Palladacycles: synthesis and catalysis
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Citation for published version (APA):

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Chapter 5

[Pd$^0$(Ar-bian)(\eta$^2$-Alkene)] Complexes Catalyze Chemo- and Stereoselective Partial Hydrogenation of Functional 1,2-Dienes

Abstract

Several zerovalent palladium catalysts bearing bis(arylimino)acenaphthene and alkene ligands were employed in the partial hydrogenation of various functionalized allenes to give the corresponding trisubstituted alkenes. These catalysts provided excellent activities as well as chemo- and positional selectivities but variable stereoselectivities to trisubstituted (Z)-1-alkenyl phosphonates (85-95%) and trisubstituted (Z)-1-alkenyl esters (20-93%). The palladium pre-catalyst bearing the 4-MeO-C$_6$H$_4$-bis(arylimino)acenaphthene and dimethylfumarate as ligands showed higher activities, chemo-, positional and stereoselectivities. Some Z-E isomerization was observed after initial stereoselective hydrogenation. However, no over-reduction was observed in the partial hydrogenation of 1,2-dienyl phosphonates and 2,3-dienoates employing this catalytic system.

5.1 Introduction

Allenes (n,n+1-dienes) are an important class of compounds with many applications in organic chemistry.\textsuperscript{2} In spite of the fact that the catalytic hydrogenation of unsaturated hydrocarbons has been extensively studied,\textsuperscript{3} the hydrogenation of allenes has been reported in only a very limited number of studies. Moreover this reaction is very challenging since there are issues of chemo- and stereoselectivity like for alkyne semi-hydrogenation, but also an issue of positional selectivity\textsuperscript{4} (Scheme 5-1). The chemoselective hydrogenation is an important method for removing allenes from distillate oil, especially the selective hydrogenation in C\textsubscript{3} streams of methylacetylene and propadiene to propene.\textsuperscript{5}

Scheme 5-1. The hydrogenation of allenes.

Several heterogeneous and homogeneous catalysts have been developed or used for this reaction such as the Wilkinson-Osborn catalyst RhCl(PPh\textsubscript{3})\textsubscript{3},\textsuperscript{6,7} the cationic Rh(I) systems of Schrock and Osborn or of Selke,\textsuperscript{7} the MoS\textsubscript{2} catalyst,\textsuperscript{8} hydrogenation with diimide.\textsuperscript{9} Moreover, palladium catalysts have also been reported such as heterogeneous palladium catalysts\textsuperscript{10} and some allylpalladium(II) derivatives.\textsuperscript{11} So far the selectivity in the reported cases is low.\textsuperscript{12}

In recent years, stereoselective semi-hydrogenation of alkynes by zerovalent palladium catalyst bearing either a Ar-bian ligand (Ar-bian = bis(arylimino)acenaphthene) or a NHC ligand (NHC = nitrogen heterocyclic carbene), that are able to homogeneously hydrogenate a wide variety of alkynes to the corresponding (Z)-alkenes have been reported by our group (Scheme 5-2).\textsuperscript{13,14}
observed selectivity towards (Z)-alkenes is very high under very mild conditions (25°C, 1 bar H₂).

Scheme 5-2. Palladium(0)-NHC catalyst generated in situ\textsuperscript{14} and [Pd(bis(p-methoxyphenylimino)acenaphtene)(η\textsuperscript{2}-dimethylfumarate)].\textsuperscript{13}

The objective of this study was to investigate whether or not [Pd(Ar-bian)(η\textsuperscript{2}-alkene)] complexes are suitable catalysts for the hydrogenation of allenes, which would be an interesting and valuable extension of the known semi-hydrogenation of isomeric alkynes. If so, we would be particularly interested to see whether any chemo-, positional and/or stereoselectivity would be exhibited by the [Pd(Ar-bian)(η\textsuperscript{2}-alkene)] complexes in such a hydrogenation. Similarly to the hydrogenation of alkynes, the hydrogenation of 1,2-dienes could lead to an alkene if the reduction of one double bond occurs selectively. In that case the reaction is chemoselective. The stereoselectivity or lack thereof will determine the Z/E ratio of the obtained alkene. In catalytic hydrogenation of 1,2-dienes, the chemoselectivity and the stereoselectivity are even more interesting if either the 1,2-hydrogenation or the 2,3-hydrogenation reaction is performed preferentially, this positional selectivity is represented in Scheme 5-1. In this chapter, the use of various [Pd\textsuperscript{0}(Ar-bian)(η\textsuperscript{2}-alkene)] catalysts in the selective hydrogenation of 1,2-dienyl phosphonates and 2,3-dienyl carboxylates is described.
5.2 Results and Discussion

5.2.1 [Pd\(^0\)(Ar-bian)(\(\eta^2\)-alkene)] complexes (1-8)

The complexes that have been used as hydrogenation catalysts (1-8) have been compiled in Figure 5-1. These complexes contain various Ar-bian and co-ligands, e.g. alkenes, and have been selected to study the effects of the various ligands on the activity, stability and selectivity in the hydrogenation reaction.

![Diagram of complexes](image)

**Figure 5-1.** Palladium(0)-alkene complexes used in this study as hydrogenation catalysts with dimethyl fumarate (dmfu), maleic anhydride (ma) and fumaronitrile (fn) as alkene.

5.2.2 Hydrogenation of the 1,2-dienyl phosphonates (9)

The palladium(0)-alkene complexes 1a and 3c were applied in the hydrogenation of 1,2-dienyl phosphonates 9. The hydrogenations were conducted at room temperature in THF with 1 mol % of catalyst under a hydrogen gas pressure of about 1 bar. Results of the hydrogenations using these catalysts have been compiled in
Table 5-1. Surprisingly the catalytic hydrogenation of these substrates gives only trisubstituted 1-alkenyl phosphonate 10 (Scheme 5-3).

\[
\begin{align*}
\text{Scheme 5-3. Hydrogenation of 1,2-dienyl phosphonates 9.}
\end{align*}
\]

So far, to the best of our knowledge, such activity, chemo-, stereo- and positional selectivity in homogeneous catalytic hydrogenation of allenes have not been described either with rhodium\textsuperscript{6,7} or palladium\textsuperscript{11} complexes. Hence, full positional selectivity is obtained, since the reduction proceeds via the unique 2,3-hydrogenation reaction. Moreover, the complete chemoselectivity is also noteworthy, since no overreduction is observed. In addition to the excellent chemo- and positional selectivities, excellent yields and stereoselectivities, up to 99% for the (Z)-alkene 10-(Z), are observed (entries 1 and 2, table 5-1).

Table 5-1. Hydrogenation of different 1,2-dienyl phosphonates (9a-9e) catalyzed by [Pd(Ar-bian)(\eta^5-alkene)].\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>1,2-Diene</th>
<th>Catalyst</th>
<th>Conversion (%)\textsuperscript{b}</th>
<th>10-(Z) (%)\textsuperscript{c}</th>
<th>Yield (%)\textsuperscript{d}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9a</td>
<td>1a</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td>94</td>
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<tr>
<td>2</td>
<td>9b</td>
<td>3c</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td>94</td>
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<tr>
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<td>9c</td>
<td>1a</td>
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<td>95</td>
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<td>4</td>
<td>9d</td>
<td>1a</td>
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<td>85</td>
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<tr>
<td>5</td>
<td>9e</td>
<td>1a</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td>91</td>
</tr>
<tr>
<td>6</td>
<td>3c</td>
<td>1a</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reaction conditions 0.2 mmol 1,2-diene, 3 mL THF, 1 mol % of catalyst, 1 atm H\textsubscript{2}, 20°C. \textsuperscript{b} Conversion determined by \textsuperscript{1}H NMR. \textsuperscript{c} Determined by \textsuperscript{1}H NMR. \textsuperscript{d} Isolated yields.
Substitution at C-3 by methyl or ethyl groups does not affect the positional selectivity (2,3-hydrogenation) and the stereoselectivity (entries 1, 3 and 4). Meanwhile, slight modification of the substituents R₁ on the carbon 1 does not change the observed stereoselectivity (entries 1, 5 and 7) the effect of the phosphonate moieties is apparently predominant to determine the stereoselectivity.

Contrary to the hydrogenation of the n-butyl-substituted 1,2-dienyl phosphonate 9a (entries 1 and 2) in which both of the catalysts (1a and 3c) were highly active and selective, the results of the hydrogenations of the methyl-substituted 1,2-dienyl phosphonate 9d (entries 5 and 6) are marked by the lack of activity of 3c. This complete absence of reaction could be attributed to the lack of activation of the pre-catalyst 3c, which may result from the stronger coordination of the fumaronitrile ligand to the palladium as compared to dimethylfumarate homologue. Indeed, the strength of the alkene-palladium bonds decreases in the order: maleic anhydride > fumaronitrile > dimethylfumarate.¹⁵

5.2.3 Hydrogenation of the 2,3-dienoates (11 and 13)

The palladium(0)-alkene complexes 1-8 were applied in the hydrogenation of 2,3-dienoates 11 and 13. The hydrogenations were conducted at room temperature in THF with 1 mol% of catalyst under a hydrogen gas pressure of about 1 bar. Results of the hydrogenations using these catalysts have been compiled in Table 5-2. The same excellent chemo- and positional selectivity as was obtained for the 1,2-dienyl phosphonates 9 is observed, since only trisubstituted 1-alkenyl esters 12 and 14 are formed (Scheme 5-4).

\[
\begin{align*}
\text{R} & \quad \text{COOEt} \\
\text{H}_2 & \quad \text{[Pd]} \\
\text{THF} & \quad \text{R} \\
\end{align*}
\]

\[
\begin{align*}
\text{11} & \quad \text{R} = \text{Bn} \\
\text{13} & \quad \text{R} = \text{nBu}
\end{align*}
\]

\[
\begin{align*}
\text{12-}(Z) & \quad \text{12-}(E) \\
\text{14-}(Z) & \quad \text{14-}(E)
\end{align*}
\]

Scheme 5-4. Hydrogenation of 2,3-dienoates 11 and 13.

With this substrate, the chemo- and positional selectivity of the hydrogenation is conserved, but we observe a lack of stereoselectivity. Indeed, the Z/E ratio typically
varies between 80/20 and 93/7. In some cases an opposite selectivity is observed with a ratio $Z/E$ varying between 20/80 and 40/60.

Table 5-2. Hydrogenation of Ethyl 2-benzylbuta-2,3-dienoate 11 and of Ethyl 2-n-butylbuta-2,3-dienoate$^{16}$ 13 catalyzed by [Pd(Ar-bian)(η$^2$-alkene)].$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>2,3-Dienoate</th>
<th>Catalyst</th>
<th>Time (h)</th>
<th>Conversion (%)$^b$</th>
<th>Ratio $Z/E$ (%)$^c$</th>
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<td>12</td>
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<td></td>
<td></td>
<td></td>
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<td>&gt;99</td>
<td>90/10</td>
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<tr>
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<td>88/12</td>
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<td>91/9</td>
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<td></td>
<td>24</td>
<td>&gt;99</td>
<td>~20/80</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions 0.2 mmol 2,3-dienoate, 3 mL THF, 1 mol % of catalyst, 1 bar H$_2$, 20ºC. $^b$ Conversion determined by $^1$H NMR. $^c$ Determined by $^1$H NMR.
The complex \([\text{Pd}(\rho-\text{MeO-C}_6\text{H}_4-\text{bian})(\eta^2-\text{dmfu})]\) (1a) (entries 1 and 8, Table 5-2) turned out to be one of the most selective catalyst for the hydrogenation of 2,3-dienoates 11 and 13. Meanwhile, for the hydrogenation of ethyl 2-benzylbuta-2,3-dienoate 11 (entries 1-7, Table 5-2), the highest selectivity with full conversion was obtained with \([\text{Pd}(\rho-\text{NO}_2-\text{C}_6\text{H}_4-\text{bian})(\eta^2-\text{dmfu})]\) (2a) (entry 4), \([\text{Pd}(\rho-\text{Me-C}_6\text{H}_4-\text{bian})(\eta^2-\text{dmfu})]\) (3a) (entry 5), \([\text{Pd}(m,m'-\text{Me}_2-\text{C}_6\text{H}_3-\text{bian})(\eta^2-\text{dmfu})]\) (5a) (entry 2) and 1a. From these results, it seems that the electronic effect induced by the substituent on the aryl group of the ligand does not have a major effect on the stereoselectivity of the hydrogenation. However, the stereoselectivity seems higher with the \([\text{Pd}(\text{Ar-bian})(\eta^2-\text{dmfu})]\) type catalyst (a) compared to the \([\text{Pd}(\text{Ar-bian})(\eta^2-\text{ma})]\) type (b) (entries 4 and 5, and regarding entries 8 and 9). The hydrogenation of these two 1,2-dienoates shows a large substrate dependence concerning the activity. Employing 1a as the catalyst, the hydrogenation of ethyl 2-n-butylbuta-2,3-dienoate 13 is faster than that of the benzyl analogue 11; after 1.75 hours full conversion is obtained for 13, whereas after 5 hours only 34% conversion of 11 (respectively entries 8 and 1, Table 5-2) had been obtained. This substrate dependence does not seem to affect the observed stereoselectivity of the semi-hydrogenation, which is approximately the same, however after 24 hours of reaction in both cases the ratio \(Z/E\) decreased significantly. This tendency is clearly confirmed by using the maleic anhydride derivative (entry 9).

5.2.4 Stereoselectivity and \(Z/E\) isomerization

Most of the studies refer to simple cyclic or acyclic allenes such as propadiene,\(^\text{11}\) 1,2-cyclononadiene\(^\text{6}\) or eventually monofunctionalized as the 1-methoxy-propa-1,2-diene.\(^\text{7}\) The allenes that have been used in this study are slightly different to that, their functionalization with group as phosphonate, ester or sulfone\(^\text{1}\) conjugated to the insaturation, allows delocalisation of the electron density that could be at the origin of the complete positional selectivity. Even if the positional selectivity is the same, the complex constants with palladium from ethyl 2-benzylbuta-2,3-dienoate 11 and of ethyl 2-n-butylbuta-2,3-dienoate 13 are different, this thermodynamic consideration should explain the substrate dependence observed.
The main question was how to explain the low stereoselectivity observed in some cases? Two hypotheses were taken into consideration; (i) a real lack of stereoselectivity of our catalysts and (ii) an isomerization process occurring after the semi-hydrogenation of the allene. Regarding all the results, the steric and electronic effects induced by the catalyst are not deemed to be the origin of the, in some cases, seemingly 'reversed' stereoselectivity. More probably, Z-E isomerization has taken place after initial stereoselective hydrogenation. Indeed, the second hypothesis has been confirmed by a simple experiment: after full conversion of the allene into alkene (and the determination of the stereoselectivity by proton NMR on the crude mixture immediately after reaction), the reaction mixture (including the Pd-complex) was subsequently stirred for another period (4 hours) under nitrogen atmosphere. Monitoring of the Z/E ratio showed that it was changing in favour of the (E)-isomer, even in the absence of hydrogen pressure. Hence, the (Z)-alkene is the primary reaction product, from which the minor product (E)-alkene may be formed by an H2-assisted palladium-catalyzed isomerization reaction13b or, as we observed, without the assistance of H2. Hence, when we employed this and similar palladium catalysts and reaction times of 24 hours, we can assume that the observed stereoselectivity is somewhat smaller than the real stereoselectivity of the catalyst. So, the numbers in Table 5-2 for reactions proceeding during 24 h represent minimum values as far as the amount of the (Z)-alkene is concerned.

The 2,3-dienoates 11 and 13 seem to be more sensitive toward isomerization than the 1,2-dienyl phosphonates 9. Isomerization occurs under mild conditions. The differences in the apparent stereoselectivity may be explained by considering two factors involved: (i) the higher thermodynamic stability of the (E)-alkene relative to the (Z)-isomer and (ii) the higher complex constant between palladium and the alkene 12 and 14 compared to the complex constant of palladium with the alkene 10.

5.2.5 Mechanistic aspects

Since we have not studied the kinetics, nor have any experiments aimed at trapping of intermediates been performed, the mechanism of the selective hydrogenation of allenes using [Pd(Ar-bian)(η2-alkene)] catalysts remains largely unknown. However, we suspect that the mechanism might in part be similar to the mechanism proposed for the semi-hydrogenation of alkynes using this type of
catalysts. On the basis of these and previous results, a mechanism for this reaction is proposed in Scheme 5-5.

Scheme 5-5. Proposed catalytic cycle for the selective hydrogenation of allenes.

The catalytic cycle starts by the activation of the catalyst precursor A by hydrogenation of the coordinated alkene. Next, the more electron rich C=C bond in B coordinates to palladium instead of the alkene ligand to form a [Pd(Ar-bian)(η²-allene)] complex C. In analogy with the mechanism for the alkyne hydrogenation, we propose heterolytic hydrogen cleavage by C to afford the monohydridopalladium complex D. This intermediate D may undergo highly stereoselective hydropalladation to generate the palladium hydride E₁ or E₂ after transfer of the N–H hydrogen atom to Pd. A new [Pd(Ar-bian)(η²-alkene)] complex F is produced by reductive elimination from E₁ or E₂. The final product G is obtained by dissociation of the product alkene from the intermediate F, at the same time regenerating the catalytically active species C through the coordination of the starting allene. The stereoselectivity observed supports the idea that the reaction most likely proceeds via the intermediate E₁, in which the mutual trans orientation of the palladium and phosphonates or ester moieties may determine the stereoselectivity. Substitution of the generated (Z)-alkene
by allene (F → C) is crucial for the chemoselectivity of the reaction. This substitution process is acceptable since a complete chemoselectivity is observed during our experiments, the complex constant is probably higher in the case of the palladium \( \eta^2 \)-allene complex than for the palladium \( \eta^2 \)-alkene complex.

### 5.3 Conclusion

The use of pre-catalyst complexes, consisting of palladium(0), a rigid bidentate nitrogen ligand and an alkene, for the reaction of hydrogenation of different functionalized allenes has been explored. Hydrogenation of 1,2-dienyl phosphonates 9a-9e has been performed successfully with high chemo-, positional and stereoselectivity leading to di- or trisubstituted (Z)-1-alkenyl phosphonates 10-(Z). The same full chemo- and positional selectivities were observed for the hydrogenation of the 2,3-dienoates 11 and 13, but a lower stereoselectivity was obtained in forming the (Z)-1-alkenyl esters (12-(Z) and 14-(Z)). The high chemoselectivity towards the alkene can be explained by the higher preference for coordination of the allene to palladium compared to the resulting alkene. Testing similar [Pd\(^0\)(Ar-bian)] catalysts revealed that the coordination strength of the alkene co-ligands has an influence on the stereoselectivity. An isomerization process of the (Z)-alkene to its (E)-isomer on palladium species resulting from catalyst decomposition is most certainly involved in this decrease of observed stereoselectivity. For all active [Pd(Ar-bian)(\( \eta^2 \)-alkene)] catalysts, over-reduction is absent. This could be interesting for applications regarding oil purification processes or for the synthesis of trisubstituted alkenes that are otherwise difficult to obtain.

### 5.4 Experimental Section

#### 5.4.1 General considerations

All reactions were carried out by using standard Schlenk techniques under an atmosphere of dry nitrogen unless otherwise specified. The solvents were dried according to standard procedures\(^{18}\) and distilled before use. \(^1\)H and \(^{13}\)C NMR spectra were recorded at 298K on a Varian Mercury 300 spectrometer (300.13 and 75.48
MHz respectively). The chemical shift values are referenced to external TMS with high frequency shifts signed positive. Chemical shifts (δ) and coupling constants (J) are expressed in ppm and in Hertz (Hz) respectively and the multiplicity as s = singulet, d = doublet, dd = double doublet, t = triplet, pst = pseudo triplet, m = multiplet, br = broad; data in parenthesis are given in the following order: multiplicity, number of protons, labelling of the proton and coupling constants in Hz.

Dimethylfumarate (Merck), maleic anhydride (Acros), fumaronitrile (EGA), were used as received. Pd(dba)$_2$,\textsuperscript{19} $p$-MeO-C$_6$H$_4$-bian,\textsuperscript{20} $p$-NO$_2$-C$_6$H$_4$-bian,\textsuperscript{20} $p$-Me-C$_6$H$_4$-bian,\textsuperscript{20} $p$-NMe$_2$-C$_6$H$_4$-bian,\textsuperscript{20} o.o'-Me-C$_6$H$_4$-bian,\textsuperscript{20} m,m'-Me-C$_6$H$_4$-bian,\textsuperscript{20} m,m'-CF$_3$-C$_6$H$_4$-bian,\textsuperscript{20} Ph-bian,\textsuperscript{20} palladium(0)-alkene complexes 1-8,\textsuperscript{15} 1,2-dienyl-phosphonates,\textsuperscript{21} 2,3-dienoates,\textsuperscript{22} were prepared according to literature procedures.

5.4.2 Hydrogenation experiments

The hydrogenation reactions were performed by dissolving, in a Schlenk tube, 0.2 mmol of the relevant allene and 0.02 mmol of the appropriate palladium complex in 3 mL of dry THF, under nitrogen atmosphere. Subsequently, the Schlenk tube was connected to a gas inlet and flushed with hydrogen to set a hydrogen atmosphere (1 atm) and the solution was stirred at 20ºC for 24h. The reaction mixture was then filtered over celite and the crude mixture was analysed by $^1$H NMR spectroscopy. The solvent was removed in vacuo and flash chromatography on silica gel with a mixture petroleum ether/diethyl ether (1/2) as the eluent afforded the correspondent product.

5.4.3 Acknowledgement

Many thanks to Prof. Shengming Ma and Hao Guo for the allenes and the discussions on the obtained results.
5.5 References


(16) IUPAC: Ethyl-2-vinylidene-hexanoate


