Chapter 4

Effect of the bite angle of bidentate phosphine ligands on the regioselectivity in allylic alkylation of crotyl complexes.

The DFT calculations in chapter 3 showed that the Pd(η3-allyl) bond is distorted, when the allyl moiety is substituted. In this chapter we study the effect on the structure and reactivity of the presence of one substituent on the allyl moiety for the case of two phosphorus donor atoms.

Abstract

The natural bite angle of bidentate phosphine ligands influences the isomer distribution (syn and anti) in (crotyl)Pd(bisphosphine) OTf complexes. It was found (31P- and 1H-NMR studies) that the syn/anti ratio changes from 12 (dppp) to 1.3 (Sixantphos). Molecular orbital calculations (PM3(tm) level) indicate that for ligands inducing a large bite angle, the phenyl rings of the ligand embrace the allyl moiety, thereby influencing the syn / anti ratio. This bite angle effect on the syn / anti ratio is transferred to the regioselectivity in stoichiometric allylic alkylation. Ligands inducing large bite angles direct the regioselectivity towards the formation of the branched product 2. Catalytic alkylation of trans-2-butenyl acetate (crotyl acetate) showed that for ligands with a small bite angle the regioselectivity of the catalytic and stoichiometric alkylation are in good agreement. This correspondence is less pronounced for ligands with a larger bite angle, which is rationalised in terms of the relative rates of syn / anti isomerization and the alkylation reaction. The ligand with the largest bite angle (Sixantphos) gives the most active catalytic species.
4.1 Introduction

The palladium-catalysed allylic alkylation reaction receives much interest\cite{1,7}. Most of the research in this field focuses on asymmetric induction. Less effort is put into understanding the regioselectivity found in the alkylation of non-symmetrically substituted allyl-fragments\cite{8,13}. Åkerman\cite{8} has shown that the cone-angle of substituted phenantroline has a large influence on both the isomer distribution of crotyl-Pd complexes and the regioselectivity of stoichiometric alkylation. The methyl substituents on the 2,9-dimethyl-1,10-phenanthroline ligand interfere with the methyl substituent on the allyl-moiety. This causes the anti-isomer of the complex to prevail over the otherwise more stable syn-isomer. It was shown that stoichiometric alkylation of the syn-complex resulted in almost exclusive formation of the linear trans-product (1). The anti-complex reacted to the branched (2) and the linear cis-product (3) in an approximately 1:1 ratio.

![Figure 1. Generic Xantphos structure](image)

In our group much research has been conducted concerning the effect of the natural bite angle\cite{20} ($\beta_n$) of bidentate phosphine ligands on transition metal catalysed reactions\cite{15}. This research led to the development of a new class of ligands that enforces (very) large bite angles up to 110° (the Xantphos type ligands; see figure 1). Significant dependencies of the catalyst performance on the natural bite angle have been observed in reactions such as the rhodium catalysed hydroformylation\cite{8} and the nickel catalysed hydrocyanation\cite{9}. Previously, we communicated on the effect found in the alkylation of trans-2-hexenyl acetate with sodium diethyl 2-methylmalonate\cite{11}. Ligands with a large natural bite angle were found to direct the regioselectivity to the linear trans-product 1 resulting in smaller amounts of the branched product (figure 2). The results were rationalized in terms of steric hindrance. In this chapter we will explore the limits of the used model by studying the influence of the bite angle on the allylic alkylation of the much smaller crotyl moiety.
P-P ligands, crotyl complexes

Figure 2. Numbering scheme and formation of regio isomers in the stoichiometric alkylation of (crotyl)Pd(bisphosphine) OTf complexes

4.2 Stoichiometric alkylation

4.2.1 Synthesis and characterization of the catalyst

In order to investigate the nature of this bite angle effect, we have prepared and isolated Pd(crotyl)(bisphosphine)OTf complexes of several bisphosphine ligands. NMR studies (1H and 31P) of these compounds show that they exist as an equilibrium mixture of the syn and anti isomers. The syn / anti ratio is dependent on the bite angle of the ligand and is significantly lower in complexes of ligands inducing larger bite angles (table 1).

To understand the effect of the P-Pd-P angle (β) on the structure of the Pd-allyl complex, molecular orbital calculations (semi-empirical PM3(tm) level) were carried out on the cationic (crotyl)Pd(bisphosphine)+ complexes. The P-Pd-P angle (β), taken from the calculated structures, varies from 85° (dppe) to 110° (Sixantphos). The allyl moiety is found to be embraced by the phenyl rings of the ligand. When the bite angle is larger, the embracing becomes more pronounced. This is visualised in figure 3.
In all the complexes studied using molecular modelling, the syn-isomer has a lower energy than the anti-isomer. The energy difference between the syn- and anti-isomer, however, decreases with larger bite angle. This is in agreement with the experimental data: a lower syn/anti ratio is observed when ligands inducing larger bite angles are applied (table 1). The embracing effect in complexes of ligands inducing a small bite angle, however, is of minor influence. The relatively high syn/anti ratio of (crotyle)Pd(dppp)OTf is therefore the result of electronic rather than steric effects. Detailed DFT modeling studies are in progress to investigate the nature of this effect.

4.2.2 Stoichiometric alkylation

Table 1. Relation between the bite angle and 1) $\Delta E$ (syn-anti) calculated by molecular modelling (PM3(tm) level) and obtained from experimental data (NMR), and 2) the regioselectivity in stoichiometric alkylation of the equilibrium mixtures of (crotyle)Pd(bisphosphine)OTf complexes

<table>
<thead>
<tr>
<th>complex (ligand)</th>
<th>$\beta^a(\degree)$</th>
<th>%syn</th>
<th>%anti</th>
<th>$\Delta E$(NMR) (kJ.mole$^{-1}$)</th>
<th>$\Delta E$($^{[b]}$(pm3(tm)) (kJ.mole$^{-1}$)</th>
<th>% 1</th>
<th>% 3</th>
<th>% 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>I (dppe)</td>
<td>85</td>
<td>90</td>
<td>10</td>
<td>-5.4</td>
<td>-23.7</td>
<td>70.0</td>
<td>8.9</td>
<td>21.1</td>
</tr>
<tr>
<td>II (dppp)</td>
<td>95</td>
<td>92</td>
<td>8</td>
<td>-6.1</td>
<td>-21.9</td>
<td>79.2</td>
<td>4.6</td>
<td>16.2</td>
</tr>
<tr>
<td>III (dppb)</td>
<td>99</td>
<td>86</td>
<td>14</td>
<td>-4.5</td>
<td>-20.0</td>
<td>71.7</td>
<td>8.0</td>
<td>20.3</td>
</tr>
<tr>
<td>IV (dpff)</td>
<td>106</td>
<td>78</td>
<td>22</td>
<td>-3.1</td>
<td>-18.9</td>
<td>68.9</td>
<td>8.9</td>
<td>22.2</td>
</tr>
<tr>
<td>V DPEphos</td>
<td>108</td>
<td>72</td>
<td>28</td>
<td>-2.3</td>
<td>-15.4</td>
<td>66.4</td>
<td>9.6</td>
<td>24.0</td>
</tr>
<tr>
<td>VI Sixantphos</td>
<td>110</td>
<td>57</td>
<td>43</td>
<td>-0.7</td>
<td>-12.5</td>
<td>54.5</td>
<td>12.4</td>
<td>33.1</td>
</tr>
</tbody>
</table>

$^[a]$: $\beta$ obtained from the calculated (crotyle)Pd(bisphosphine) complexes

$^[b]$: the relative large energy difference in the calculations is most likely the result of the absence of solvent and anion

Figure 3. The embracing effect of the phenyl rings cause the substituent on the allyl moiety to bend out of the allyl plane. Left = syn, right = anti.
P-P ligands, crotyl complexes

The syn / anti ratio governs the regioselectivity of the stoichiometric alkylation (table 1, figure 4). In (crotyl)Pd(bisphosphate) OTf complexes of ligands inducing a small bite angle the syn isomer largely prevails and the relative amount of the linear trans product 1 is high. Going to a larger bite angle (from dppe to Sixantphos), the percentage syn isomer as well as the selectivity to 1 drops, whereas the selectivity to the branched product 2 increases. The percentage of 3 remains almost constant along the bite angle range studied.

![Figure 4](image.png)

Figure 4. Relation between isomer distribution in cationic (crotyl)Pd(bisphosphine)OTf complexes and the regioselectivity of stoichiometric alkylation

It has been suggested\(^{[1]}\) that in allylic alkylation reactions the structure of the allyl complex determines the (enanti)selectivity in an early transition state. Recent developments\(^{[4, 6, 12-15]}\), however, indicate that in many cases a late transition state is more likely. In an early transition state, not only the electronic properties of the allyl moiety are important for the regioselectivity (chapter 3), but also the relative steric accessibility of the two carbon atoms C1 and C3. Due to steric hindrance between the substituent on the allyl moiety and the ligand, it will be bent out of the allyl plane, away from the palladium centre. Therefore the substituted allyl carbon atom C3 will be less accessible for nucleophilic attack and consequently alkylation of the unsubstituted allyl carbon atom C1 will prevail.

In a late transition state, nucleophilic attack of the malonate anion at the substituted allyl carbon atom C3 will cause a change in the hybridisation on C3 from sp\(^2\) to sp\(^3\). This causes the substituent to bend towards a phenyl ring of the ligand. A large bite angle results in an increase of the steric hindrance in this stage of the reaction (figure 3), which hampers the formation of 2\(^{[1]}\).

Using a small group like a methyl substituent on the allyl moiety the steric hindrance during the nucleophilic attack is of less influence. Consequently, electronic factors may become more important. This would explain the good correlation between the syn / anti ratio and the observed regioselectivity.
Therefore it is concluded that in the alkylation of (crotyl)Pd(bisphosphine)OTf complexes the transition state of the reaction is not late. The relative importance of steric and electronic factors is dependent on the nature of the ligand and the (syn or anti) orientation of the substituents on the allyl moiety.

4.3 Catalytic alkylation

4.3.1 Rate of reaction

In addition to these stoichiometric experiments we have also carried out the catalytic alkylation of crotyl acetate (table 2). The catalytic experiments have been performed using the isolated (crotyl)Pd(bisphosphine)OTf complexes, instead of using a precursor, such as Pd(dba)$_2$, or Pd(OAc)$_2$, and the ligand. This procedure excludes an incubation step which is necessary for the formation of the catalytically active species, as well as the possibility of pre-equilibria via complexation of dba to palladium$^{17}$. The retarding effect of dba is clear, if we compare the reaction rates presented in table 2 with the reaction rates presented in a previous communication of the bite angle effect on allylic alkylation$^{11}$. The difference in the rate of reaction is at least one order of magnitude$^{16}$. Remarkably, the observed trend in reaction rate does not remain the same. Starting from the isolated (crotyl)Pd(bisphosphine)OTf complex, Sixanthos is found to yield the most active catalytic species, whereas use of Pd(dba)$_2$ results in DPEphos or dppb to yield the most active catalyst$^{11}$. Obviously, the catalytically active species is less easily formed from Pd(dba)$_2$ when a rigid ligand inducing a large bite angle is used.

In contrast to most literature procedures for allylic alkylation reactions only one equivalent of ligand per palladium atom is used. When a precursor, such as Pd(OAc)$_2$ is used, an additional equivalent of ligand might be required to reduce the Pd$^{III}$ to the active Pd$^{II}$ species$^{16}$. The presence of an excess of ligand will also reduce the rate of the reaction, by complexation to the Pd$^{II}$ species which is formed after alkylation. Before coordination of the substrate dissociation of the extra ligand is necessary. This can retard the overall reaction rate.

4.3.2 Regioselectivity

The bite angle effect as observed in the stoichiometric alkylation of (crotyl)Pd(bisphosphine)OTf complexes is less obvious in the catalytic alkylation of crotyl acetate. The starting complex enters the catalytic cycle via alkylation of the starting (crotyl)Pd(bisphosphine)OTf complex. The next step involves oxidative addition of the substrate to the thus formed Pd$^{II}$ species. As the substrate configuration is mainly trans (95%), initially the syn (crotyl)Pd(bisphosphine)OAc complex is formed as the main
product. This complex is cationic, so the acetate leaving group will remain as a counterion in the coordination sphere. Interaction of the counterion with the palladium centre is known to increase the rate of dynamic behaviour of the allyl moiety\cite{18}. This results in an isomerization of the syn complex to the anti complex and vice versa. The resulting regioselectivity of the catalytic reaction (table 2) is dependent on the relative rates of syn-anti isomerization and alkylation.

NMR experiments with the (crotyl)Pd(bisphosphine)OTf complexes used in the alkylation reactions, indicate that the syn-anti isomerization in these complexes is slow relative to stoichiometric alkylation. The isomerization, however, may play a significant role when acetate instead of the weakly co-ordinating triflate is the counterion, as is the case in the catalytic experiments.

The correlation between the regioselectivity in stoichiometric and catalytic alkylation is good for ligands inducing a small bite angle, such as dppe and dpp, but also for dppf (table 1 and 2). Going to a larger bite angle, the selectivity follows a different trend than observed in the stoichiometric reaction. The Sixantphos ligand directs the regioselectivity towards 85% of the linear trans product. This can be rationalised in terms of a fast alkylation rate, relative to isomerization, of the complexes with ligands inducing a large bite angle.

Table 2. Catalytic alkylation of crotyl acetate using the equilibrium mixtures of (crotyl)Pd(bisphosphine)OTf complexes

<table>
<thead>
<tr>
<th>complex(ligand)</th>
<th>$\beta^{[a]}(\circ)$</th>
<th>t.o.f.$^{[b]}$</th>
<th>yield$^{[c]}$(%)</th>
<th>% 1</th>
<th>% 3</th>
<th>% 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>I (dppe)</td>
<td>85</td>
<td>2.0</td>
<td>37.3</td>
<td>68.8</td>
<td>11.1</td>
<td>20.0</td>
</tr>
<tr>
<td>II (dppp)</td>
<td>95</td>
<td>2.9</td>
<td>37.1</td>
<td>76.0</td>
<td>6.6</td>
<td>17.4</td>
</tr>
<tr>
<td>III (dpp)</td>
<td>99</td>
<td>8.9</td>
<td>90.3</td>
<td>79.0</td>
<td>3.1</td>
<td>17.9</td>
</tr>
<tr>
<td>IV (dppf)</td>
<td>106</td>
<td>8.0</td>
<td>81.5</td>
<td>74.1</td>
<td>2.5</td>
<td>23.4</td>
</tr>
<tr>
<td>V (DPEphos)</td>
<td>108</td>
<td>8.7</td>
<td>86.0</td>
<td>80.1</td>
<td>2.5</td>
<td>17.4</td>
</tr>
<tr>
<td>VI (Sixantphos)</td>
<td>110</td>
<td>9.1</td>
<td>88.3</td>
<td>85.7</td>
<td>1.4</td>
<td>12.9</td>
</tr>
</tbody>
</table>

$^{[a]}$: $\beta$ obtained from the calculated (crotyl)Pd(bisphosphine) complexes

$^{[b]}$: t.o.f. initial turn over frequency, determined after 10 minutes reaction time, in $10^3$ mole$^{-1}$ h$^{-1}$

$^{[c]}$: based on the formation of 1,2 and 3, as determined after 30 minutes by GC, using the internal standard method

The catalytic reactions were performed in THF (10 mL), using 0.05 mol% of catalyst (0.00050 mmole), 1.0 mmole of substrate and 2.0 mmole of sodium diethyl 2-methylmalonate. The reaction was monitored by GC using decane as the internal standard.
4.4 Conclusion

In conclusion, we have shown that for (crotyl)\text{Pd(bisphosphine)OTf} complexes with ligands inducing a large bite angle the syn / anti ratio is much lower than in the corresponding complexes with ligands having a small bite angle. Molecular modelling studies indicate that this is caused by an increasing embrace of the allyl moiety by the phenyl rings of the ligand. This bite angle effect on the syn / anti ratio can be transferred to the regioselectivity in stoichiometric allylic alkylation. Ligands inducing large bite angles direct the regioselectivity towards the formation of 2. In the \textit{catalytic} alkylation of crotyl acetate, however, the regioselectivity is also determined by the relative rates of syn-anti isomerization and alkylation. The correlation between the regioselectivity found in the stoichiometric and the catalytic alkylation is best for ligands inducing a small bite angle. The ligands with the largest bite angle (Sixantphos) is found to result in the most active catalytic species, indicating an enhanced electrophilicity of the allyl moiety (see chapter 3).
4.5 Experimental section

$^1$H NMR (300 MHz, TMS, CDCl$_3$), $^{31}$P($^1$H) (121.5 MHz external 85% H$_3$PO$_4$, CDCl$_3$) were recorded on a Bruker AMX-300 spectrometer. Elemental analyses were performed on an Elementar Vario EL (Foss Electric).

All calculations were carried out using the commercially available SPARTAN program (version 5.0.3).

The geometry optimisation was performed on the semi-empirical pm3(tm) level.

The product distribution was measured on a Interscience Mega2 apparatus, equipped with a DB1 column, length 30 m, inner diameter 0.32 mm, film thickness 3.0 µm, and a F.I.D detector.

All experiments were carried out using standard Schlenk techniques. All solvents were freshly distilled prior to use.

Sodium diethyl 2-methylmalonate (0.5 M in THF) was prepared from diethyl 2-methylmalonate and NaH in THF at 273 K.

The stoichiometric alkylation reactions were performed by adding an excess of sodium diethyl 2-methylmalonate (0.1 ml of a 0.5 M solution in THF) to a solution of 10 mg of the Pd-complex in 1 ml of THF. Reaction was instantaneous and after one minute, the mixture was worked up with water, filtered over silica and analysed by GC.

The catalytic reactions were performed in THF (10 mL), using 0.05 mol% of catalyst (0.00050 mmole), 1.0 mmole of substrate and 2.0 mmole of sodium diethyl 2-methylmalonate. The reaction was monitored by quenching samples from the reaction mixture with flash chromatography which were analysed by GC using decane as the internal standard.

The Pd-complexes were prepared in CH$_2$Cl$_2$ from [(crotyl)-Pd-$\mu$Cl]$_2$ by adding 2 equiv. of ligand and abstracting the Cl-atom with AgOTf. The complexes were isolated in a quantitative yield (white microcrystalline powder) as their analytically pure equilibrium mixtures and were used as such in the alkylation reaction. The syntheses of DPEphos and Sixanphos have been published elsewhere$^{[6]}$. Dppe, dppp, dppb and dppf were obtained from Acros chemicals and used as received.

Analytical data of the (crotyl)-Pd-(ligand)OTf complexes are given for their equilibrium mixtures. The NMR signals of the syn and anti isomers could easily be distinguished. The syn / anti ratio was determined by comparing the intensities of the signals of the Me-substituent on the allyl moiety. NMR-data of the complexes were obtained in CDCl$_3$ ($\delta$ in ppm).
Chapter 4

Pd(dppe)(crotyl)OTf (Ia+s) was obtained in syn/anti ratio of 90/10. El.anal. (Ia+s) found: C: 52.08%, H: 4.30% (calc. C: 52.51%, H: 4.38%)

Pd(dppe)(syn-crotyl)OTf (Is): \( ^1H \): 1.69 (ddd, \( J_1 = 6.3 \) Hz, \( J_2 = 8.4 \) Hz, \( J_3 = 8.4 \) Hz, 3H(Me)), 2.4-3.0 (m, 4H, 2CH= bridge), 3.1 (ddd, \( J_1 = 12.1 \) Hz, \( J_2 = 12.1 \) Hz, 1H(Ha)), 4.37 (m, 1H(Hc)), 4.6 (dd, \( J_1 = 7.2 \) Hz, \( J_2 = 7.2 \) Hz, 1H(Hb)), 5.7 (ddd, \( J_1 = 7.4 \) Hz, \( J_2 = 13.1 \) Hz, \( J_3 = 13.1 \) Hz, 1H(Hd)), 7.3-7.7 (m, 20H(Ar)), \[^{31}P\] \( ^1H \): 48.5 (d, \( J = 33 \) Hz), 49.6 (d, \( J = 33 \) Hz).

Pd(dppe)(anti-crotyl)OTf (la): \( ^1H \): 0.9 (ddd, \( J_1 = 6.9 \) Hz, \( J_2 = 7.0 \) Hz, \( J_3 = 7.0 \) Hz, 3H(Me)), 2.4-3.0 (m, 4H, 2CH= bridge), 3.5 (dd, 1H(Ha)), 4.15 (m, 1H(Hc)), 4.7 (dd, 1H(Hb)), 5.6 (m, 1H(Hd)), 7.3-7.7 (m, 20H(Ar)).

Pd(dppe)(anti-crotyl)OTf (IIa): \( ^1H \): 0.88 (ddd, \( J_1 = 7.1 \) Hz, \( J_2 = 7.1 \) Hz, \( J_3 = 7.1 \) Hz, 3H(Me)), 2.6-3.0 (m, 4H, 2CH= bridge), 3.2 (dd, \( J_1 = 7.0 \) Hz, 1H(Ha)), 4.0 (dd, \( J_1 = 6.9 \) Hz, \( J_2 = 6.9 \) Hz 1H(Hb)), 4.0 (dd, \( J_1 = 6.9 \) Hz, \( J_2 = 6.9 \) Hz, 1H(Hb)), 4.7 (m, 1H(Hc)), 5.5 (m, 1H(Hd)), 7.2-7.6 (m, 20H(Ar)).

Pd(dppe)(anti-crotyl)OTf (IIa): \( ^1H \): 7.1 (d), 7.9 (d)

Pd(dppe)(anti-crotyl)OTf (IIa): \( ^1H \): 6.75 (d, \( J = 65.3 \) Hz), 8.01 (d, \( J = 65.3 \) Hz)

Pd(dppe)(anti-crotyl)OTf (IIa): \( ^1H \): 0.88 (ddd, \( J_1 = 7.1 \) Hz, \( J_2 = 7.1 \) Hz, \( J_3 = 7.1 \) Hz, 3H(Me)), 2.6-3.0 (m, 4H, 2CH= bridge), 3.2 (dd, \( J_1 = 7.0 \) Hz, 1H(Ha)), 4.0 (dd, \( J_1 = 6.9 \) Hz, \( J_2 = 6.9 \) Hz 1H(Hb)), 4.0 (dd, \( J_1 = 6.9 \) Hz, \( J_2 = 6.9 \) Hz, 1H(Hb)), 4.7 (m, 1H(Hc)), 5.5 (m, 1H(Hd)), 7.2-7.6 (m, 20H(Ar)).

Pd(dppe)(anti-crotyl)OTf (IIa): \( ^1H \): 7.1 (d), 7.9 (d)

Pd(dppe)(syn-crotyl)OTf (Is): \( ^1H \): 1.14 (ddd, \( J_1 = 6.7 \) Hz, \( J_2 = 8.9 \) Hz, \( J_3 = 8.9 \) Hz, 3H(Me)), 2.6-3.0 (m, 4H, 2CH= bridge), 3.0 (dd, \( J_1 = J_2 > 7 \) Hz, 1H(Ha)), 3.65 (dd, \( J_1 = J_2 < 7 \) Hz, 1H(Hb)), 4.2 (m, 1H(Hc)), 5.5 (dd, \( J_1 = 12.4 \) Hz, \( J_2 = 12.4 \) Hz, \( J_3 = 7.4 \) Hz, 1H(Hd)), 7.2-7.6 (m, 20H(Ar)).

Pd(dppe)(anti-crotyl)OTf (IIa): \( ^1H \): 0.6 (ddd, \( J_1 = 6.7 \) Hz, \( J_2 = 6.7 \) Hz, \( J_3 = 6.7 \) Hz, 3H(Me)), 2.6-3.0 (m, 4H, 2CH= bridge), 3.5 (dd, 1H(Ha)), 4.15 (m, 1H(Hc)), 4.7 (dd, 1H(Hb)), 5.6 (m, 1H(Hd)), 7.2-7.6 (m, 20H(Ar)).

Pd(dppe)(anti-crotyl)OTf (IIa): \( ^1H \): 20.4 (d, \( J = 20.8 \) Hz), 21.2 (d, \( J = 20.8 \) Hz).

Pd(dppe)(anti-crotyl)OTf (IIa): \( ^1H \): 0.64 (ddd, \( J_1 = 6.7 \) Hz, \( J_2 = 6.7 \) Hz, \( J_3 = 6.7 \) Hz, 3H(Me)), 1.7-2.0 (m, 4H, 2CH= bridge), 2.5-2.8 (m, 4H, 2CH= bridge), 2.95 (dd, \( J_1 = 11.3 \) Hz, \( J_2 = 11.3 \) Hz, 1H(Ha)), 3.7 (dd, \( J_1 = 6.5 \) Hz, \( J_2 = 6.5 \) Hz, 1H(Hb)), 4.85 (m, 1H(Hc)), 5.5 (ddd, \( J_1 = 7.4 \) Hz, \( J_2 = 13.0 \) Hz, \( J_3 = 13.0 \) Hz, 1H(Hd)), 7.4-7.7 (m, 20H(Ar)).

Pd(dppe)(anti-crotyl)OTf (IIa): \( ^1H \): 20.7 (d, overlap with syn-complex), 21.2 (d, overlap with syn-complex)
Pd(dpff)(crotyl)OTf (IV s+a) was obtained in syn/anti ratio of 78 / 22. El.anal. (IVa+s) found: 53.71%, H: 4.11% (calc.: C: 54.15 %, H: 4.05 %)
Pd(dpff)(syn-crotyl)OTf (IVs): 1H: 1.08 (ddd, J1= 6.7 Hz, J2 = 6.7 Hz, J3 = 10.3 Hz, 3H (Me)), 3.23 (dd, J1 = 11.0 Hz , J2 = 11.0 Hz, 1H (Ha)), 3.50 (dd, J1 = 4.0 Hz, J2 = 4.0 Hz, 1H (Hb)), 3.83 (s, 1H (FcH)), 3.94 (s, 1H (FcH)), 4.27 (s, 1H (FcH)), 4.32 (s, 1H (FcH)), 4.35-4.55 (m, contains FcH and Hc), 4.37 (s, 1H (FcH)), 4.46 (s, 1H (FcH)), 4.63 (s, 1H (FcH)), 4.83 (s, 1H (FcH)), 5.64 (ddd, J1 = 12.9 Hz, J2 = 12.9 Hz, J3 = 7.4 Hz, 1H (Hd)), 7.3-7.8 (m, 20H, Ar, syn and anti)

31P{1H}: 24.9 (d, J=47.5 Hz), 23.6 (d, J=47.5 Hz),
Pd(dpff)(anti-crotyl)OTf (IVa): 1H: some signals appear as shoulders on IVs, some however appear as separate signals: 0.90 (ddd, J1=J2=J3 = 6.8 Hz, 3H (Me)), 3.2 (shoulder on IVs(Ha), Ha), 3.93 (s, 1H (FcH)), 4.35-4.55 (m, contains FcH), 4.40 (s, 1H (FcH)), 4.43 (s, 1H (FcH)), 4.51 (s, 1H (FcH)), 4.56 (s, 1H (FcH)), 4.66 (s, 1H (FcH)), 4.74 (ddd, J1 = J2 = J3 = 6.8 Hz, 1H, (He)), 7.3-7.8 (m, 20H, Ar, syn and anti)

31P{1H}: signals appear as shoulders on IVs.

Pd(DPEphos)(crotyl)OTf (V s+a) was obtained in syn/anti ratio of 72 / 28. El.anal. (Va+s) found: C: 57.60%, H: 4.08% (calc.: C: 57.99%, H: 4.15%)
Pd(DPEphos)(syn-crotyl)OTf (Vs): 1H: 1.1 (ddd, J1 = 10.7 Hz, J2 = 6.6 Hz, J3 = 6.6 Hz, 3H(Me), 3.4 (m, 2H(Ha and Hb)), 4.4 (m, 1H, Hc)), 5.6 (ddd, J1 = 7.4 Hz, J2 = 12.7 Hz, J3 = 12.7 Hz, 1H(Hd)), 6.4-7.6 (m, Ar)

31P{1H}: 10.3 (d, J=39.6 Hz), 17.1 (d, J= 39.6 Hz),
Pd(DPEphos)(anti-crotyl)OTf (Va): 1H: 0.9 (ddd, J1 = 6.6 Hz, J2 = 6.6 Hz, J3 = 6.6 Hz, 3H(Me), 3.0 (dd, J1=9.1 Hz, J2 = 14.1 Hz, 1H(Ha)), 4.2 (dd, J1 = 6.4 Hz, J2 = 6.1 Hz, 1H(Hb)), 4.4 (m, 1H, Hc)), 5.8 (ddd, J1=14.0 Hz, J2 = 7.7 Hz, J3=7.7 Hz, 1H(Hd)), 6.4-7.6 (m, Ar)

31P{1H}: 10.6 (d, J=40 Hz), 16.4 (d, J=40 Hz)

Pd(Sixantphos)(crotyl)OTf (VI s+a) was obtained in syn/anti ratio of 57 / 43. El.anal. (VIa+s) found: C: 56.31%, H: 4.35% (calc.: C: 55.88%, H: 4.46%)
Pd(Sixantphos)(syn-crotyl)OTf (Vis): 1H: 0.57 (s, 3H(Me-Si)), 0.61 (s, 3H(Me-Si)), 0.8 (ddd, J1=11.3 Hz, J2=6.3 Hz, J3=6.3 Hz, 3H(Me)), 3.4 (dd, J1=11.7 Hz, J2=11.7 Hz, 1H(Ha)), 3.55 (dd, J1=6.4 Hz, J2=6.4 Hz, 1H(Hb)), 4.4 (m, 1H(Hc)), 5.4 (ddd, J1=12.8 Hz, J2=12.8 Hz, J3=7.3 Hz, 1H(Hd)), 6.9-7.5 (m, Ar(syn and anti)), 7.7 (q, Ar(syn and anti))

31P{1H}: 9.8 (d, J=39.3 Hz), 10.6 (d, J=39.3 Hz)
Pd(Sixantphos)(anti-crotyl)OTf (Via): 1H: 0.57 (s, 3H(Me-Si)), 0.61 (s, 3H(Me-Si)), 0.9 (ddd, J1=6.2 Hz, J2=6.2 Hz, J3=6.2 Hz, 3H(Me)), 3.4 (dd, J1=11.7 Hz, J2=11.7 Hz, 1H(Ha)), 3.7 (dd, J1=7.1 Hz, J2=7.1 Hz,
\( \text{IH(Hb)}, 4.65 (\text{m}, \text{1H(Hc)}), 5.9 (\text{ddd}, J_1=13.8 \text{ Hz}, J_2=8.0 \text{ Hz}, J_3=8.0 \text{ Hz}, \text{1H(Hd)}), 6.9-7.5 (\text{m}, \text{Ar(syn and anti)}), 7.7 (\text{q}, \text{Ar(syn and anti)})) \)

\( ^{31}\text{P}[1\text{H}]: 5.8 (\text{d}, J=35.2 \text{ Hz}), 7.0 (\text{d}, J=35.2 \text{ Hz}) \)

4.6 References

[19] \( \beta \) obtained from the calculated (crotyl)Pd(bisphosphine) complexes

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