Palladium and rhodium allyl complexes in catalysis

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Chapter 11
Rhodium-allyl chemistry

Abstract

In the previous chapters we have described the use of palladium catalysts and the mechanisms of the alkylation and carbonylation reaction. In this chapter, we present an exploratory study of the use of rhodium based catalysts in the same reactions.

To this end, we have prepared several novel rhodium complexes and we have studied the structure in detail, using NMR and modeling techniques. We found that three coordination modes are possible: the known $\eta^1$ and $\eta^3$ mode and the newly found $\eta^1\cdot\eta^3$ mode. A crystal structure of the $(\eta^3$-C$_3$H$_5$)Rh(Xantphos)Cl$_2$ complex shows many similarities to the crystal structure of the analogous palladium complex in chapter 7. The reactivity of these complexes was tested in the stoichiometric alkylation and in high pressure NMR experiments. We showed that these novel complexes are active in the allylic alkylation reaction. Under a pressure of CO (10-40 bar), we found that insertion of CO is a facile process and we have obtained the corresponding novel acyl complexes, which are presumably the intermediates in the catalytic carbonylation reaction.
11.1 Introduction

Previous studies in our group concerning the effect of the bite angle of bidentate phosphine ligands in the rhodium catalyzed hydroformylation of styrene, showed an interesting influence on the rate of this reaction.\textsuperscript{[1]} The reaction rate was relatively low when ligands were used that enforce a medium bite angle (95-105°). Other ligands enforcing either a smaller or a larger bite angle resulted in a more active catalyst. For the intermediate rhodium-styrene complex, an equilibrium has been postulated between an η\textsuperscript{1}-styril (A) and an η\textsuperscript{3}-styril complex (B).\textsuperscript{[2]} Hydroformylation of A yields the non-chiral linear aldehyde, whereas after the required η\textsuperscript{1}-η\textsuperscript{3} rearrangement to C, the hydroformylation of C can yield the chiral branched product (figure 1). In view of our previous results with Pd(η\textsuperscript{1}-allyl) complexes, it occurred to us, that a relatively stable η\textsuperscript{3}-styril complex of ligands enforcing a medium bite angle could explain the observed effect of the bite angle on the rate of the reaction.\textsuperscript{[1]}

![Figure 1: Influence of an η\textsuperscript{3}-styril complex (B) on the course of hydroformylation of η\textsuperscript{1}-styril (A and C) complexes.](image)

A reaction that involves a similar Rh-allyl intermediate is the allylic alkylation (figure 2).\textsuperscript{[3, 5]} Although palladium is the metal of choice for many homogeneously catalyzed organic transformations, the interest for the use of catalysts based on other metals, such as rhodium and iridium, is increasing.\textsuperscript{[4, 5]} Recently, rhodium based catalysts showed unusual regioselectivity in the allylic alkylation of monosubstituted allyl moieties.\textsuperscript{[5]} Most palladium catalysts, favor the non-chiral linear product, whereas the rhodium system shows a high preference for the formation of the chiral branched product.
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Figure 2: Regioselectivity in allylic alkylation of cinnamyl chloride.

Although for the palladium catalyst the reaction is known to proceed via an $\eta^3$-allyl complex, for the rhodium system an $\eta^1$-allyl complex was postulated as the catalytically active species. The alkylation on such a species would take place via an $S_N2'$ attack of the nucleophile on the $\gamma$-carbon of the allyl (figure 3). Alkylation of an allyl moiety with a substituent on the $\gamma$-carbon would then yield the branched product.

Figure 3: The postulated $S_N2'$ mechanism for the rhodium catalyzed allylic alkylation via a Rh($\eta^1$-cinnamyl) species (left) and the alternative pathway via a Rh($\eta^3$-cinnamyl) species (right).
The rhodium catalysts in the reported alkylation studies were prepared in situ using an excess of monodentate phosphine ligands. For these systems, \( \eta^1 \)-allyl complexes have indeed been observed,\[^6\] but similar complexes bearing \textit{bidentate} phosphine ligands have not been studied yet. Inspired by the results of the hydroformylation,\[^1\] we reasoned that for bidentate ligands, the \( \eta^1 \)-allyl coordination may not be favored over the \( \eta^3 \)-allyl coordination. Furthermore, Cole-Hamilton has reported the rhodium catalyzed carbonylation of allyl halides using PEt\(_3\) as the ligand.\[^7\] In the late sixties (Vrieze and co-workers) and the early eighties (Fryzuk and co-workers) several studies have been reported concerning the synthesis and structure of allyl-rhodium complexes.\[^8\] Encouraged by these findings we decided to synthesize \textit{(diphosphine)}rhodium-allyl complexes and study their structure and their reactivity in the allylic alkylation and towards CO.

11.2 Results

11.2.1 Choice of ligands and allyl moieties

To study the effect of the bite angle of the ligand on the geometry of \((PP)\text{Rh}^{III}\)(allyl)Cl\(_2\) complex, four ligands were used (figure 4) that mainly differ in their preferred bite angle. Besides alkane bridged dppe (2), which enforces a relatively small bite angle and has a rather flexible backbone, the other three ligands are tri-aryl phosphines: o-dppb (1), which is a rigid ligand enforcing a small bite angle, DPEphos (3), which enforces an intermediate bite angle and has a flexible backbone and Xantphos (4), which enforces a large bite angle and has a more rigid backbone.

To study the effect of the substituent on the allyl moiety, the small unsubstituted \( \text{C}_3\text{H}_5 \) moiety (a) was used and the large phenyl substituted cinnamyl moiety (3-Ph-\( \text{C}_3\text{H}_4 \)) (b). The numbering scheme of the complexes used in this study is presented in figure 4.

![Figure 4: Numbering scheme of the complexes used in this study.](image)
11.2.2 Synthesis

Starting from a Rh\(^+\) precursor, several routes were explored to synthesize \((PP)\text{Rh}^{11}(\text{allyl})\text{Cl}\)_2 complexes. The most convenient and versatile route proceeds via oxidative addition of the appropriate allyl chloride to \((PP)\text{Rh}^{11}(\text{COD})\text{Cl}\).\(^{[8]}\)

The oxidative addition proceeded smoothly for each complex. For the DPEphos complex a small amount (< 5 \%) of an unidentified side product was formed that could not be removed.

11.2.3 Characterization, general remarks

In the previous chapters, the characterization of Pd(allyl) complexes has been discussed in detail. The NMR spectra of the rhodium-allyl complexes show similarities, but also differences compared to those of the palladium complexes. Some rhodium complexes clearly showed an \(\eta^3\)-coordination mode, whereas other complexes seemed to be \(\eta^1\)-complexes. To facilitate the characterization of the \((PP)\text{Rh}^{11}(\text{allyl})\text{Cl}\)_2 complexes described in this chapter, some general remarks concerning the \(^1\text{H}-\text{NMR}\) spectra of palladium allyl complexes may prove useful for the unambiguous assignment of the observed signals. The two coordination modes of the allyl moiety (\(\eta^1\)- or \(\eta^3\)-fashion (figure 5)) can be distinguished by several differences in the \(^1\text{H}\)-NMR spectra.

![Figure 5: Bonding modes of the allyl moiety and numbering scheme of the hydrogens (left \(\eta^3\) and right \(\eta^1\)).](image)

11.2.4 \(\eta^3\)-allyl-palladium (see also chapter 4-8)

The results in the previous chapters and the work of others show, that the five hydrogens on the allyl moiety are inequivalent in non-symmetrical complexes, whereas in symmetrical complexes \((\text{H_{anti}}\) and \(\text{H_{anti'}}\) and \((\text{H_{syn}}\) and \(\text{H_{syn'}}\) are equivalent. The anti hydrogens are closer to palladium and show a signal at lower ppm-value than the syn-hydrogens. In general, the signal for \(\text{H_{anti}}\) is typically found between 2 and 3.5 ppm, whereas the signal for \(\text{H_{syn}}\) is mostly observed between 2.5 and 3.9 ppm. The signal of \(\text{H_{meso}}\) almost always appears above 5 ppm, but below 6.5 ppm. In some cases, the \(\eta^3\)-allyl moiety shows fluxional behavior and via a \(\eta^3\cdot\eta^1\)-\(\eta^1\) rearrangement, \(\text{H_{anti}}\) and \(\text{H_{syn}}\) become equivalent, which results in only one signal for the anti- and syn-hydrogens appearing at the averaged frequency.
The presence of a phenyl substituent at the allyl moiety (cinnamyl) disrupts the symmetry of allyl and all four protons show different signals. The phenyl can be oriented anti or syn with respect to H_{meso}, but in the complexes described in this thesis, only the syn-orientation has been observed. The signals of H_{anti} and H_{syn}, as compared to the C_{2}H_{5} moiety, are in general slightly shifted to a higher ppm value. The shift of the signal of the anti hydrogen next to the phenyl is much larger, because of the partial double bond character of the C2-C3 bond (figure 4). The doublet may be observed even at higher chemical shift (between 5.9 and 6.8 ppm) than the signal of H_{meso}, which is found between 5.8 and 6.6 ppm.

11.2.5 \( \eta^1 \)-allyl-palladium

So far, only a few (\( \eta^1 \)-C_{5}H_{5})Pd complexes have been reported. The \(^1\)H-NMR spectrum resembles that of organic allyl compounds e.g. allyl chloride. The aliphatic CH_{2}-unit appears as one signal; the olefinic signals are magnetically inequivalent. The fine structure on and the chemical shift of the signal of H_{meso} resembles that found for H_{meso} in \( \eta^1 \)-allyl complexes. The main difference, therefore, between an \( \eta^1 \)- and an \( \eta^1 \)-allyl will be found in the fine structure on the signal of the olefinic CH_{2}-unit. The signal consists of two double doublets around 5 ppm, whereas this is not observed for the \( \eta^1 \)-allyl complex.

The situation is slightly more complicated for cinnamyl complexes. In (triphos)Pd(\( \eta^1 \)-cinnamyl)Cl, the cinnamyl is bonded to the metal via the CH_{2} unit, with a trans configuration of the allylic C=C bond. The \(^1\)H-NMR spectrum of these complexes shows one signal for the CH_{2}-unit, a multiplet for H_{meso} and a doublet for H_{olefinic} (H_{olefinic} is bonded to the terminal carbon atom). In other words: it yields a spectrum potentially similar to that of an \( \eta^1 \)-cinnamyl group in which H_{anti} and H_{syn} are equivalent or rapidly exchanging. Contrary to the \( \eta^3 \)-cinnamyl group, the \( \eta^1 \)-cinnamyl moiety does not show a phosphorus coupling on the olefinic hydrogen next to the phenyl group. Another tool to distinguish between the two coordination modes is the relative chemical shift of H_{meso} and H_{olefinic}. In the \( \eta^1 \)-allyl complex, the chemical shift of H_{olefinic} is higher than that of H_{meso}, whereas in the \( \eta^1 \)-allyl complex, it is the other way round.

11.2.6 Characterization of the rhodium complexes

Using the guidelines of the previous paragraph, we have assigned the structure of the rhodium complexes (tables 1 and 2). The interpretation of the \(^1\)H-NMR spectrum of the o-dpb cinnamyl complex 1b, is hampered by the overlap of H_{olefinic} and the aromatic hydrogens. Because of the similarities between the NMR spectra of 1b, 1a and 2b, the signals have been assigned to an \( \eta^1 \)-cinnamyl moiety. Also the Xantphos bearing complex, 4b, binds the cinnamyl in an \( \eta^1 \)-fashion. Both DPEphos modified complexes, 3a and 3b, have been identified as \( \eta^1 \)-allylic complexes.
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Table 1: Assignment of (C₃H₅)Rh(PP)Cl₂ complexes (room temperature).

<table>
<thead>
<tr>
<th>number</th>
<th>PP ligand</th>
<th>hapticity</th>
<th>P's equivalent?</th>
<th>remarks</th>
</tr>
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<tbody>
<tr>
<td>1a</td>
<td>o-dppb</td>
<td>η¹</td>
<td>yes</td>
<td></td>
</tr>
<tr>
<td>2a</td>
<td>dppe</td>
<td>η¹</td>
<td>yes</td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>DPEphos</td>
<td>η³</td>
<td>no</td>
<td>all hydrogens inequivalent</td>
</tr>
<tr>
<td>4a</td>
<td>Xantphos</td>
<td>η³</td>
<td>yes</td>
<td>broad ³¹P-NMR signal</td>
</tr>
</tbody>
</table>

Table 2: Assignment of (3-Ph-C₃H₄)Rh(PP)Cl₂ complexes (room temperature).

<table>
<thead>
<tr>
<th>number</th>
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<th>hapticity</th>
<th>P's equivalent?</th>
<th>remarks</th>
</tr>
</thead>
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<tr>
<td>1b</td>
<td>o-dppb</td>
<td>probably η¹</td>
<td>yes</td>
<td>H₃oefine under aromatic signals</td>
</tr>
<tr>
<td>2b</td>
<td>dppe</td>
<td>η¹</td>
<td>yes</td>
<td></td>
</tr>
<tr>
<td>3b</td>
<td>DPEphos</td>
<td>η¹</td>
<td>no</td>
<td>broad signals in ¹H-NMR</td>
</tr>
<tr>
<td>4b</td>
<td>Xantphos</td>
<td>η¹</td>
<td>yes</td>
<td></td>
</tr>
</tbody>
</table>

In most complexes the two phosphorus atoms show only one signal in the ³¹P-NMR spectra, which is indicative of a symmetric complex geometry. Rhodium(III) can adopt several geometries: octahedral, square pyramidal and trigonal bipyramidal. Although the coordination mode of the allyl is clearly identified by ¹H-NMR, the geometry around the rhodium is not resolved. Because the chemical shift of ¹⁷⁷Rh is known to be dependent on the geometry around the metal center, attempts were made to measure the ¹⁷⁷Rh-NMR signal. Due to broad signals, even at low temperature, the measurements were not conclusive.

11.2.7 Variable temperature NMR

Several complexes show broad signals in the ¹H-NMR, which is indicative of fluxional behavior of the allyl moiety. Because more insight in the coordination of the allyl ligand at low temperature may provide information about the geometry around rhodium, variable temperature NMR experiments were carried out using complexes 1-4a (figures 6-9, following pages).
Figure 6: VT-NMR of $1\text{a} ((\text{o-dppb})(\text{C}_3\text{H}_5)\text{RhCl}_2)$, left $^1\text{H}$-NMR, right $^{31}\text{P}$-NMR.

Figure 7: VT-NMR of $2\text{a} ((\text{dppe})(\text{C}_3\text{H}_5)\text{RhCl}_2)$, left $^1\text{H}$-NMR, right $^{31}\text{P}$-NMR.
Figure 8: VT-NMR of 3a ((DPEphos)(C₃H₅)RhCl₂), left ¹H-NMR, right ³¹P-NMR.
Both 1a (o-dppb) and 2a (dppe) are η1-allyl complexes at room temperature and show similar 1H-NMR spectra at lower temperatures. Cooling the o-dppb-complex 1a to 218 K (figure 6), the signals in the olefinic region do not shift and are slightly broadened, but the signal of the CH₂ unit is split into two separate multiplets, each representing one hydrogen. In contrast, the signals in the olefinic region of the dppe-complex 2a do shift (figure 7). At room temperature three overlapping multiplets are observed, whereas at 218 K the signals are split in one multiplet at 5.0 ppm (presumably H_meso) and a double doublet and a triplet at 4.6 and 4.4 ppm respectively. In addition, the 31P-NMR spectra of 1a and 2a showed a single doublet at high temperature, but at low temperature two doublets were observed. It is clear that the species at low temperature is neither the η1-allyl species observed at room temperature nor an η2-allyl species. We propose an η1-η2-type coordination for the observed complex (figure 10). At low temperature, the signals of the η1-part (2.8 ppm) are split into two signals, one for each hydrogen. Thus, if the structure would be that of an η1-η2-allyl, the rotation about the Rh-C and the C1-C2 bond is restricted. The possible occurrence of this coordination mode is supported by the crystal structure of 4a (Xantphos, see below) and modeling studies.
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Complex 3a (DPEphos, figure 8) showed five separate signals for all hydrogens of the C₃H₅ moiety at room temperature. Lowering the temperature did not affect the \(^1\)H and \(^31\)P NMR-spectra of 3a, but the signals of the minor side product (< 5 %) sharpened and appeared to be very similar to the spectrum of 3a.

At room temperature, the \(^1\)H-NMR spectrum of complex 4a (figure 9) shows one coalesced signal for all hydrogens except H\(_{\text{meso}}\). At low temperature, this coalesced signal splits in three broad multiplets in a 2 : 1 : 1 ratio, of which the multiplet with relative intensity 2 overlaps with one other multiplet. At low temperature, the CH₃ groups on the backbone of the ligand appear as two multiplet patterns, one at 1.2 ppm and one at 1.8 ppm. The inequivalence of the methyl groups of the backbone has been observed before in similar palladium complexes (chapter 7) and can be attributed to endo and an exo methyl groups of the bent xanthene moiety. The assignment of the multiplet signals to the CH₃ groups is discussed in section 11.2.8.

At first glance, the allyl region of the \(^1\)H-NMR spectrum is rather complicated. In contrast to the spectra of 1a and 2a, there are no signals in the olefinic region (except H\(_{\text{meso}}\)), indicating that the structure is still very similar to the \(\eta^1\)-allyl observed at room temperature. At room temperature, the \(^1\)H-NMR spectrum is similar to that of an \(\eta^2\)-C₃H₅ moiety with fast exchange of all 4 terminal hydrogen atoms. At low temperature, the signal at 5.5 ppm reveals two signals for H\(_{\text{meso}}\), indicating the existence of two isomeric complexes. One of the isomers shows a spectrum similar to that observed at room temperature and can be assigned to a symmetrically bonded \(\eta^2\)-C₃H₅ moiety, in which one average signal is observed for all four terminal hydrogens due to a fast dynamic exchange. The other isomer, however, shows two different multiplet signals for the terminal hydrogen atoms. One possible explanation would be that one of the two multiplets can be assigned to the syn-protons, and the other multiplet to the anti-protons. This explanation would imply for this isomer a slow \(\eta^2\)-\(\eta^1\)-\(\eta^3\) rearrangement relative to the apparent allyl rotation rearrangement, which is not observed often.
A second, more plausible explanation involves a dissymetrically $\eta^3$-bonded allyl moiety (towards $\eta^1$-$\eta^3$) as found in the crystal structure of 4a (see below). In this complex, two phenyl rings of the Xantphos ligand are stacked in a perpendicular fashion, unlike the parallel orientation which was found in the crystal structure of the analogous palladium complex (chapter 7). A non-selective $\eta^3$-$\eta^1$-$\eta^3$ rearrangement involving both Cl and C3 of the allyl moiety accounts for the two broad multiplets; one multiplet for each CH$_2$-unit. This explanation would imply a slow allyl-rotation rearrangement for this isomer, which may seem unlikely, but has been observed before in analogous palladium complexes (chapters 4-8).

In the $^{31}$P-NMR spectrum recorded at low temperature, two doublets are observed in a 1:1 ratio. Apparently, the slight distortion of the $\eta^1$-character of the Pd-ally bond is not reflected in the $^{31}$P-NMR spectrum at the lowest temperature used (218 K).

A summary of the assignments at low temperature is presented in table 3.

![Figure 11: Selective $\eta^3$-$\eta^1$-$\eta^3$ rotation about the Rh-C$_a$ bond in 4b.](image)

<table>
<thead>
<tr>
<th>number</th>
<th>PP ligand</th>
<th>hapticity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>o-dppb</td>
<td>$\eta^1$-$\eta^2$</td>
</tr>
<tr>
<td>2a</td>
<td>dppe</td>
<td>$\eta^1$-$\eta^2$</td>
</tr>
<tr>
<td>3a</td>
<td>DPEphos</td>
<td>$\eta^3$</td>
</tr>
<tr>
<td>4a</td>
<td>Xantphos</td>
<td>$\eta^1$-$\eta^2$ and $\eta^3$</td>
</tr>
</tbody>
</table>
11.2.8 Crystal structure of 4a

After recrystallization of (Xantphos)Rh(Cl$_2$)(η$^3$-C$_3$H$_5$) 4a from CH$_2$Cl$_2$ / hexane, crystals were obtained that were suitable for X-ray crystallography (figure 12). The structure of 4a is rather similar to the crystal structure of the analogous cationic (Xantphos)Pd(η$^3$-C$_3$H$_5$)OTf complex described in chapter 7 (figure 13).

Geometrical data of both complexes are presented in table 4.

Figure 12: Crystal structure of 4a (three points of view)
Figure 13: Crystal structure of the palladium analogue of $4a$ (Xantphos)Pd($C_3H_5$) $^+\text{OTf}^-$ (three points of view).

Figure 14: Numbering scheme in crystal structures, $M = \text{Rh or Pd}$. 

P1 $\vdots$ M $\vdots$ P2

1 2 3
Table 4: Selected geometrical data of the crystal structures of 4a (figure 12) and (Xantphos)Pd(C₃H₅)⁺ OTf⁻ (figure 13). The numbering scheme is presented in figure 14. Distances in Å, angles in °.

<table>
<thead>
<tr>
<th></th>
<th>rhodium</th>
<th>palladium</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(M-C1)</td>
<td>2.232(11)</td>
<td>2.17(1)</td>
</tr>
<tr>
<td>d(M-C2)</td>
<td>2.186(14)</td>
<td>2.16(1)</td>
</tr>
<tr>
<td>d(M-C3)</td>
<td>2.241(11)</td>
<td>2.17(1)</td>
</tr>
<tr>
<td>d(C1-C2)</td>
<td>1.414(18)</td>
<td>1.34(2)</td>
</tr>
<tr>
<td>d(C2-C3)</td>
<td>1.442(18)</td>
<td>1.34(2)</td>
</tr>
<tr>
<td>∠(C1-C2-C3)</td>
<td>124.9(14)</td>
<td>120.4(15)</td>
</tr>
<tr>
<td>d(M-P1)</td>
<td>2.394(2)</td>
<td>2.372(2)</td>
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<tr>
<td>d(M-P2)</td>
<td>2.437(2)</td>
<td>2.372(2)</td>
</tr>
<tr>
<td>d(Rh-Cl) (above in figure)</td>
<td>2.351(3)</td>
<td>2.372(2)</td>
</tr>
<tr>
<td>d(Rh-Cl) (below in figure)</td>
<td>2.363(2)</td>
<td>2.372(2)</td>
</tr>
<tr>
<td>∠(P-M-P)</td>
<td>106.89(7)</td>
<td>108.11(7)</td>
</tr>
<tr>
<td>∠(Cl-Rh-Cl)</td>
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<tr>
<td>angle between xanthene planes</td>
<td>16.6571</td>
<td>27.352</td>
</tr>
<tr>
<td>d(M-O)</td>
<td>3.320(6)</td>
<td>3.445(7)</td>
</tr>
<tr>
<td>∠((P-M-P)- (C1-C2-C3))</td>
<td>58.9154</td>
<td>99.368</td>
</tr>
<tr>
<td>d(C1-(P-M-P))</td>
<td>-0.2723 (below)</td>
<td>+0.349</td>
</tr>
<tr>
<td>d(C2-(P-M-P))</td>
<td>+0.3136</td>
<td>+1.008</td>
</tr>
<tr>
<td>d(C3-(P-M-P))</td>
<td>-0.2195</td>
<td>+0.349</td>
</tr>
</tbody>
</table>

*: M=Rh for 4a and M=Pd for (Xantphos)Pd(C₃H₅)⁺ OTf⁻.

The rhodium complex has a trigonal bipyramidal structure, with the two chloride ligands in the axial positions, the two phosphine atoms cis to one another and the allyl in the equatorial plane bonded in an η³-fashion. In contrast to the palladium complex, the rhodium complex has no C₅ symmetry, probably because of the non-symmetric π-π interactions between the phenyl rings of the ligand. Compared to the palladium complex, the metal to allyl distance is larger and the C-C bonds in the allyl moiety are longer. Although the longer C-C bonds may suggest a less olefinic character of the allyl moiety, the C-C-C angle of the allyl is larger. In addition, the angle between the P-M-P plane and the allyl C-C-C plane is much smaller. The coordination mode of the allyl group may thus indicate a decreased bonding and an increased backbonding interaction compared to the palladium complex. The P-Rh-P bite angle is similar to the calculated natural bite angle and to the bite angle found in other rhodium complexes of Xantphos derivatives.[1]
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The dynamic behavior observed in $^1$H-NMR can be explained in terms of $\pi-\pi$ interactions of the cinnamyl with the phenyl rings of the ligand (see above). The dissymmetric stacking observed in the crystal structure of 4a causes an $\eta^1$-$\eta^1$-coordination of the allyl moiety at low temperature.

The perpendicular stacking (lines represent phenyl rings) of the phenyl rings may explain the low chemical shift in the $^1$H-NMR spectrum (1.2 ppm) of one of the multiplet signals of the CH$_3$ groups of the ligand. A different orientation of the phenyl rings causes a different folding of the Xanthene backbone and also a different ring current experienced by the methyl groups. In figure 12 and 13 it is shown that because of the large folding of the Xanthene backbone in the rhodium complex 4a, the difference between the endo and exo methyl group is smaller than in the analogous palladium complex. Therefore, we assign each of the two multiplet NMR-signals of the CH$_3$ groups to an endo-exo combination of the same isomer. In the analogous palladium complex, the signals of the CH$_3$ groups was found between 1.4-1.9 ppm. Because of the different orientation of the phenyl rings and the resulting different effect of ring current, we propose that the multiplet signal of 1.2 ppm should be assigned to the $-\parallel$ stacked isomer.

11.2.9 DFT studies

To study the effect of the bite angle on the geometry in more detail, DFT calculations on model complexes were performed on the B3LYP/LANL2DZ level of theory, which is a commonly accepted level of theory for DFT calculations of organometallic compounds.$^{10}$

The bonding of the allyl to the [Rh(PH$_3$)$_2$Cl$_2$] fragment was studied for both the complex bearing the non substituted [C$_3$H$_5$] 5 and the substituted [3,3-(CH$_3$)$_2$-C$_3$H$_3$] moiety 6. The latter was used as a model for the cinnamyl complexes. The influence of the bite angle of the ligand was investigated by changing the P-Rh-P angle incrementally from 90-180°.

For both allyl moieties, two minima were found in the energy curve (figure 15, table 5). The global minimum for 5 (figure 16) and a local minimum for 6 (figure 18) correspond to the $\eta^3$-complex (bite angle $\sim$ 100°, trigonal bipyramid, figure 16). The local minimum of 5 (figure 17) and the global minimum of 6 (figure 19) correspond to an $\eta^1$-geometry (bite angle $\sim$ 170°, square pyramidal). The relative stability of the $\eta^1$-structure for 6 compared to 5, is most likely caused by the more stable C=C double bond.

Table 5: Heat of formation (in kJ/mole) of the minimized structures of the $\eta^3$ and the $\eta^1$ isomers of 5 and 6.

<table>
<thead>
<tr>
<th>Complex (bite angle)</th>
<th>5 (C$_3$H$_5$)</th>
<th>6 (3,3-(CH$_3$)$_2$-C$_3$H$_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E \eta^3$ ($\sim$100°)</td>
<td>-717048</td>
<td>-923257</td>
</tr>
<tr>
<td>$\Delta E \eta^1$ ($\sim$170°)</td>
<td>-717022</td>
<td>-923258</td>
</tr>
<tr>
<td>$\Delta E (\eta^3-\eta^1)$</td>
<td>-26</td>
<td>+1</td>
</tr>
</tbody>
</table>

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Figure 15: Plot of the heat of formation of $(\text{C}_3\text{H}_5)\text{Rh}(\text{PH}_3)_2\text{Cl}_2$ (5) at different values of the P-Rh-P angle. For complex 6, the global minimum is found at a bite angle of $\sim 170^\circ$.

Figure 16: The $\eta^3$-geometry of $(\text{C}_3\text{H}_5)\text{Rh}(\text{PH}_3)_2\text{Cl}_2$ (5) corresponding to the global minimum (two views).

Figure 17: The $\eta^1$-geometry of $(\text{C}_3\text{H}_5)\text{Rh}(\text{PH}_3)_2\text{Cl}_2$ (5) corresponding to the local minimum.
Although complex \((\text{C}_5\text{H}_9)\text{Rh}(\text{PH}_3)_2\text{Cl}_2\) (5) has a symmetric \(\eta^3\)-structure in the global minimum, the symmetry is slightly distorted for larger values of the bite angle. Going from 100\(^\circ\) to 140\(^\circ\) the geometry of the complex slowly changes from trigonal bipyramidal to square pyramidal and the coordination of the allyl slowly changes from the \(\eta^3\)-mode to the \(\eta^1\)-mode. This distortion is more pronounced for the substituted \([3,3-(\text{CH}_3)_2\text{C}_3\text{H}_3]\) moiety (figure 18) and increases further for a larger bite angle. The deviation from \(\eta^3\) to \(\eta^1\)-\(\eta^7\) of the Rh-allyl bond is stronger than found for the analogous Pd-allyl bond (chapter 7) (figure 20). For the \(\eta^3\)-geometry, the bond distances in the Rh-(\(\eta^3\)-\text{C}_3\text{H}_5) bond are similar to those of the corresponding palladium complex (table 6). However, for the palladium complex, d(Pd-C1) is shorter than d(Pd-C2).
whereas for the rhodium complex, \( d(\text{Rh-C2}) < d(\text{Rh-C1}) \). This indicates that for the Rh-allyl bond, the contribution of the allyl-to-rhodium electron donation is relatively more pronounced than the rhodium-to-allyl back donation.

Increasing the bite angle leads to a strong increase of the Rh-allyl distance. The C-C distances in the allyl moiety are smaller, indicating a decrease of the allyl-to-rhodium electron donation. The Mulliken charge of the allylic carbon atoms resembles that of the analogous palladium complex, although for the rhodium complex the electron density on C1 / C3 is slightly higher and that on C2 is slightly lower (table 7). An increase of the bite angle does not result in a significant change of the charge on the allylic carbon atoms.

![Figure 20: Comparison of distortion of \( \eta^3 \)-bonding fashion in 6 (120°) viewed along the Cl-Rh-Cl axis (left) and its palladium analogue Pd(C\text{5}H\text{9})(PH\text{3})\text{2} (120°) (right).](image)

<table>
<thead>
<tr>
<th>bond \ bite angle</th>
<th>80°</th>
<th>100°</th>
<th>120°</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d(\text{Rh-C1}) )</td>
<td>2,198</td>
<td>2,217</td>
<td>2,163</td>
</tr>
<tr>
<td>( d(\text{Rh-C3}) )</td>
<td>2,383</td>
<td>2,421</td>
<td>2,752</td>
</tr>
<tr>
<td>( d(\text{Pd-C1}) )</td>
<td>2,187</td>
<td>2,195</td>
<td>2,191</td>
</tr>
<tr>
<td>( d(\text{Pd-C3}) )</td>
<td>2,374</td>
<td>2,425</td>
<td>2,527</td>
</tr>
</tbody>
</table>
Table 7: Mulliken charge of allylic carbon atoms in 5 Rh(C3H5), 6 Rh(3,3-(CH3)2-C3H3) and the analogous cationic palladium complexes resp. 5Pd and 6Pd.

<table>
<thead>
<tr>
<th>atom</th>
<th>bite angle</th>
<th>5</th>
<th>6</th>
<th>5Pd</th>
<th>6Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>100 (η1)</td>
<td>-0.5027</td>
<td>-0.5286</td>
<td>-0.4915</td>
<td>-0.5252</td>
</tr>
<tr>
<td>C2</td>
<td>100 (η1)</td>
<td>-0.0379</td>
<td>-0.1769</td>
<td>0.0154</td>
<td>-0.1678</td>
</tr>
<tr>
<td>C3</td>
<td>100 (η1)</td>
<td>-0.5027</td>
<td>0.3119</td>
<td>-0.4915</td>
<td>-0.3240</td>
</tr>
<tr>
<td>C1</td>
<td>170 (η1)</td>
<td>-0.4361*</td>
<td>-0.4297**</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td>170 (η1)</td>
<td>-0.0179*</td>
<td>-0.2961**</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C3</td>
<td>170 (η1)</td>
<td>-0.5606*</td>
<td>0.3842**</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*: taken from the structure at the local minimum (bite angle = 172.01°).

**: taken from the structure at the local minimum (bite angle = 171.44°).

Comparing the Mulliken charges of the allylic carbon atoms (table 7), shows that the η1-C3H5 complex 5 resembles the palladium analogue 5Pd (C3H5)Pd(PH3)2+. The charge distribution in the substituted analogue 6, however, is much more shifted to the η1-like distribution than in the palladium analogue 6Pd (3,3-(CH3)2-C3H5)Pd(PH3)2+. As a result of the relatively large geometrical distorion, the relative electrophilicity of the substituted carbon atom C3 in 6 is larger than in 6Pd.

For the η1-structure of 5 the Mulliken charge of the C1 atom is more positive than for the η1-structure, whereas the charge on C3 is more negative than in the η1-structure. For the substituted complex 6, both C1 and C3 become more positively charged.

Based on the modeling studies, it is expected that alkylation of the η1-structure of a substituted allyl moiety of rhodium complexes results in a higher regioselectivity for the branched product than its palladium analogue. For the η1-C3H5 complex 5, the distribution of the Mulliken charge is not in favor of an S_N2' attack on C3. For the substituted complex η1'-6, however, nucleophilic attack via the S_N2' mechanism is plausible.

11.2.10 Reactions: Allylic alkylation

For palladium(allyl) complexes, it has been shown that nucleophilic attack takes place exclusively on an η1-coordinated allyl moiety[131] and that for substrates such as cinnamyl, in most cases the linear product is obtained (chapters 3-9 and references therein). In contrast, studies of the allylic alkylation using rhodium phosphine complexes as the catalyst yield a very high portion (99%) of the chiral branched product.[15] It has been suggested that the reaction does not proceed via an attack on a η1'-coordinated allyl, but via an S_N2' attack on a η1-allyl (figure 2 and 3). To investigate these postulations, we used complexes 1b, 4a, 4b and the
palladium analogue of 4b in the stoichiometric alkylation with sodium diethyl 2-methylmalonate, which is the nucleophile we also used for the studies with palladium (table 8).

Furthermore, complexes 4a and 4b were used in the catalytic alkylation of respectively allyl chloride and cinnamyl chloride (table 9). Because the rhodium catalyzed reactions proceed relatively slower, a slightly more concentrated reaction mixture was used.

Table 8: Stoichiometric alkylation of rhodium complexes using sodium diethyl 2-methylmalonate as the nucleophile (for reaction conditions: see experimental section).

<table>
<thead>
<tr>
<th>complex</th>
<th>branched (%)</th>
<th>linear (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1b (o-dppb) (cinnamyl)</td>
<td>88</td>
<td>12</td>
</tr>
<tr>
<td>4b (Xantphos) (cinnamyl)</td>
<td>23</td>
<td>77</td>
</tr>
<tr>
<td>4a (Xantphos) (allyl)</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Pd(Xantphos)(cinnamyl)OTf</td>
<td>8</td>
<td>92</td>
</tr>
</tbody>
</table>

Table 9: Catalytic allylic alkylation using sodium diethyl 2-methylmalonate as the nucleophile (for reaction conditions: see experimental section).

<table>
<thead>
<tr>
<th>complex</th>
<th>TOF&lt;sub&gt;in&lt;/sub&gt;*</th>
<th>% product**</th>
<th>branched (%)**</th>
<th>linear (%)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a (allyl)</td>
<td>107</td>
<td>44</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>4b (cinnamyl)</td>
<td>15</td>
<td>13</td>
<td>21</td>
<td>79</td>
</tr>
</tbody>
</table>

*: determined after 45 minutes

**: determined after 4 hours.

The stoichiometric and the catalytic reactions show that both η<sup>3</sup>- and η<sup>1</sup>-allyl complexes are alkylated. In the stoichiometric alkylation, the regioselectivity for the formation of the branched product is high for the o-dppb complex 1b (88 %), whereas the Xantphos complex 4b shows the reverse regioselectivity (23%). Nevertheless, the selectivity to the branched product found using 4b is significantly higher than that found using its palladium analogue (Xantphos)(cinnamyl)OTf (only 8% branched product). In the catalytic reaction of complex 4b, the same regioselectivity is found as in the stoichiometric reaction, suggesting that the reaction proceeds via the same intermediate. Using Xantphos, the reaction proceeds faster for allyl chloride than for cinnamyl chloride and at a rate similar to that of the palladium complex.

11.2.11 Reaction with CO: High pressure-NMR

To study the influence of an η<sup>3</sup>- or η<sup>1</sup>-coordination of the allyl on the interaction of the complexes with CO, the complexes 1-4a were treated with elevated pressures of ¹³C enriched CO.

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For complexes 1a, 2a and 4a, at room temperature, the NMR spectra showed the slow formation of a new complex (figures 21, 22 and 24 respectively). Upon heating to 313 K, the reaction proceeded faster and conversion was complete within 3 hours. During the reaction the $^{31}$P-NMR spectrum showed the formation of several transient complexes. The signals in the $^1$H-NMR spectrum are too broad to be conclusive; we postulate a Rh-CO complex, in which the allyl is bonded in an $\eta^1$-fashion. Several isomeric structures may exist for such complexes, which may account for different signals in the $^{31}$P-NMR spectra.

Figure 21: NMR spectra of the formation of an acyl complex of 1a (o-dppb).

Figure 22: NMR spectra of the formation of an acyl complex of 2a (dppe).
Rhodium-allyl Rhodium-allyl chemistry.

Figure 23: HP-NMR spectra of the reaction of complex 3a (DPEphos) with CO.

Figure 24: NMR spectra of the formation of an acyl complex of 4a (Xantphos).
The $^{13}$C-NMR spectra of the final product showed a doublet at 212 ppm ($J_{\text{Rh-C}} = 29$ Hz) (1a and 2a) or 217 ppm ($J_{\text{Rh-C}} = 27$ Hz, 4a). These values are similar to those of a reported acyl species (Rh(PPh$_3$)$_2$(C(O)(C$_2$H$_5$))Cl)$_2$.[7b, 11] In all cases the $^1$H-NMR showed a characteristic \(-\text{CH}_2-\text{CH}=\text{CH}_2\) pattern, with the signals of the CH$_2$-unit at a higher ppm value than those in the starting complexes. The $^{31}$P-NMR showed that the two phosphorus atoms in the new complex are equivalent, indicating either an equatorial-equatorial coordination of the ligand in a trigonal bipyramidal or a square pyramidal structure. From this we concluded that the acyl species were formed.

After release of the CO pressure, the novel acyl complexes remained stable for a short time. The acyl product resulting from complex 4a, showed in the infrared spectrum a signal at 1676 cm$^{-1}$, which is in the range of metal-acyl complexes.

The $^1\eta$-allyl complex 3a, showed a different interaction with CO (figure 23). Several new complexes were formed, but the reaction did not proceed to form a single product.

### 11.3 Discussion

#### 11.3.1 Structure

The modeling studies show that both an $\eta^3$ and an $\eta^1$ coordination of allyl to rhodium are possible and they support the feasibility of a significant distortion of the $\eta^3$ coordination to $\eta^1$-$\eta^1$. For the non substituted C$_3$H$_5$ allyl moiety, the global minimum is found for the $\eta^1$-complex, whereas the $\eta^1$-structure is more favored for the substituted allyl moiety. For both allyl groups, the $\eta^1$ structure is favored for a bite angle smaller than 130-140° and the $\eta^1$ structure for larger values.

#### 11.3.2 dppe and o-dppb

Although the calculations predict an $\eta^1$-allyl for the used ligands, the experiments show a different result. The calculated $\eta^1$-coordination is found for DPEphos and Xantphos, but an $\eta^1$-coordinated allyl is found for dppe and o-dppb. Obviously, the Rh(PH$_3$)$_2$(C$_3$H$_5$)Cl$_2$ complex is not a good model for our system or the B3LYP/LANL2DZ level of theory is not a good method to study the geometry for small values of the bite angle (< 100°). Although the calculations show that a trigonal bipyramidal structure is favored for small bite angles, in experimental systems, such a coordination may put too much strain on the backbone of the ligand and / or may cause too much steric hindrance for the substituents on the phosphorus atom. The geometry around the rhodium for o-dppb and dppe may therefore differ from trigonal bipyramidal and be more towards a square pyramidal geometry with the phosphorus functionalities cis to one another. The latter coordination would indeed explain the formation of $\eta^1$-complexes for these ligands.
11.3.3 DPEphos

NMR spectroscopy shows that for DPEphos, both complex 3a and 3b are \( \eta^3 \)-structures and that a trigonal bipyramidal geometry is most likely. The NMR studies show, that in contrast to the other ligands, the two phosphorus atoms in the C\(_3\)H\(_5\) complex 3a are not equivalent, which indicates that the Rh-allyl bond is not symmetric. This has been observed before in crystal structures of cationic (DPEphos)Pd(allyl) complexes (chapter 7). It appeared that the backbone of the DPEphos ligand is folded, such that one of the aromatic rings of the backbone has a \( \pi-\pi \) interaction with one of the phenyl rings of the phosphorus atom that is bonded to the other backbone ring.

11.3.4 Xantphos

According to NMR spectroscopy, the Xantphos complexes 4a and 4b differ in structure and presumably also in the geometry around the rhodium. The crystal structure clearly shows a trigonal bipyramidal geometry for 4a, but for the \( \eta^1 \)-complex 4b the calculations predict a square pyramidal complex. It remains unclear whether the two phosphorus atoms are cis or trans to one another. A trans coordination of Xantphos, with a coordinated oxygen, has been observed in cationic palladium complexes\(^{[12]}\), but seems less likely in a neutral rhodium complex. We therefore propose a cis coordination of the Xantphos ligand in complex 4b. The different coordination of C\(_3\)H\(_5\) and cinnamyl to the rhodium is presumably caused by steric hindrance. In chapter 7, it was described that a large cone angle of the ligand influences the coordination of the allyl group. A strong steric interaction between Xantphos and the cinnamyl may therefore explain the difference in structure of 4a and 4b.

11.3.5 Allylic alkylation reaction

It has been suggested that, in contrast to palladium, rhodium allyl complexes react via an \( S_N2' \) attack on the \( \gamma \) carbon of the \( \eta^1 \)-allyl moiety. We found that both \( \eta^1 \)- and \( \eta^3 \)-complexes react with sodium diethyl 2-methylmalonate to form the corresponding alkylated products. Attack on the substituted \( \gamma \)-carbon of the \( \eta^1 \)-cinnamyl of o-dppb complex 1b results in a high regioselectivity for the branched product (88%). Remarkably, the alkylation of the analogous Xantphos \( \eta^1 \)-complex 4b results in the formation of only 23% of the branched product. This relatively low regioselectivity is more easily explained by a nucleophilic attack on an \( \eta^1 \)-allyl moiety (\( S_N2 \)) than by the \( S_N2' \) mechanism. Possibly, complex 4b undergoes a rearrangement from \( \eta^1 \) to \( \eta^3 \) in the alkylation mixture. The increased polarity of the solution and an interaction between the sodium of the nucleophile and a chloride of 4b, may cause the formation of an intermediate rhodium complex with an enlarged Rh-Cl distance, which would enhance the possibility of \( \eta^3 \)-coordination of the cinnamyl. The possibility of nucleophilic attack on a rhodium allyl complex is evidenced by the successful
reaction between the \( \eta^3 \)-allyl complex 4a and malonate. If 4b reacts via the \( \eta^1 \)-structure, the high selectivity for the branched product (23%) relative to the palladium analogue Pd(Xantphos)(cinnamyl)OTf (8%) can be explained by the large distortion of the Rh-cinnamyl bond (see above).

The catalytic alkylation of cinnamyl chloride using complex 4b shows the same regioselectivity as in the stoichiometric reaction, which indicates that the reactions proceed via the same intermediate. The alkylation of cinnamyl chloride using 4b proceeds relatively fast, even compared to palladium complexes (chapter 6). If complex 4b reacts via the \( \eta^3 \)-mechanism, the high reaction rate could be explained by the instability of the intermediate \( \eta^3 \)-cinnamyl complex and the large distortion of the Rh-cinnamyl bond. Furthermore, the modeling studies showed that for the \( \eta^3 \)-allyl complex, the backbonding interaction may be relatively small compared to the analogous palladium complex. In chapter 3 it was shown that a smaller backbonding interaction enhances the reactivity towards nucleophilic attack. The overall regioselectivity may therefore be a result of a competition between the S_{N2}' mechanism and the \( \eta^3 \)-mechanism. For \( \eta^1 \)-complexes, a larger bite angle of the ligand will result in an increase of the reactivity and the \( \eta^3 \)-mechanism may be favored over the S_{N2}' mechanism.

11.3.6 Reaction with CO

Previous studies in our group to the rhodium catalyzed hydroformylation of styrene showed a remarkable dependency of the reaction rate on the bite angle of the ligand.\(^{11} \) The reaction proceeded slowly for ligands with a medium bite angle and fast for ligands with either a smaller or a larger bite angle. Our present study towards the interaction between the isolated rhodium allyl complexes and CO show the same trend. A facile insertion of CO was observed for complexes 1a and 2a, bearing ligands enforcing a small bite angle (o-dppb and dppe) and for complex 4a, bearing the large-bite-angle Xantphos ligand. The DPEphos complex 3a does show an interaction with CO, but no insertion product could be observed.

Since in complexes 1a and 2a the allyl is coordinated in an \( \eta^1 \)-fashion, not all the coordination sites of the rhodium atom are occupied. Coordination of CO will therefore be a relatively facile process. In contrast, the allyl moiety in the Xantphos bearing complex is bonded in an \( \eta^3 \)-fashion. In studies of CO insertion (chapter 10) using analogous palladium complexes it was found that a distorted symmetry of the metal-allyl bond and a low barrier for \( \eta^3 \)-\( \eta^1 \) isomerization facilitate the reaction with CO. The same factors may govern the different behavior of complexes 3a and 4a. In the NMR studies, no \( \eta^1 \)-\( \eta^1 \)-\( \eta^3 \) rearrangement could be observed for the DPEphos complex 3a, whereas this isomerization is an easy process for the Xantphos complex 4a. We tentatively propose an \( \eta^3 \)-\( \eta^1 \) rearrangement of the allyl moiety of 4a prior to the coordination and insertion of CO (figure 25).
Rhodium-allyl chemistry.

Figure 25: Proposed mechanism of reaction of 4a with CO.

If our proposed mechanism for the carbonylation with Rh\textsuperscript{III} complexes is applicable to the Rh\textsuperscript{I} species in the reaction mixture of the hydroformylation of styrene and if the insertion of CO is rate determining (figure 1), we expect that for ligands enforcing an intermediate bite angle, the $\eta^3$-styryl species may be relatively stable. If this is the case, the catalytic reaction with ligands enforcing either a smaller or a larger bite angle will then show a different rate determining step. To date, no such kinetic studies have been reported.

11.4 Conclusion

We have synthesized and isolated a series of novel Cl\textsubscript{2}Rh\textsuperscript{III}(diphosphine)allyl complexes. The hapticity of the rhodium-allyl bond ($\eta^1$, $\eta^3$ or $\eta^1$-$\eta^2$) is highly dependent on the ligand and the substituents on the allyl moiety. The Rh(allyl) complexes react with malonate to form the alkylated product and with CO to form the CO-inserted acyl complex. The nature of the rhodium-allyl bond influences the mechanism of these reactions. In the allylic alkylation, an $\eta^1$-complex reacts via the $S_N2'$ mechanism whereas an $\eta^3$-complex reacts via nucleophilic attack on the $\eta^3$-allyl moiety. DFT calculations suggest that the $S_N2'$ mechanism may not be the favored pathway for non substituted allyl moieties.

For the reaction with CO, no insertion products could be observed for the $\eta^3$-allyl DPEphos complex 3a. For palladium complexes, the $\eta^3$-allyl square planar cationic geometry is favored whereas the crystal structure of 4a shows that neutral penta-coordinated complexes are formed for rhodium. The possibility for rhodium to adopt different geometries facilitates the formation of $\eta^1$-allyl complexes and causes a much stronger distortion of the $\eta^3$-coordination to $\eta^1$-$\eta^2$ than observed for palladium. For palladium, $\eta^1$-allyl complexes can only be formed in using tridentate ligands and coordinating counterions, and these $\eta^1$-allyl species have shown to be unreactive towards nucleophiles. In contrast, $\eta^1$- and $\eta^3$-allyl rhodium complexes described in this chapter react readily to form the alkylation product with a moderately high regioselectivity for the chiral, branched product.

Thus, we have studied the structure and reactivity of a series of novel Rh(III)(allyl) complexes. Further studies are needed to reveal more details of the mechanism of the reactions and to explore the scope of the potential use as homogeneous catalysts.
11.5 Experimental Section

11.5.1 General procedure:

All reactions were performed in an atmosphere of argon unless stated otherwise. Dichloromethane was distilled under nitrogen atmosphere from P₂O₅; pentane, hexane, toluene and benzene were distilled from sodium, THF and diethyl ether from sodium/benzophenone. [RhCl₂·3H₂O] was obtained from ABCR and used as obtained. [Rh(Acac)(CO)₂] was obtained from Merck and used as received. bis-1,2-(diphenylphosphino)-ethane and bis-1,2-(diphenylphosphino)-benzene were purchased from Aldrich and used as received. Allylchloride and cinnamylchloride were obtained from ACROS and used as received. [Rh(COD)Cl]₂, was synthesised according to literature procedure. ¹H-, ³¹P{¹H}- and ¹³C-NMR spectra were recorded at 300, 121 and 75 MHz respectively on a Varian FT NMR spectrometer. Variable temperature NMR experiments were performed on a Brucker DRX-300 FT NMR spectrometer equipped with a variable temperature unit. Cosy-spectra were recorded at 500 MHz on a Varian Inova500 FT NMR spectrometer. Chemical shifts are reported in δ units (ppm) and referenced to the residual deuterated solvent signal for ¹H- and ¹³C-NMR spectroscopy, external H₃PO₄ (δ = 0 ppm) for ³¹P{¹H}-NMR spectroscopy.

11.5.2 Computational Details

The DFT/HF-hybrid calculations were performed using the Gaussian98 program. The geometries were optimised using the B3LYP / LANL2DZ level of theory. All optimalisations were performed in redundant internal coordinates. No symmetry was used.

11.5.3 Synthesis and characterization

![Diagram](image)

Figure 26: Numbering scheme for ¹H-NMR data.

Rh(o-DPPB)(COD)Cl

25 mg of [Rh(COD)Cl]₂ (0.05 mmol) was dissolved in 5 ml of dry toluene. To this solution 47 mg of o-DPPB (0.10 mmol) in 15 ml of toluene was added. After addition the solution was stirred for 30 minutes at
room temperature, during which an orange solid precipitated. The liquid was removed and the solid was washed twice using 25 ml of pentane. The product was dried under vacuum.

$^1$H-NMR(CDC$_3$): 8.0 - 6.2 (24H, m, aromatic protons o-DPPB), 3.9 (4H, bs, olefinic protons COD), 2.2 (4H, bs, exo - protons COD), 1.6 (4H, bd, $J$(H,H) = 8 Hz, endo – protons COD)

$^{31}$P$^1$H$^1$-NMR (CDCl$_3$): 75 (d, $J$(Rh,P) = 198 Hz)

**Rh(DPPE)(COD)Cl**

16.1 mg of [Rh(COD)Cl]$_2$ (0.06 mmol) was dissolved in 5 ml of THF. To this solution 26.5 mg of DPPE (0.06 mmol, 97%) was added while stirring. The solution was stirred for 30 minutes. The solvent was removed in vacuo and the solid was washed twice using 10 ml of pentane.

$^1$H-NMR(CD$_2$CN): 8.0 - 7.0 (20H, m, aromatic protons DPPE), 4.1 (4H, bs, olefinic protons COD), 3.5 (2H, m, backbone protons DPPE), 2.3 (4H, bs, aliphatic protons COD), 2.1 (2H, m, backbone protons DPPE), 1.7 (4H, bs, aliphatic protons COD).

$^{31}$P$^1$H$^1$-NMR (CD$_2$CN): 63 (d, $J$(Rh,P) = 133 Hz)

**Rh(Xanthphos)(COD)Cl**

25 mg of [Rh(COD)Cl]$_2$ (0.05 mmol) was suspended in 5 ml of dry Ether. To this suspension 58 mg of Xantphos was added as a finely ground solid. After addition the solution was stirred for 30 minutes at room temperature, during which an orange solid precipitated. The orange solid was washed twice using 20 ml of Ether. The product was dried under vacuum.

$^1$H-NMR(Toluene-D$_8$): 8.0 - 7.0 (26H, m, Aromatic protons Xantphos), 4.5 (4H, bs, olefinic protons COD), 1.9 (4H, bs, aliphatic protons COD), 1.6 (6H, bs, methyl-protons Xantphos), 1.3 (4H, bs, aliphatic protons COD)

$^{31}$P$^1$H$^1$-NMR (Toluene-D$_8$): 7.6 (d, $J$(Rh,P) = 91 Hz)

**Rh (C$_3$H$_5$(o-DPPB)Cl$_2$**:

50 mg of [Rh(COD)Cl]$_2$ (0.10mmol) was suspended in 5 ml of toluene. To this suspension 90.1 mg of o-di(diphenylphosphino)-benzene (0.20 mmol) in 15 ml of toluene was added dropwise. After addition, the solution was stirred for 1 hour, during which the product precipitated as an orange solid. 0.05 ml of allylchloride (0.65 mmol, a large excess) was added. The mixture was stirred for another hour at room temperature, during which the colour of the suspension changed from orange to yellow. 15 ml of pentane were added to facilitate precipitation. The liquids were removed and the solid was washed twice using 20 ml of pentane. The solid was dried under vacuum.

$^1$H-NMR(CDCl$_3$): 8.0 - 6.2 (24H, m, aromatic protons o-DPPB), 5.1 (1H, m, He), 5.0 (1H, dt, $J$(H,2H) = 4 Hz; $J$(H,H) = 14 Hz; Ha), 4.9 (1H, dt, $J$(H,2H) = 3 Hz; $J$(H,H) = 6Hz, Hb), 2.6 (2H, d, $J$(H,H) = 8 Hz, Hd and He)

$^{31}$P$^1$H$^1$-NMR (CDCl$_3$): 62 (bd, $J$(Rh,P) = 124 Hz)

HR-MS (FAB): C$_3$H$_5$P$_2$Cl$_2$Rh$^+$ requires m/z = 660.0176, found: 625.0491 (loss of one Cl)
Rh(C₃H₅)(DPPE)Cl₂ 2a
29 mg of Rh(DPPE)(CO)Cl (0.05 mmol) was dissolved in 5 ml of THF. To this suspension 0.05 ml of allylchloride (0.65 mmol, a large excess) was added dropwise. The mixture was stirred for 30 minutes at room temperature. The solvent was removed in vacuo and the product was washed twice using 10 ml of pentane. The yellow product was dried in vacuo.

^1^H-NMR (CDCl₃): 8.0 - 7.0 (20H, m, aromatic protons DPPE), 5.0 (1H, m, Hc), 4.8 (2H, m, Ha and Hb), 3.1 (2H, m, Backbone protons DPPE), 2.9 (2H, bs, Hd and He), 2.5 ppm (2H, m, Backbone protons DPPE)

^3^P[^1^H]-NMR (CDCl₃): 66 (bd, J(Rh,P) = 105 Hz)

Rh(DPEphos)(C₃H₅)Cl₂ 3a
25 mg of [Rh(COD)Cl]₂ (0.05 mmol) was suspended in 5 ml of dry ether. To this suspension 55 mg of DPEphos (0.10 mmol) was added as a finely ground solid. After addition the solution was stirred for 30 minutes at room temperature, during which a red solid precipitated. The solid was washed twice using 20 ml of ether. This solid was then suspended in 3 ml of THF. To this suspension 0.05 ml of allylchloride (0.65 mmol, a large excess) was added dropwise. The mixture was stirred for 2 hours during which the colour of the solution changed from red to yellow and finally a yellow solid precipitated. The liquid was removed and the solid was washed twice using 20 ml of pentane. The solid was dried under vacuum.

^1^H-NMR (CDCl₃): 8.5 - 6.0 (aromatic protons DPEphos), 5.3 (1H, m, Hc), 4.5 (1H, dd, J(H,H) = 13 Hz, J(H,H) = 10 Hz, Hb), 4.2 (1H, dd, J(H,H) = 7 Hz, J(H,H) = 7 Hz, He), 3.1 (1H, d, J(H,H) = 7 Hz, Hd), 3.0 (1H, d, J(H,H) = 12 Hz, Ha)

^3^P[^1^H]-NMR (CDCl₃): 30 (1P, dd, J(Rh,P) = 115 Hz, J(P,P) = 9 Hz), 12 (1P, dd, J(Rh,P) = 144 Hz, J(P,P) = 9 Hz)

HR-MS (FAB): C₉ₓHₓₜₙₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖₖ₆
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solution was stirred for 1 hour, during which the product precipitated as an orange solid. 0.10 ml of cinnamylchloride (1.3 mmol, a large excess) was added. The mixture was stirred for two hours at room temperature. 15 ml of pentane were added to facilitate precipitation. The liquids were removed and the solid was washed twice using 20 ml of pentane. The solid was dried under vacuum.

\[ ^1H\text{-NMR (CDCl}_3\text{): 8.0 - 7.0 (30H, m, aromatic protons o-DPPB and phenyl cinnamyl-group), 5.6 (1H, dt, } J(H,H) = 8 \text{ Hz, } J(H,2H) = 11 \text{ Hz, Hc), 2.3 (2H, d, } J(H,H) = 11 \text{ Hz, Hd and He) } \]

\[ ^{31}P\text{-NMR (CDCl}_3\text{): 64 (d, } J(Rh,P) = 164 \text{ Hz) } \]

**Rh(DPPE)(C\text{\textsubscript{3}}H\text{\textsubscript{4}}Ph)Cl\text{\textsubscript{2}} 2b**

28 mg of Rh(DPPE)(CO)Cl (0.05 mmol) was dissolved in 5 ml of THF. To this solution 0.05 ml of cinnamylchloride (0.65 mmol, a large excess) was added dropwise. The mixture was stirred for 30 minutes at room temperature. The solvent was removed in vacuo and the product was washed twice using 10 ml of pentane. The yellow product was dried in vacuo.

\[ ^1H\text{-NMR (CDCl}_3\text{): 8.0 - 7.0 (25H, m, aromatic protons DPPE and phenyl protons cinnamyl), 6.1 (1H, d, } J(H,H = 25 \text{ Hz, Ha}), 5.7 (1H, dt, } J(H,H) = 25 \text{ Hz, } J(H,2H) = 8 \text{ Hz, Hc), 4.5 (2H, d, } J(H,H) = 8 \text{ Hz, Hd and He), 3.3 (2H, m, backbone protons DPPE), 2.3 (2H, m, backbone protons DPPE) } \]

\[ ^{31}P\text{-NMR (CDCl}_3\text{): 69 (d, } J(Rh,P) = 145 \text{ Hz) } \]

**Rh(DPEnphos)(C\text{\textsubscript{3}}H\text{\textsubscript{4}}Ph)Cl\text{\textsubscript{2}} 3b**

25 mg of [Rh(COD)Cl\text{\textsubscript{2}} (0.05 mmol) was suspended in 5 ml of dry ether. To this suspension 55 mg of DPEnphos (0.10 mmol) was added as a finely ground solid. After addition the solution was stirred for 30 minutes at room temperature, during which a red solid precipitated. The solid was washed twice using 20 ml of ether. This solid was then suspended in 3 ml of Toluene. To this suspension 0.1 ml of cinnamylchloride (0.66 mmol, a large excess) was added. The solution was stirred at room temperature for 2 hours. The product was precipitated using 20 ml of pentane. The liquids were removed, and the solid was washed twice, using 20 ml of pentane. The product was dried in vacuo.

\[ ^1H\text{-NMR (CDCl}_3\text{): 8.0 - 7.0 (33H, m, aromatic H's Xantphos and phenyl cinnamyl-group), 6.1 (1H, bs, Hb), 5.8 (1H, m, Hc), 3.7 (1H, bs, Hd), 3.4 (1H, bs, He) } \]

\[ ^{31}P\text{-NMR (CDCl}_3\text{): 44 (1P, dd, } J(Rh,P) = 180 \text{ Hz, } J(P,P) = 15 \text{ Hz), 32 (1P, dd, } J(Rh,P) = 134 \text{ Hz, } J(P,P) = 15 \text{ Hz), 11 (0.1P, d, } J(Rh,P) = 121 \text{ Hz, minor product) } \]

**Rh(Xantphos)(C\text{\textsubscript{3}}H\text{\textsubscript{4}}Ph)Cl\text{\textsubscript{2}} 4b**

40 mg of Rh(Xantphos)(COD)Cl (0.05 mmol) was suspended in 5 ml of toluene. To this suspension 0.1 ml of cinnamylchloride (0.66 mmol, a large excess) was added. The reaction mixture was stirred for 2 hours at room temperature. The solvent was removed in vacuo, and the yellow solid was washed twice using 10 ml of pentane. The product was dried under high vacuum (5*10\textsuperscript{-5} mbar).
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$^1$H-NMR (CDCl$_3$): 8.0 – 7.0 (31H, m, aromatic H's Xantphos and phenyl cinnamyl-group), 6.7 (1H, d, J(H,H) = 16 Hz, Hb), 6.6 (1H, m, He), 4.4 (2H, bs, Hd and He), 1.7 (6H, s, methyl-protons Xantphos)

$^{31}$P($^1$H)-NMR (CDCl$_3$): 16 (bd, J(Rh,P) = 117 Hz)

HR-MS (FAB): C$_{48}$H$_{41}$Cl$_2$OP$_2$Rh$^+$ requires m/z = 868.1065, found: 833.1384 (loss of one Cl)

11.5.4 High-Pressure NMR

**Rh(C$_3$H$_5$)(o-DPPB)Cl$_2$ 1a**

34 mg of Rh(C$_3$H$_5$)(o-DPPB)Cl$_2$ (0.05 mmol) was dissolved in 2 ml of CDCl$_3$. The solution was transferred to a 10 mm sapphire high-pressure NMR-tube. The tube was pressurised using 4 bar of $^{13}$CO and 36 bar of $^{12}$CO. $^1$H- and $^{31}$P($^1$H)-spectra were taken every 15 min throughout the experiment. $^{13}$C-spectra were taken every hour. After 2 hours the mixture was heated to 50°C in the spectrometer. The solution was heated for 1 hour, during which time the reaction went to completion. Afterwards the solution was cooled to room temperature and $^1$H- and $^{31}$P($^1$H)-NMR spectra were obtained.

**Rh(C$_3$H$_5$)(DPPE)Cl$_2$ 2a**

32 mg of Rh(NBD)(DPPE)Cl (0.05 mmol) was dissolved in 2 ml of CD$_2$CN. To this solution 0.05 ml of allylchloride (1.3 mmol, a large excess) was added and the mixture was stirred thoroughly. The solution was transferred to a 10 mm sapphire high-pressure NMR-tube. The tube was pressurized using 4 bar of $^{13}$CO and 36 bar of $^{12}$CO. $^1$H- and $^{31}$P($^1$H)-NMR spectra were obtained at room temperature before heating to 50°C. NMR-spectra were obtained after 20 min., 45 min., 1:20 h. and 1:30 h. The solution was then cooled to room temperature. $^1$H- and $^{31}$P($^1$H)-NMR spectra were taken 20 min., 40 min. and 75 min. after cooling.

**Rh(C$_3$H$_5$)(DPEphos)Cl$_2$ 3a**

37 mg of Rh(C$_3$H$_5$)(DPEphos)Cl$_2$ (0.05 mmol) was dissolved in 2 ml of CDCl$_3$. The solution was transferred to a 10 mm sapphire high-pressure NMR-tube. The tube was pressurized to 8 bar using $^{13}$CO. The $^1$H-, $^{31}$P($^1$H)- and $^{13}$C($^1$H)-NMR measurements were taken at room temperature. The solution was heated to 50°C for 1 hour in the spectrometer, after which another set of measurements was taken. The NMR-tube was pressurized further using 36 bar of $^{12}$CO and was heated to 50°C for another hour. The mixture was analysed using $^1$H-, $^{31}$P($^1$H)- and $^{13}$C($^1$H)-NMR.

**Rh(C$_3$H$_5$)(Xantphos)Cl$_2$ 4a**

41 mg of Rh(C$_3$H$_5$)(Xantphos)Cl$_2$ (0.05 mmol) was dissolved in 2 ml of CDCl$_3$. The solution was transferred to a 10 mm sapphire high-pressure NMR-tube. The tube was pressurized to 8 bar using $^{13}$CO. The $^1$H- and $^{31}$P($^1$H)-NMR spectra were taken every 15 min. for 3 hours at room temperature, $^{13}$C-NMR spectra were obtained every hour. Afterwards, the solution was heated to 40°C in the spectrometer for 1 hour, during
which time the reaction was completed. The solution was cooled to room temperature and $^1$H-, $^{31}$P-$^1$H- and $^{13}$C-NMR spectra from the final product were obtained.

11.5.5 Crystal structure determination of 4a:

$$\text{C}_{42}\text{H}_{77}\text{Cl}_{2}\text{OP}_{2}\text{Rh, } M_w=793.5, \text{monoclinic, } P2_1/c, a=16.516(3), b=13.218(2), c=16.908(2) \text{Å, } \beta=101.15(1)^\circ, V=3621.5(10) \text{Å}^3, Z=4.$$ 

$$\lambda(\text{CuK}\alpha)=1.5418 \text{Å, } \mu(\text{CuK}\alpha)=62.56 \text{ cm}^{-1}, F(000)=1624, \text{room temperature, } \text{Final } R=0.074 \text{ for } 5558 \text{ reflections.}$$

A crystal with dimensions 0.15 x 0.20 x 0.45 mm approximately was used for data collection on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated CuKα radiation and $\omega$-2θ scan. A total of 7453 unique reflections was measured within the range $-20 \leq h \leq 20, 0 \leq k \leq 16, -21 \leq l \leq 0$. Of these, 5558 were above the significance level of 4σ($F_{\text{obs}}$) and were treated as observed. The range of $(\sin \theta)/\lambda$ was 0.031-0.627 Å

$$(2.7 \leq 0 \leq 75.3^\circ).$$

Two reference reflections ([2 1 4],[2 1 1]) were measured hourly and showed no decrease during the 132 h collecting time. Unit-cell parameters were refined by a least-squares fitting procedure using 23 reflections with 39.91 ≤ θ ≤ 41.00. Corrections for Lorentz and polarisation effects were applied. Absorption correction was performed with the program PLATON, following the method of North et al. using Ψ-scans of five reflections, with coefficients in the range 0.356-0.954. The structure was solved by the PATTY option of the DIRDIF99 program system. The hydrogen atoms were calculated. Full-matrix least-squares refinement on F, anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms keeping the latter fixed at their calculated positions with an atomic displacement parameter of U = 0.10 Å$^2$, converged to R=0.074, R$_w$=0.081, (Δ/σ)$_{\text{max}}$=0.18, S=1.07. A weighting scheme $w=[15. + 0.01*\sigma(F_{\text{obs}})]^2 + 0.01/(\sigma(F_{\text{obs}}))]^{-1}$ was used. A final difference Fourier map revealed a residual electron density between −2.43 and 1.66 eÅ$^3$ in the vicinity of the Rh. Scattering factors were taken from Cromer and Mann. International Tables for X-ray Crystallography. The anomalous scattering of Rh, P and Cl was taken into account. All calculations were performed with XTAL3.7, unless stated otherwise.
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11.6 References and notes

[8] Many different procedures have been reported for the synthesis of such complexes and we have tried many. Our novel route was the only method that was succesful for all ligands and all allyls. For other procedures see for instance:
[13] R. J. van Haaren: characterization of (triphos)Pd(η¹-cinnamyl)Cl: ¹H-NMR: 2.3-2.6 (2 multiplets, 4H, backbone), 2.7 (m, 2H, Pd-CH₂), 3.0-3.3 (m(ddd), 4H, backbone), 5.1 (dd, J₁ = 15.3 Hz, J₂ = 5.6 Hz, 1H, =CH-Ph), 5.8 (dt, J₁(d) = 15.0 Hz, J₂(t) = 6.3 Hz, 1H, Pd-CH2=CH-Ph), 7.0-7.8 (m, 30 H, aromatic H); ³¹P-NMR: 47 (d, J = 48 Hz, 2P, -PPh₂), 99 (temperature, J = 48 Hz, 1P, PPh₂-P(Ph)-PPh₂); This palladium complex and other Pd(η¹-cinnamyl) complexes are not reactive in the stoichiometric and the catalytic allylic alkylation.
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