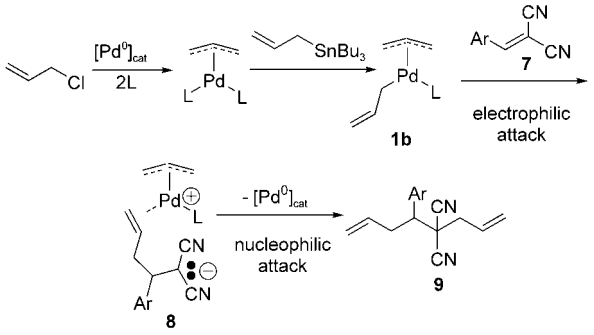
Yamamoto and co-workers[7,11] described a catalytic asymmetric version of the allylation reaction of aldimines. In this process the bis(allyl)palladium intermediate **6** is formed from an (1*S*)-β-(−)pinene-based mono-allylpalladium complex **5** (Scheme 11). Subsequently, this complex undergoes electrophilic attack by aldimines affording homoallylamines with up to 91% enantiomeric excess. The best results were accomplished by using benzylimine derivatives. It was found that the chiral information from the η^3-allyl ligand is propagated in the electrophilic attack involving bis(allyl)palladium intermediate **6**.

Electrophilic Attack Followed by Nucleophilic Attack on Bis(allyl)palladium Intermediates

The palladium-catalyzed reaction of a 1:1 mixture of allyl chloride and allyl stannane reagents with alkylidene malonitriles results in a double allylated product.[6,9] The mechanism of this reaction is particularly interesting. The first step of the reaction is an oxidative addition of the palladium(0) catalyst to allyl chloride to give a mono-allylpalladium complex (Scheme 12). This complex undergoes transmetallation providing the bis(allyl)palladium intermediate (**1b**) of the



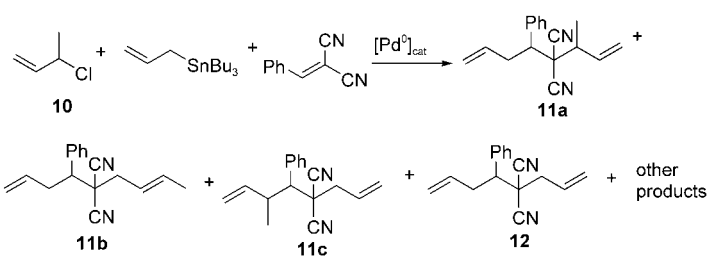
Scheme 11. Asymmetric allylation of aldimines in the presence of a chiral allyl–palladium catalyst.



Scheme 12. Bis-allylation reaction of alkylidene malonitriles (**7**).

reaction. Subsequently, the arylated carbon of alkylidene malonitrile **7** attacks the η^1-allyl moiety of **1b**. This electrophilic attack generates a mono-allylpalladium complex and a malonitrile anion (**8**). This malonitrile derivative undergoes a second allylation step by nucleophilic attack of the mono-allylpalladium complex to give compound **9**. This peculiar behavior of bis(allyl)palladium complexes (such as **1b**) involving an initial electrophilic attack followed by a nucleophilic attack is classified as amphiphilic (or ambiphilic) reactivity.

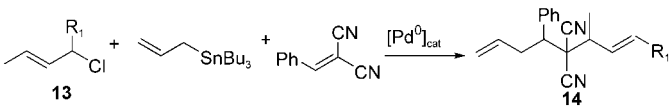
Control of the regioselectivity becomes an important issue when substituted allyl chlorides and allyl stannanes are employed as reagents. An interesting feature is that the reaction with mono-alkyl-substituted precursors usually gives a poor regioselectivity.[8,13,14,40] For example the bis-allylation process with methyl allyl chloride **10** gives a complex reaction mixture involving both cross-coupling (**11a–c**) and homocoupling (**12**) products (Scheme 13).[13] On the other hand, an excellent regiochemistry was obtained using 1,3-dialkyl-substituted allylic precursors, such as **13**. This reaction gives a single regioisomer **14**; the homocoupled product (**12**) was not detected (Scheme 14).[13] A similar regioselectivity



Scheme 13. Employment of mono-alkyl-substituted allyl chloride **10** with allylstanne gives poor regio- and chemoselectivity in the palladium-catalyzed bis-allylation reaction.

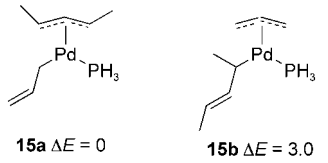
was obtained for the palladium-catalyzed bis-allylation of isocyanates with allyl chlorides and allyl stannanes.[14]

The high regioselectivity with allylic precursor **13** could be explained by the destabilizing ef-



Scheme 14. The bis-allylation reaction proceeds with an excellent regioselectivity using dialkyl allyl chlorides **13**.

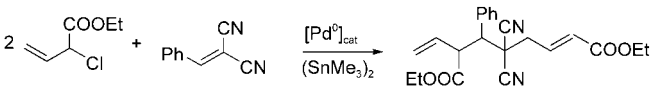
fects of the alkyl substituents on the η^1-allyl moiety.[13] In the presence of spectator ligands (approximated by PH_3) the reaction of **13** and allylstannane with palladium(0) catalyst (Scheme 15) may generate two isomeric η^1,η^3-bis(allyl)palladium complexes **15a** and **15b**. Complex **15a**, with an unsub-



Scheme 15. Alkyl substituents on the η^1-allyl moiety destabilize the bis(allyl)palladium complexes.

stituted η^1-allyl moiety, is more stable than its alkyl-substituted counterpart **15b**. Since the double allylation reaction is initiated by an electrophilic attack (Scheme 12) at the phenyl-substituted carbon atom of **7** (Ar = Ph), the second attack will take place on the substituted allyl moiety with a high regioselectivity. It was also shown that the activation energy of the initial electrophilic attack is lower on **15a** than on **15b**; this further improves the regioselection in the bis-allylation reaction.[13]

Bis-allylation reactions can also be performed by using only the functionalized allyl chloride precursor together with hexamethylditin (Scheme 16).[15,16] This catalytic transformation also proceeds with a very high regioselectivity. A



Scheme 16. Triple-catalytic approach for bis-allylation with functionalized allyl chloride in the presence of hexamethylditin.

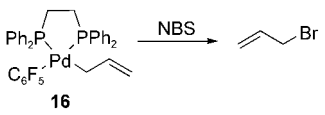
particularly interesting mechanistic aspect of this reaction is that palladium catalyzes three processes in each catalytic cycle: 1) generation of the allylstannane precursor from allyl chloride and hexamethylditin, 2) the electrophilic attack (c.f. Scheme 12), and 3) the nucleophilic attack.

Electrophilic Substitution via Mono-allylpalladium Complexes

Although catalytic transformations via bis(allyl)palladium intermediates have found many important synthetic applications, the diverse reactivity of the bis(allyl)palladium complexes imposes serious limitations to the scope of these reactions. As mentioned above, formation of unsymmetrically substituted bis(allyl)palladium complexes may lead to difficulties in controlling the regioselectivity of the reaction (c.f. Scheme 13). A further important problem is that bis(allyl)-palladium complexes may undergo allyl–allyl (Stille) coupling instead of reaction with electrophiles.[10,26,32] Accordingly, further development of the palladium-catalyzed electrophilic substitution reaction requires that the catalytic transformations proceed entirely via mono-allylpalladium intermediates without involvement of bis(allyl)palladium species. However, development of such catalytic transformations poses a great challenge, since mono-allylpalladium complexes are usually considerably more stable as η^3-coordinated species (Scheme 1a).[41] On the other hand, the theoretical calculations clearly indicate[12] that the electrophilic attack occurs at the η^1-allyl moiety of the complex, while the η^3-coordinated allyl moiety and L (**1b**) are considered as spectator ligands. Accordingly, the nucleophilic reactivity of the η^1-allyl moiety could be maintained by replacement of the η^3-allyl moiety and L with strongly coordinating electron-supplying ligands.

Stoichiometric Reactions with η^1-Allylpalladium Complexes

Although the majority of the reactions involving mono-allylpalladium complexes have been performed with nucleophiles, certain mono-allylpalladium complexes have been reported to undergo electrophilic attack. Kurosawa and co-workers showed that the η^1-allyl moiety of complex **16** was nucleophilic, and therefore it readily reacts with electrophilic reagents. For example, the reaction of **16** with HCl and Br_2 afforded propene and allylbromide, respectively (Scheme 17).



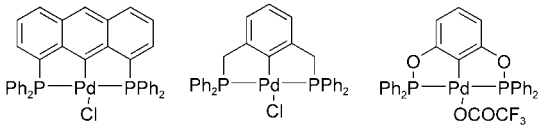
16

Scheme 17. Electrophilic substitution at the η^1-allyl moiety of mono-allylpalladium complex **16** with *N*-bromosuccinimide (NBS).

It is important to note that the electrophilic allylation reactions reported by Kurosawa and co-workers[42,43] require the use of stoichiometric amounts of palladium complex **16**, which considerably limits the synthetic scope of these transformations.

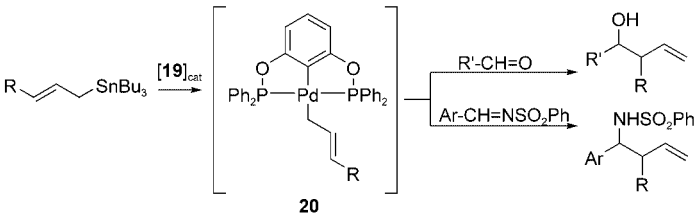
Catalytic Electrophilic Allylation via Mono-allylpalladium Complexes

Recently, Szabó and co-workers[18] reported a new palladium-catalyzed electrophilic substitution reaction proceeding entirely via mono-allylpalladium intermediates without involvement of bis(allyl)palladium species. In these processes so-called "pincer complexes"[44–46] (**17**–**19**, Scheme 18) were used to catalyze the electrophilic substitution reaction of allylstannanes with aldehyde and imine electrophiles (Scheme 19).



17 18 19

Scheme 18. So-called "pincer complexes" employed in catalytic allylation of electrophiles.



20

Scheme 19. Palladium-catalyzed electrophilic substitution via a mono-allylpalladium intermediate.

The allyl–palladium intermediate (**20**) of the catalytic transformation is generated by transmetallation of the allylstannane with the corresponding pincer complex. This intermediate was observed under the reaction conditions of the catalytic process.[47] In complex **20** palladium is complexed by a strongly coordinating terdentate ("pincer") ligand, and therefore the allyl moiety is constrained to an η^1-coordination state required for the nucleophilic reactivity (c.f. Scheme 5b). Furthermore, the aryl group in **20** is an efficient σ-donor ligand ensuring a high electron density on palladium; this increases the nucleophilicity of the allyl moiety. The catalytic activity of the various pincer complexes depends on the electronic effects of the heteroatom in the pincer ligand and on the coordination ability of the counterion. Phosphorus-containing pincer complexes with weakly coordinating counterions, such as **19**, exhibit a high catalytic activity in electrophilic substitution reactions.

Conclusion and Outlook

Palladium-catalyzed electrophilic allylation reactions represent a conceptually new approach in allyl–palladium chemistry. This approach involves tuning the reactivity of the allyl moiety by choice of the spectator ligands on palladium. Commonly used monodentate ligands (such as phosphanes)

in η^3-coordinated allyl–palladium complexes provide electrophilic allyl moieties, which react with nucleophiles (Schemes 1a and 5a). However, the η^1-moiety in bis(allyl)-palladium complexes (**1b**) and in specially constructed aryl-palladium complexes (such as **16** and **20**) is electrophilic, and therefore these complexes react with a great variety of electrophilic reagents, such as aldehydes, imines, and Michael acceptors. Bis(allyl)palladium complexes can be readily generated under catalytic conditions, and thus many synthetic applications have been presented for single and even for double allylation of electrophiles (Schemes 7–9 and 14). These reactions can be performed by using simple precursors involving conjugated dienes, allyl stannanes, allyl chlorides, and allyl acetates. Catalytic generation of chiral bis(allyl)palladium complexes offer an attractive new method for asymmetric catalysis (Scheme 11). The synthetic scope of the palladium-catalyzed electrophilic substitution reactions can be extended by use of pincer complex catalysts (Scheme 19). These catalysts operate via mono-allylpalladium complexes eliminating the side-reactions arising from the diverse reactivity of bis(allyl)palladium complexes.

The future development of the palladium-catalyzed electrophilic allylation reactions will certainly involve new regio-, stereo-, and enatioselective processes. The unique amphiphilic reactivity of the bis(allyl)palladium complexes can be employed to bis-allylation of Michael acceptors (Scheme 12) and related systems. The level of the selectivity of the electrophilic attack on the allylic precursor can be further increased by employment of various pincer complexes or analogue catalysts. The majority of the above-mentioned electrophilic allylation reactions proceed under mild and neutral conditions without the occurrance of redox processes in the palladium catalyst; therefore, these reactions can also be combined with other catalytic reactions to develop new multicatalytic systems (c.f. Scheme 9).

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