Palladium-catalyzed C-H and C-N bond formation

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Chapter 4

Palladium(0) Complexes with Bidentate Nitrogen and Phosphorus Ligands for the Stereoselective Hydrogenation of 1-Phenyl-1-propyne to (Z)-1-phenyl-1-propene

4.1 Introduction

The catalytic hydrogenation of unsaturated hydrocarbons has been extensively studied. In recent years chemo- and stereoselective hydrogenations of unsaturated carbon-carbon double and triple bonds have taken a fundamental role in organic synthesis, both in laboratory as well as in industry. The hydrogenation of carbon-carbon double bonds has been mostly described. Although the selective hydrogenation of internal alkynes to (Z)-alkenes is a very desirable tool, the hydrogenation of triple bonds has received much less attention. Various catalysts are suitable for this semi-hydrogenation reaction, many of which are heterogeneous, such as the Lindlar catalyst, nickel boride, and the "P2Ni" catalyst. There are also examples of homogeneous systems with various metals and ligands, but only a few exhibit a good selectivity towards a variety of alkynes with different functional groups. Examples of homogeneous catalysts with a high selectivity for the (Z)-alkene are the cationic Rh(I) systems of Schrock and Osborn, and the Cr(arene)(CO)3 complexes by Sodeoka and Shibasaki. Surprisingly little is known about the effect of the ligands on this reaction and very few systematic studies concerning this aspect have been reported in literature. In Chapter 2 the selective homogeneous Pd(0)-catalyzed hydrogenation of alkynes to (Z)-alkenes was reported, a

reaction tolerant of functional groups that proceeds under very mild conditions (25 °C, 1 bar H₂ pressure).

The precatalysts employed are the Pd(Ar-bian)(alkene) compounds, which had previously been used in the homogeneous hydrogenation of electron poor alkenes and in carbon-element bond formation reactions. This type of Pd(0) complex is able to hydrogenate a wide variety of alkynes to the corresponding (Z)-alkenes, with good to excellent selectivities (Scheme 4.1). Moreover, the complexes are completely stable under hydrogen until the substrate has been semi-hydrogenated to the alkene. It was observed that the selectivity in the hydrogenation of 1-phenyl-1-propyne strongly depends on the nature of the substituents attached to the imine nitrogens of the bian ligand. It was reported by Pelagatti et al. that the homogeneous hydrogenation of alkenes and alkynes can be also accomplished, under mild conditions, by using Pd(II) complexes containing potentially tridentate ligands as pre-catalysts for the acetylenic substrates a good chemoselectivity to the corresponding alkenes was found.

This chapter deals with the use of bidentate and tridentate nitrogen ligands of the pyridine-2-carbaldimine (pyca) type, of bipyridine (bipy) and of bidentate phosphorus-nitrogen ligands, as well as bidentate phosphorus ligands. The synthesis of a series of Pd(0) complexes of the type Pd(LL)(η²-alkene) complexes and their use as...
catalysts in the homogeneous stereoselective semi-hydrogenation of alkynes is also discussed. The pyca type ligands have already been applied before in the synthesis of Pd(0) complexes stabilized by electron-poor alkenes and the equilibrium of the alkene exchange has been studied. The only example known of homogeneous hydrogenation catalyzed by Pd(NN)(η²-alkene) complexes where NN is a di-imine or a pyridyl-imine ligand, apart from those reported, has been reported by Ruffo, employing diimines containing carbohydrate substituents as catalyst for the hydrogenation of several alkenes in water. It was found that the homogeneity of this process is strongly dependent on the pH of the reactant solution. The other types of ligands have not been applied before in the hydrogenation of alkynes. The pyca type ligands may, due to their expected hemilability, more or less readily promote an open coordination position for activation of hydrogen. This also applies to bipy and to the non rigid P-N ligands and 5d. Also the presence of two different donor sites allows for variable coordination of the two donor sites to incipient Pd-species dependent on the type of donor atom required for a stable intermediate, and might therefore lead to a more stable and active catalyst.

[Diagram with structures and labels]

Chart 4.1: The various ligands that were employed.
For a good comparison of the effect of different donor atoms, also the bidentate phosphorus ligands dppe and dppf were applied. We synthesized a variety of bidentate ligands and their palladium(0) complexes with dimethylfumarate (dmfu) as ancillary ligand (Chart 4.1).

Furthermore, the effect of a third nitrogen donor atom was studied (ligands 1), since these tridentate ligands might stabilize the incipient zerovalent Pd-species by forming tricoordinate 16-electron Pd(NNN) complexes.

4.2 Results and discussion

4.2.1 Ligand and complex synthesis

The pyca-ligands have been prepared by condensation of the pyridyl-2-carbonyl compound with the appropriate amine, in the presence of molecular sieves and, where necessary, a catalytic amount of \( p \)-toluenesulfonic acid.

![Scheme 4.2: Synthesis of P-N ligands 5c and 5d.](image-url)
The P-N ligands were prepared using a variety of techniques. The ligands 5c and 5d were prepared starting from 2-bromobenzaldehyde (Scheme 4.2).

First the aldehyde function was protected with ethyleneglycol, yielding the acetal, after which the diphenylphosphine moiety was introduced via a Grignard reaction. After deprotection of the aldehyde and condensation with the appropriate amine 5c and 5d were obtained. Ligand 6 was synthesized starting from benzonitrile, which was converted into the phenyloxazoline via a reaction with 2-aminoalcohol using zinc chloride as a template (Scheme 4.3)

\[
\text{Ph} \rightarrow \text{CH} \rightarrow \text{N} \rightarrow \text{PPh}_2
\]

Scheme 4.3: Synthesis of ligand 6.

The phosphine compound was obtained by ortho-lithiation using n-butyllithium and a subsequent reaction with chlorodiphenylphosphine. The same reaction using sec-butyllithium did not yield the desired product. Ligand 7 was obtained starting from 8-aminoquinoline which was converted into 8-bromoquinoline via the diazonium salt (Scheme 4.4).

\[
\text{Ph} \rightarrow \text{N} \rightarrow \text{PPh}_2
\]

Scheme 4.4: Synthesis of ligand 7.

The phosphine moiety was introduced by reaction with sec-butyllithium and chlorodiphenylphosphine after earlier attempts via a Grignard and also comparable routes using n-butyllithium and tert-butyllithium, which yielded a mixture of at least ten different phosphine compounds. Palladium complexes were obtained by reaction of Pd(dba)$_2$ (dba = dibenzylidene acetone) with the appropriate ligand, in the presence of
dimethylfumarate (dmfu) as ancillary ligand in a 1:1.1:1.1 molar ratio, according to Scheme 4.5 and Scheme 4.6

Scheme 4.5: Synthesis of Pd\(^{0}\)(NN)(dmfu) complexes.

Three different methodologies were followed: (i) stirring all reactants at room temperature in dry acetone for 8 to 36 hours, (ii) stirring the solution of the NN-ligand and dmfu in dry acetone while small portions Pd(dba)\(_2\) are added at 45 °C over several hours, or (iii) stirring all reagents in dry tetrahydrofuran (THF) for 2 hours. Most complexes could be obtained by the first method, except 11d, for which an extensive release of palladium black was observed without any formation of the complex. This was thought to arise from steric repulsions between the demanding t-Bu group bonded to the imine nitrogen and the ester groups of the dmfu; then the synthesis was attempted using the less steric maleic anhydride as ancillary ligand, but also here palladium black was formed and no product formation could be detected. However, when the second method was applied complex 11d was obtained in 58% yield, without extensive formation of palladium black. Also 12c could not be obtained using the first method, but it was successfully synthesized using the second method. Later on during the investigation the
third method, which involves the use of THF as solvent at room temperature, was adopted.

![Chemical structures and reactions]

Scheme 4.6: Synthesis of Pd^0(P-N)(dmfu) complexes.

This procedure proved to be superior to the former methods, since the reactions were complete within 2 hours, higher yields were obtained and the work-up was much easier. It was therefore extended to the synthesis of all complexes and also gave good results for 11d and 12c. However, the complex containing ligand 3d could not be obtained with any of the aforementioned methods, in this case extensive precipitation of palladium was observed (vide infra). NMR spectroscopy

Pd-complexes containing Bidentate Nitrogen Ligands

The $^1$H NMR spectra of the pyca-complexes (Table 4.1) all show similar characteristics. There is a noticeable, but not uncommon, low frequency shift of the alkene resonances of the dmfu, caused by the $\pi$-back donation of palladium into the alkene $\pi$-orbital. The
two halves of the alkene are not equivalent, they either show a broadened signal, indicating slow alkene rotation on the NMR time scale, as in 10a,b, 11e-g and 12a,b or two signals, as in 11c,d, 12c and 13c, that couple with each other to give doublets. The latter can only be explained assuming a rigid coordination of the dmfu to the palladium in these complexes, i.e. no or very slow rotation around the Pd-alkene axis occurs on the NMR time scale. The $^{3}J_{HH}$ coupling of about 9 to 10 Hz can be determined for the alkene protons of 11c,d, 12c and 13c, whereas for the complexes 10a, 11e-g, and 12a,b the severe broadening of the same signals does not allow determination of any coupling constant in those cases. The dmfu in complexes 11c,d, 12c and 13c experience hindrance from the sterically demanding i-Pr or t-Bu group, preventing the dmfu from freely rotating around the Pd-alkene bond. This leads to the non-equivalence of the alkene protons and thus to two anisochronous resonances and the $^{3}J_{HH}$ coupling is observed. In the case of complexes 10a,b, 11e-g and 12a,b with the less sterically demanding R-groups on the imine, the rotation is less hindered, leading to a severe broadening of the alkene signals. In complex 12c one can imagine that the methyls of the i-Pr group are placed so as to reduce the steric repulsions with the methoxy group of the dmfu and the methyl group of the imine carbon, and the rotation around the N(imine)-CH(CH$_{3}$)$_{2}$ bond is consequently hampered. Since the complexes 10a and 10b are not stable under hydrogenation conditions (vide infra), their dynamic behavior was not further investigated. In the case of complexes 11c, 12c and 13c, containing an i-Pr group on the imine, the i-Pr methyl groups become diastereotopic upon coordination of the ligand, and indeed two signals are observed for these methyl groups. Due to the low solubility of the complexes in most common non-chlorinated NMR solvents and to their extensive decomposition in chlorinated solvents, within the time required to obtain $^{13}$C-NMR spectra (usually more than 1 hour), high quality $^{13}$C-NMR data have been obtained only for 11c, 11d and 11g. At low temperatures (-20 °C), the solubility dropped so considerably that decent $^{13}$C-NMR signals were not observed even after measuring for 18 hours.
Table 4.1: Selected $^1$H NMR data for compounds 10-13.

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| a) In brackets are reported the coupling constants. b) JC=N 8.68 (s, 1H); Ph 7.40(m, 5H). c) CH(Me)$_2$ + 1H alkene 3.87 (m, 2H); CH$_3$ 1.46 (d, 3H, $^3$J$_{HH}$ = 6.0 Hz), 1.24 (d, 3H, $^3$J$_{HH}$ = 6.0 Hz). d) t-Bu 1.42 (s, 9H). e) N(CH$_3$)$_2$ 3.31 (s, 6H). f) N-CH$_2$CH$_3$ 3.90-3.70 (br, 2H); N-CH$_2$CH=CH$_2$ 1.88 (m, 2H); CH$_2$-CH$_3$ 0.97 (t, 3H, $^3$J$_{HH}$ = 7.5 Hz). g) CH$_2$CH$_2$OH 4.10-3.70 (br, 4H). h) Ph 7.44 (d, 2H, $^3$J$_{HH}$ = 7.4 Hz), 7.38 (pst, 1H, $^3$J$_{HH}$ = 7.4 Hz), 7.41 (d, 2H, $^3$J$_{HH}$ = 7.4 Hz). i) p-An 7.05 (d, 2H, $^3$J$_{HH}$ = 8.7 Hz), 6.92 (d, 2H, $^3$J$_{HH}$ = 8.7 Hz). k) CH(Me)$_2$ 4.10 (sep, 1H, $^3$J$_{HH}$ = 6.3 Hz), CH$_3$ 1.49 (d, 3H, $^3$J$_{HH}$ = 6.0 Hz), 1.17 (d, 3H, $^3$J$_{HH}$ = 6.0 Hz). l) CH(Me)$_2$ 3.86 (m), CH(CH$_3$)$_2$ 1.49 (d, 3H, $^3$J$_{HH}$ = 6.3 Hz), 1.24 (d, 3H, $^3$J$_{HH}$ = 6.3 Hz)

**Pd-complexes containing Bidentate P-N ligands**

The $^1$H NMR spectra of the different P-N complexes (14 c,d, 15 and 16) basically show the same features as the complexes containing pyca-type ligands. There is a very significant low-frequency shift of the alkene resonances of the dmfu and a broadening
of the alkene signal, indicative of slow alkene rotation on the NMR time scale in complex 15, or two separate alkene signals that couple with each other, as can been seen in complexes 14c,d and 16. This is indicative of slow or no rotation around the Pd-alkene axis on the NMR time scale. The alkene protons of 14c,d and 16 exhibit a $^{3}J_{HH}$ coupling of between 10.0 and 10.3 Hz and are comparable or somewhat larger than the corresponding pyca type complexes. The splitting of the alkene complexes in the complexes 14c and 14d can be explained by the steric hindrance experienced by the dmfu from the sterically demanding i-Pr and i-Bu group on the imine, preventing the alkene from freely rotating around the Pd-alkene bond, leading to the nonequivalence of the alkene protons and therefore to two anisochronous resonances with a $^{3}J_{HH}$ coupling. In the less sterically demanding ligand of complex 15 a very severe broadening of the alkene signal is observed, indicating a hindered rotation, but not so hindered as to lead to different signals. For complex 16, steric hindrance also leads to the splitting of the alkene proton resonances. In this system there is no sterically demanding R-group on the N-donor, which is a quinoline, but this is the only P-N ligand which forms a five membered ring with palladium upon coordination and is therefore likely to give rise to more steric crowding than comparable ligands that form a six membered ring upon coordination such as 14c,d and 15. Add to this the relatively bulky diphenylphosphine group and there is apparently enough steric crowding in 16 to lead to the two different signals for the alkene protons. For all four of the P-N complexes $^{13}$C-NMR data could be obtained, due to the higher stability of these complexes in chlorinated solvents. This can be attributed to the higher stabilizing qualities of phosphine donors as compared to nitrogen donors, due to the very good donor-acceptor qualities of phosphine donors. A very significant upfield shift of between 86 and 90 ppm is observed for the alkene carbons of the dmfu upon coordination, whereas the carbonyl carbons exhibit a downfield shift of about 9 ppm upon coordination. For all four complexes (14c,d, 15 and 16), the two alkene signals of the dmfu are different, indicating that the rotation of the alkene around the Pd-alkene axis is slow on the carbon NMR time scale. This splitting of the alkene signal was also observed with hydrogen NMR for complexes 14c,d and 16, but not for 15. The carbonyl signals are also split in 14c and 16, but not in complexes 14d and 15.
4.2.2 X-ray Crystal Structure of 12c

Single crystals of 12c·0.5 CH₂Cl₂ suitable for X-ray diffraction were obtained from a refrigerated dichloromethane solution. The compound crystallizes with two independent complex molecules and one dichloromethane molecule in the asymmetric unit. The pair of complex molecules, which do not display significant geometric differences, is related by a non-crystallographic two-fold axis parallel to z, simulating an orthorhombic Pnca space-group, perturbed by distortion of β to 93.369(2)°. The coordination sphere around the 16-electron Pd(0)center is formally square-planar, based on the NN chelation of ligand 3c and on a η² interaction with the alkene, with the N,N,C-C,Pd system planar within 0.08Å in both cases. However, the coordination may be conveniently described also as trigonal planar, by taking the midpoint M of the alkenic C-C bond as third coordination position: the ligand bite angle is 76.4(1) and 76.0(1)° respectively for the two complexes, and the Pd-M directions form angles ranging from 137.9(1) to 145.9(1)° with the Pd-N bonds. The geometry of ligand 3c can be compared with the one observed for analogous aldimine and cyclo-ketimine compounds (pyridineketimine)Pd(II)·(Cl)(CH₃C(O))¹⁸ and Pd(0)(aldimine)(fn) (fn = fumaronitrile = (E)-1,2-dicyano-ethene)¹⁹ complexes. In our system, the bond lengths C(Ar)-C(CH₃) = 1.489(5), 1.485(5), C(CH₃)=N = 1.282(5), 1.282(5), N-C(i-Pr) = 1.483(5), 1.486(5) Å are perfectly comparable with those observed for the above mentioned Pd(II) and Pd(0) compounds (ranges: 1.418-1.484, 1.262-1.286, 1.473-1.497 Å for the three bonds), showing that the metal oxidation state does not greatly influence either the electron distribution on the ligand conjugate system, or the Pd-N bond lengths, which in the Pd(0)-alkene systems (2.115, 2.160Å in the Pd(aldimine)(fn) complex, 2.120-2.165Å in the present compound) are comparable to the average of those shown by the Pd(II) complexes (ranges: 2.062-2.081Å for trans-Cl, 2.171-2.275Å for trans-C bonds) This is accomplished by the two above Pd(0) systems by extensive back donation into the highly electron withdrawing η* orbitals of the alkenes fn and dmfu. The C=C bond in the alkenic ligands is remarkably weakened, being 1.427Å for fn,¹⁹ and 1.422(5) and 1.423(5)Å in the present dmfu complex. The latter C=C bond is significantly weaker than the one observed in the only other Pd(0)(dmfu) complex structurally known (Pd(dmfu)(dimethylamino)ethyl-diphenyl-phosphino-ferrocene)²⁰ (1.409Å), while the
Pd-C bonds are correspondently stronger (2.055, 2.077 Å for 12c and 2.083, 2.154 Å for the phosphine containing system). The dmfu molecule is in this case slightly twisted around the C=C bond: C15-C11-C12-C13 = 154.8(3), C31-C27-C28-C29 = 154.6(4)°. The comparison of Pd-N distances between 12c and the above similar Pd(0)(aldimine)(fn) compound suggests that the replacement of the aldimine HC=N with a methyl group affects the strength of the Pd-N(imine) bond, which is stronger in Pd(0)(aldimine)(fn)) (2.115 Å) than in 12c (2.143(3) and 2.165(3) Å) respectively, whereas the reverse is observed for the Pd-N (pyridine) bond (2.160 Å in Pd(0)(aldimine)(fn) and 2.120(3) and 2.123(3) Å in 12c). The solid-state structure of one complex molecule is depicted in Figure 4.1.

Figure 4.1: X-ray crystal structure of 12c.

Selected bond lengths and angles for the structure are given in Table 4.2.
Table 4.2: Selected bond lengths and angles for 12c.

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</table>

Regarding the intramolecular arrangement of ligand 3c and dmfu around Pd in 12c, the shortest contact observed is between i-Pr and the nearest methoxy oxygen of dmfu: C9...O4 = 3.622(5) and C25...O6 = 3.622(6)Å for the two independent molecules, and in both cases the pair of i-Pr methyl groups point towards the oxygen atom, rather than being pushed away from it. This is a consequence of the steric hindrance of the CH₃C=N methyl group, which restricts the freedom of rotation of the i-Pr around N-C in the range Pd-N-C(H)-CH₃ = 25-90° for a minimum repulsive contact of 3.4Å (observed value 74° for both molecules). The oscillation of i-Pr group is further reduced between 65° and 90°.
by the presence of the CH₃O- group of the dmfu ligand (a rotation of the i-Pr group below 65° implies a close contact between i-Pr and CH₃O- of less than 3.4 Å). This could explain the fact that the obtainment of a stable complex containing the steric demanding ligand 3d is not possible. The equivalence of Pd-N-C-CH₃ torsion angles in the two independent molecules (73.6(4)° and 74.2(4)°) suggests that the shape and the moderately positive charge distributions on the methyls of the i-Pr group is capable to interact with the local partial negative charge on the methoxy oxygen, by means of medium range favorable electrostatic interaction. This would explain why in both molecules one i-Pr...dmfu distance is shorter than the other (3.622, 4.077 and 3.62, 3.992 for C(i-Pr)...O(dmfu) in the two molecules). A displacement from the arrangement found in the solid state would decrease the electrostatic attraction and increase the repulsive effect. This also explains why the rotation of the alkene around the bond to Pd is hindered in solution on the NMR time-scale.

4.2.3 Hydrogenation

The Pd(LL)(dmfu) complexes have been used in the hydrogenation of 1-phenyl-1-propyne as the substrate (Scheme 4.7).

![Scheme 4.7: Hydrogenation of 1-phenyl-1-propyne.](image)

This substrate was chosen because it gave, in the corresponding Pd(Ar-bian)(dmfu) catalyzed hydrogenations, a high, but not complete selectivity to (Z)-1-phenylpropene with concomitant formation of some (3-7%) of the (E)-isomer and 1-phenylpropane (6-35%). Hence, comparison would be relevant for this substrate. The results have been collected in Table 4.3.
### Table 4.3: Hydrogenation of 1-phenyl-1-propyne.

<table>
<thead>
<tr>
<th>Complex</th>
<th>% (Z)-alkene</th>
<th>% (E)-alkene</th>
<th>% alkane</th>
<th>% Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>10a(^b)</td>
<td>Immediate decomposition</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10b(^c)</td>
<td>Immediate decomposition</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11c</td>
<td>87</td>
<td>3</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>11d</td>
<td>78</td>
<td>3</td>
<td>6</td>
<td>87</td>
</tr>
<tr>
<td>11e</td>
<td>50</td>
<td>-</td>
<td>3</td>
<td>53</td>
</tr>
<tr>
<td>11f</td>
<td>68</td>
<td>2</td>
<td>7</td>
<td>77</td>
</tr>
<tr>
<td>11g</td>
<td>85</td>
<td>4</td>
<td>7</td>
<td>96</td>
</tr>
<tr>
<td>12a(^c)</td>
<td>Immediate decomposition</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12b</td>
<td>28</td>
<td>3</td>
<td>46</td>
<td>77</td>
</tr>
<tr>
<td>12c</td>
<td>76</td>
<td>4</td>
<td>6</td>
<td>86</td>
</tr>
<tr>
<td>13c</td>
<td>50</td>
<td>3</td>
<td>6</td>
<td>59</td>
</tr>
<tr>
<td>14c</td>
<td>87</td>
<td>4</td>
<td>9</td>
<td>100</td>
</tr>
<tr>
<td>14d</td>
<td>87</td>
<td>13</td>
<td>&lt;1</td>
<td>100</td>
</tr>
<tr>
<td>15</td>
<td>No reaction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>No reaction</td>
<td></td>
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<tr>
<td>17</td>
<td>74</td>
<td>3</td>
<td>3</td>
<td>80</td>
</tr>
<tr>
<td>18(^d)</td>
<td>80</td>
<td>2</td>
<td>18</td>
<td>100</td>
</tr>
</tbody>
</table>

\(^a\) Referred at the catalyst decomposition. \(^b\) Decomposed immediately when the substrate was added. \(^c\) Decomposed when subjected to a hydrogen atmosphere. \(^d\) Very slow reaction, 24 hours were needed to obtain full conversion.

The hydrogenations were carried out under mild conditions, 1 bar of H\(_2\)-pressure and 25 °C, using 1 mol % of catalyst.\(^8\) All complexes exhibited catalytic activity, approximately 1-1.5 hours were needed for 100 % conversion. The one exception is the Pd(dppe)(dmfu) catalysed hydrogenation, which proceeded very slowly but steadily and 24 hours were needed to obtain full conversion. In none of the cases an induction period was observed.


Pd(0)-complexes containing pyca-type ligands

The Pd(0) complexes containing pyca type ligands (10a,b, 11c-g, 12a-c and 13c) have been chosen because of their different electronic and steric properties. In this way a good comparison could be made on the effect of the substituents and the effect of the different substituents could be determined. The substituents on the imine nitrogen range from the slightly electron withdrawing phenyl and the weakly donating p-anisyl group, to the very electron-donating dimethyl- amino group. The various complexes show a markedly diverse behavior in catalysis, especially concerning the stability of the catalyst during the hydrogenation. At first, the complexes 10a and 10b were tested. As mentioned, the tridentate ligands could potentially stabilize the corresponding Pd(0) complexes under hydrogenation conditions, thanks to their chelating effect. However, we observed that complex 10a decomposes immediately upon addition of the alkyne, even before being subjected to a hydrogen atmosphere, whereas 10b decomposes within a few seconds after the introduction of hydrogen into the system. The most resembling bidentate analogues, complexes 12a and 12b, show a higher stability during the hydrogenation: complex 12a remains stable when the substrate is added, as compared to 10a which decomposes after addition of the substrate, and 12b is stable for some time under hydrogenation conditions, as compared to 10b, which decomposes immediately when subjected to hydrogenation conditions. Hence it can be concluded that the tridentate ligands exhibit no additional stabilizing effects. Therefore, the use of the tridentate ligands was not further pursued, and the investigation was directed to the complexes containing the pyridinecarboxaldehydine (pyca) type ligands.

The most stable catalyst proved to be 11c, which decomposes only after the complete conversion of the alkyne. The selectivity observed is high, with 87% of the (Z)-alkene formed, the main side product being 1-phenylpropane resulting from the overreduction of the alkene. All other catalysts decompose prior to reaching total conversion of the alkyne, either at a very high conversion, as in the case of the complexes 11d,g and 12c, or almost immediately after the start of the reaction, as in the case of 11e or 13c. From these results it can be concluded that the stability of the catalysts strongly depends on the nature of the imine substituents, which must be the result of a delicate balance between steric and electronic effects. The four most stable catalysts, 11c,d,g and 12c, all have a
good σ-donating alkyl group on the imine nitrogen. This can be considered beneficial for its coordinating capability. When 11c is compared to 12c, it is obvious that the additional inductive effect of the CH₃ doesn't have any positive effect on the stability, since 12c decomposes before full conversion of the alkyne (86% conversion). This might stem from the increased steric requirements of the ligand, as inferred by X-ray and NMR data. Also 11d is inferior to 11c with respect to the stability under hydrogenation conditions, as it decomposes before the full conversion of the substrate (decomposition at 87% of conversion); in this case it is obvious to invoke steric factors, which then seem more important than the inductive ones. When a methyl group is added in 6-position of the pyridine moiety as in 13c, the augmented electron donating capability of the heteroaromatic ring is not sufficient to overcome the encumbrance generated in the coordination plane, and a decreased stability is observed. Complex 13c in fact, decomposes at low (59%) conversion. In the case of 11e, with the very electron donating NMe₂-group, a high selectivity is observed, but palladium precipitation occurs in an early stage of the reaction (53% conversion). When the catalysts 12a and 12b are compared, the drastic effect of the electronic features of the ligand becomes apparent. With a relatively small change in electron withdrawing capability, a rather large difference in stability is observed. The catalyst with the phenyl group (12a) decomposes immediately when subjected to hydrogenation conditions, whereas the catalyst with the p-anisyl group (12b) remains stable for a longer time during the hydrogenation, leading to a 77% conversion. Since the steric requirements are the same, it seems apparent that the more electron donating capacity of the p-anisyl group has a beneficial effect on the lifetime of the catalyst. Worth noticing is the fact that complex 12b leads to the lowest chemo-selectivity observed with the employed complexes (46% of alkane). This can be explained by considering the absence of a partial steric crowding (for 12a,b) created in the coordination plane when alkyl groups are bound to the imine nitrogen (as in 11c,d,g and 12c), which allows only the coordination of the alkyne, excluding the poorer coordinating alkene. None of these Pd(NN)(alkene) complexes are as stable as the Pd(Ar-bian)(alkene) type complexes during the hydrogenations, although their stereoselectivity in alkyne hydrogenation (i.e. the selectivity towards the (Z)-alkene) is comparable. Several of the complexes are more stable than the previously studied complexes with the bidentate nitrogen ligands
bipy and dab.\textsuperscript{8} From these results it can be concluded that, in order to obtain a stable and active catalyst containing a pyca type ligand, a not too bulky and good $\sigma$-donor group on the imine nitrogen is required; excessive steric encumbrance in the coordination plane must be avoided. Regarding the imine carbon substituent, the proton is preferred to the methyl, due to torsion within the five membered palladacycle in case of the latter, decreasing the complex stability.

$Pd(0)$-complexes containing bidentate $P-N$ ligands

Apart from $Pd(NN)$ systems also four $Pd(0)$ complexes with $P-N$ ligands have been screened in the hydrogenation of 1-phenyl-1-propyne. The first two ($14c$ and $d$) can be considered to be the $P-N$ analogues of the $N-N$ complexes $11c$ and $d$. There is a small difference insofar that the pyca type ligands form five membered rings with $Pd(0)$ and $14c$ and $d$ form six membered rings. They have the same imine function with the same $i$-Pr and $t$-Bu groups and a diphenylphosphine group as donor instead of a pyridine nitrogen and are therefore also hemilabile and able to promote an open coordination position for activation of hydrogen. Complexes $14c$ and $d$ show a high stability under hydrogenation conditions, with no decomposition observed even after total consumption of the alkyne. In this respect these complexes are more comparable to the $Pd(0)$(bian) complexes than with the $Pd(0)$(pyca) complexes. Precatalysts $14c$ and $d$ also exhibit a very high selectivity towards the ($Z$)-alkene of 87\%, which is similar to the result for the best bian system (92\%). However, there is a remarkable difference between $14c$ and $14d$. With catalyst $14c$, the alkane is the main side-product and only little isomerization to the ($E$)-alkene is observed, while with $14d$, overreduction to the alkane is almost absent but isomerization to the ($E$)-alkene is a prominent side reaction. Where this noticeable difference stems from is not clear and cannot easily be explained from the small difference between an $i$-Pr group and a $t$-Bu group. Complex $11c$ is also stable until total consumption of the alkyne, but decomposes immediately after that and the complexes with pyca type ligands do not even last that long. Clearly $14c$ and $14d$ are superior to their pyca type analogues. The higher stability of these complexes containing $P-N$ ligands can be explained by the presence of a phosphine donor with its very good donating qualities. In combination with the very flexible imine function, this results in stable and selective precatalysts which are useful for the selective hydrogenation of
alkynes. Complexes 15 and 16 however do not exhibit a measurable catalytic activity. They remain stable under hydrogen atmosphere but after eight hours of being subjected to hydrogenation conditions no consumption of the alkyne had occurred. This might be explained by the fact that these ligands are less hemilabile, in case of 15, or are quite rigid, which prevents an easy dissociation of the quinoline nitrogen as in the case of 16.

Pd(0)-complexes containing bipyridine and dppe

For a final comparison between different ligand systems containing nitrogen and phosphorus donors, the Pd(0) complexes of bipyridine (17) and dppe (18) with dmfu were tested as precatalysts in the hydrogenation of 1-phenyl-1-propyne. The bipy complex 17 is also very selective towards the (Z)-alkene as long as it remains stable. This complex, however, decomposes at about 80% conversion and has a stability that is comparable to most of the pyca type ligands except 11c. Clearly a more donating second donor atom is needed than a pyridine nitrogen. The dppe containing complex 18 is also a very stable precatalyst; the same as the other phosphorus containing complexes (14c,d, 15 and 16). It is somewhat surprising that this complex shows catalytic behaviour at all, considering the behaviour of 15 and 16, which do not exhibit any catalytic behaviour over a period of 8 hours, and the fact that 18 has two very donating atoms and can hardly be considered as a hemilabile ligand. The selectivity of 80% toward the (Z)-alkene is much less than that of all the other stable precatalysts, which exhibit a selectivity of 92% for the bian system and 87% for the other systems. There is an especially large amount of alkane being formed, which increases steadily throughout the reaction period while the underlying ratio between (Z)-alkene, (E)-alkene and alkane remains the same.

4.3 Conclusions

A variety of palladium complexes have been used for the selective hydrogenation of 1-phenyl-1-propyne. These include complexes containing bidentate N-N, P-N and P-P ligands. In general it can be said that all complexes containing a phosphorus donor are stable under hydrogenation conditions, even after total consumption of the alkyne, but when these ligands do not posses one hemilabile donor site such as the imine group in
14c and 14d, the reaction is either very slow as with the P-P ligand dppe (18), or doesn’t take place as with 15 and 16. The bidentate nitrogen ligands show a much lower stability and only one remains stable until total consumption of the alkyne (11c). All complexes, with the exception of 12b and 18, exhibit the same inherent selectivity, i.e. the selectivity before an eventual decomposition, towards the (Z)-alkene. There are very noticeable differences in the hydrogenation behaviour of the complexes with pyca-type ligands that can be explained from the steric and electronic properties of the different substituents, both those on the imine nitrogen and carbon and those on the pyridine ring. The nature of the substituent on the imine nitrogen seems to be the most determining factor regarding the stability of the various pre-catalysts under hydrogenation conditions; the better the σ-donating capacity of the substituent, the higher the stability of the complex. Furthermore, it was shown that increasing the steric bulk of the ligand results in lower stability, even when these substituents might have beneficial inductive effects. The inherent selectivities of these complexes in the hydrogenation of 1-phenyl-1-propyne, except for 12b and 18, are all comparable with each other and somewhat lower than that with the best known Pd(Ar-bian) system.8 Their stability, with the exception of 11c, 14c and 14d and 18 is inferior when compared to that of the Pd(Ar-bian) systems.

4.4 Experimental section

4.4.1 General Methods

Chemicals were obtained from Acros Chimica and Aldrich Chemical Co. All synthesis of ligands, complexes and hydrogenations were carried out in dried glasswork, using standard Schlenk techniques under an atmosphere of purified nitrogen. THF and Et₂O were distilled from sodium/benzophenone, acetone was distilled from K₂CO₃, and dichloromethane from CaH₂. Primary alkyl amines were distilled before use and stored under nitrogen on molecular sieves (4 Å). The aldehydes and ketones were distilled prior to use and stored under nitrogen. Other chemicals were used as received. The starting materials dba²¹ and Pd(dba)₂²² were prepared according to literature procedures. ¹H and ¹³C NMR data were recorded on a Bruker AMX300 or a Varian Mercury300 spectrometer (¹H: 300.13 MHz, ¹³C: 75.47 MHz), using either CDCl₃ as a solvent and as an external reference (¹H, 7.26 ppm; ¹³C, 77.0 ppm) or CD₂Cl₂ (¹H, 5.32 ppm; ¹³C, 54.0 ppm). IR-spectra were recorded on a Nicolet 5PC FT-IR or a Bio-Rad FTS-7 using a KBr pellet. The gaschromatographic analyses were performed on a Dani HP 3800 flame-ioni-
4.4.2 Ligand synthesis

Most of the ligands described below have been reported before, usually well characterized, for the ligand see the references cited: 1a, 2c,d, 2e, 2f, 2g, 2a, 23b, 23c, 23d, 23e, 23f, 4c. The ligands were synthesized using somewhat different methods than reported before, and these methods are described below. For the atom labelling of the ligands for NMR see Chart 4.1.

**2,6-di(N-phenylcarbaldimino)pyridine (1a)**

A solution of 2,6-pyridinediacetaldehyde (0.71 g, 5 mmol) and aniline (1.14 g, 12.5 mmol) in 50 ml of absolute ethanol was refluxed for half an hour. Upon cooling a white powder precipitated. The solution was filtered, and the powder was recrystallized from absolute ethanol and dried in vacuo. Yield: 0.57 g (40%) of a white powder. $^1$H NMR: δ 8.69 (s, 2H, H$_7$), 8.32 (d, 2H, H$_3$-H$_5$, $^3$J$_{HH}$ = 7 Hz), 7.96 (pt, 1H, H$_4$, $^3$J$_{HH}$ = 7 Hz), 7.34 (m, 10H, Ph). IR (cm$^{-1}$): v(C=N) = 1567 w. m.p. (°C): 134. Anal. Calc. for C$_{19}$H$_{15}$N$_3$: C, 80.07; H, 5.26; N, 14.73. Found: C, 79.55; H, 5.27; N, 14.52.

**2,6-di(N-4-methoxyphenylcarbaldimino)pyridine (1b)**

The same procedure was used as for compound 1a, using the same mole amounts, but in this case a white solid precipitated immediately; this was filtered, washed with diethyl ether and dried in vacuo. Yield: 0.35 g (72%) of a white powder. $^1$H NMR: δ 8.71 (s, 2H, H$_7$), 8.25 (d, 2H, H$_3$-H$_5$, $^3$J$_{HH}$ = 8 Hz), 7.91 (pt, 1H, H$_4$, $^3$J$_{HH}$ = 8 Hz), 7.37 (d, 4H, p-An, $^3$J$_{HH}$ = 9 Hz), 6.97 (d, 4H, p-An, $^3$J$_{HH}$ = 9 Hz), 3.85 (s, 6H, OCH$_3$). IR (cm$^{-1}$): v(C=N) = 1596 w. m.p. (°C): 156. Anal. Calc. for C$_{21}$H$_{19}$N$_3$O$_2$: C, 73.11; H, 5.55; N, 12.17. Found: C, 72.99; H, 5.40; N, 11.96.

**2-(N-2-propanecarbaldimino)pyridine (2c)**

A solution of 2-pyridinediacetaldehyde (0.55 g, 5 mmol) and 2-isopropylamine (3.0 g, 50 mmol) was stirred in 50 ml of dry diethyl ether in the presence of activated molecular sieves (4 Å) for 30 minutes. The solution was filtered, the collected mol sieves washed with dry diethyl ether and the solvent removed in vacuo. Yield: 0.14 g (97%) of a yellow oil. $^1$H NMR: δ 8.57 (d, 1H, H$_6$, $^3$J$_{HH}$ = 5 Hz), 8.33 (s, 1H, H$_7$), 7.92 (d, 1H, H$_3$, $^3$J$_{HH}$ = 8 Hz), 7.65 (pt, 1H, H$_4$, $^3$J$_{HH}$ = 8 Hz), 7.22 (pt, 1H, H$_5$, $^3$J$_{HH}$ = 5 Hz), 3.60 (sept, 1H, CH(CH$_3$)$_2$, $^3$J$_{HH}$ = 6 Hz), 1.21 (d, 6H, CH(CH$_3$)$_2$, $^3$J$_{HH}$ = 6 Hz). IR (cm$^{-1}$): v(C=N) = 1526 w.
2-(N-t-butanecarbaldimino)pyridine (2d)

The same procedure was used as for compound 2c, using the same mole amounts. The excess of amine was varied between 1.1 and 10 equivalents. Yield: 0.16 g (98%) of a yellow oil. 

$^1$H NMR: 2d, δ 8.55 (d, 1H, H₆, $^3$J_HH = 5 Hz), 8.29 (s, 1H, H₇), 7.94 (d, 1H, H₃, $^3$J_HH = 9 Hz), 7.63 (p(t, 1H, H₄, $^3$J_HH = 9 Hz), 7.20 (p(t, 1H, H₅, $^3$J_HH = 5 Hz), 1.24 (s, 9H, CH₃).

2-(N-dimethylaminocarbaldimino)-pyridine (2e)

The same procedure was used as for compound 2c, using the same mole amounts. Yield: 0.15 g (>99%) of a yellow oil. 

$^1$H NMR: δ 7.92 (d, 1H, H₆, $^3$J_HH = 5 Hz), 7.24 (d, 1H, H₃, $^3$J_HH = 8 Hz), 7.08 (p(t, 1H, H₄, $^3$J_HH = 5 Hz), 6.72 (s, 1H, H₇), 6.55 (p(t, 1H, H₅, $^3$J_HH = 5 Hz), 2.48 (s, 6H, CH₃).

2-(N-butanecarbaldimino)pyridine (2f)

The same procedure was used as for compound 2c, using the same mole amounts. Yield: 0.16 g (>99%) of a yellow oil. 

$^1$H NMR: δ 8.47 (d, 1H, H₆, $^3$J_HH = 4 Hz), 8.21 (s, 1H, H₇), 7.83 (d, 1H, H₃, $^3$J_HH = 9 Hz), 7.54 (p(t, 1H, H₄, $^3$J_HH = 9 Hz), 7.11 (p(t, 1H, H₅, $^3$J_HH = 5 Hz), 3.51 (t, 2H, CH₂-N, $^3$J_HH = 6 Hz), 1.56 (m, 2H, CH₂), 1.27 (m, 2H, CH₂), 0.78 (t, 3H, CH₃, $^3$J_HH = 7 Hz).

2-(N-2-ethanolcarbadimino)-pyridine (2g)

The same procedure was used as for compound 2c, using the same mole amounts. The resulting oil was washed with ethanol to remove the excess of the high boiling amine. Yield: 0.15 g (99%) of a yellow oil. 

$^1$H NMR: δ 8.63 (d, 1H, H₆, $^3$J_HH = 5 Hz), 8.41 (s, 1H, H₇), 7.92 (d, 1H, H₃, $^3$J_HH = 9 Hz), 7.70 (p(t, 1H, H₄, $^3$J_HH = 9 Hz), 7.30 (p(t, 1H, H₅, $^3$J_HH = 5 Hz), 3.95 (t, 2H, CH₂OH, $^3$J_HH = 6 Hz), 3.81 (t, 2H, CH₂-N, $^3$J_HH = 6 Hz), 2.75 (br, 1H, OH).

2-(N-phenylacetimino)pyridine (3a)

A solution of 2-acetylpyridine (0.61 g, 5 mmol) and a slight excess (5.5 mmol) of aniline (0.51 g) in 15 ml of dry toluene, was heated in the presence of activated molecular sieves (4 Å) to 120 oC in an Ace pressure tube for 72 hours. The reaction mixture was filtered and the solvent evaporated. The remaining oil was washed with ethanol and dried in vacuo. Yield: 0.82 g (83%) as a yellow oil. 

$^1$H NMR: δ 8.67 (d, 1H, H₆, $^3$J_HH = 5 Hz), 8.27 (d, 1H, H₃, $^3$J_HH = 8 Hz), 7.78 (p(t, 1H, H₄, $^3$J_HH = 8 Hz), 7.36 (p(t, 1H, H₅, $^3$J_HH = 5Hz), 2.36 (s, 3H, CH₃).
2-(N-4-methoxyphenylacetimino)pyridine (3b)

The same procedure was used as for compound 3a, using 0.62 g of p-anisidine. Yield 84% as a red oil. \( ^1H \) NMR: \( \delta 8.64 \) (d, 1H, H\(_6\), \(^3J_{HH} = 5 \) Hz), 8.24 (d, 1H, H\(_3\), \(^3J_{HH} = 8 \) Hz), 7.76 (p, 1H, H\(_4\), \(^3J_{HH} = 8 \) Hz), 7.34 (p, 1H, H\(_5\), \(^3J_{HH} = 5 \) Hz), 6.91 (d, 2H, p-An, \(^3J_{HH} = 7 \) Hz), 6.79 (d, 2H, p-An, \(^3J_{HH} = 7 \) Hz), 3.81 (s, 3H, OCH\(_3\)), 2.37 (s, 3H, CH\(_3\)).

2-(N-2-propaneacetimino)pyridine (3c)

The procedure was identical to that reported for 3a except for the reaction time which was 48 hours long. Yield: 0.58 g (79%) as a yellow oil. \( ^1H \) NMR: \( \delta 8.52 \) (d, 1H, H\(_6\), \(^3J_{HH} = 6 \) Hz), 7.99 (d, 1H, H\(_3\), \(^3J_{HH} = 8 \) Hz), 7.50 (p, 1H, H\(_4\), \(^3J_{HH} = 8 \) Hz), 7.22 (p, 1H, H\(_5\), \(^3J_{HH} = 6 \) Hz), 3.86 (sept, 1H, CH(\(CH_3\))\(_2\), \(^3J_{HH} = 6 \) Hz), 2.31 (s, 3H, CH\(_3\)), 1.18 (d, 6H, CH\(_3\)).

2-(N-\(t\)-butaneacetimino)pyridine (3d)

The procedure was identical to that reported for 3a except for the reaction time which was 48 hours long. Yield: 0.58 g (65%) as an orange oil. \( ^1H \) NMR: \( \delta 8.58 \) (d, 1H, H\(_6\), \(^3J_{HH} = 5 \) Hz), 7.94 (d, 1H, H\(_3\), \(^3J_{HH} = 9 \) Hz), 7.74 (p, 1H, H\(_4\), \(^3J_{HH} = 9 \) Hz), 7.40 (p, 1H, H\(_5\), \(^3J_{HH} = 5 \) Hz), 2.66 (s, 3H, C(\(CH_3\))=N), 1.31 (s, 9H, \(t\)-Bu).

2-(N-2-propanecarbaldimino)-6-methylpyridine (4c)

The same procedure was used as for compound 2c except 6-methyl-2-pyridinecarbaldehyde was used. Yield: 0.16 g (99%) of a yellow oil. \( ^1H \) NMR: \( \delta 8.35 \) (s, 1H, H\(_7\)), 7.79 (d, 1H, H\(_3\), \(^3J_{HH} = 8 \) Hz), 7.59 (p, 1H, H\(_4\), \(^3J_{HH} = 8 \) Hz), 7.14 (d, 1H, H\(_5\), \(^3J_{HH} = 7 \) Hz), 3.60 (sept, 1H, CH(\(CH_3\))\(_2\), \(^3J_{HH} = 6 \) Hz), 2.56 (s, 3H, CH\(_3\)(py)), 1.25 (d, 6H, CH(\(CH_3\))\(_2\), \(^3J_{HH} = 6 \) Hz).

2-bromobenzaldehyde-ethylene acetal

To a solution of 2-bromobenzaldehyde (20.0 g, 108 mmol) and ethyleneglycol (20 mL, 359 mmol) was added a catalytic amount of p-toluenesulphonic acid, and the solution was refluxed until no more water was produced (15 h) using a Dean-Stark apparatus. The mixture was concentrated and the resulting oil was dissolved in dichloromethane. This solution was washed twice with 2M NaOH (15mL) and three times with brine (15 mL). The solution was dried on MgSO\(_4\), filtered and concentrated. The resulting oil was destilled in vacuo giving a colorless oil. Yield: 21.54 g (94 mmol; 87%). \( ^1H \) NMR: \( \delta 7.59 \) (d, 1H, \(^3J_{HH} = 7.8 \) Hz), 7.53 (d, 1H, \(^3J_{HH} = 7.8 \) Hz), 7.33 (d, 1H, \(^3J_{HH} = 7.8 \) Hz), 7.18 (t, 1H, H, \(^3J_{HH} = 7.8 \) Hz), 6.09 (s, 1H, H\(_7\)), 3.97-4.12 (m, 4H, H\(_8\)+H\(_9\)). \( ^{13}C \) NMR: \( \delta 136.96, 133.17, 130.89, 128.16, 127.69, 123.17, 102.79 \) (CH\(_{acetal}\)), 65.67 (CH\(_2\) _acetal\)).
2-diphenylphosphino-benzaldehyde-ethylene acetal

In a three-necked flask magnesium (1.6 g, 65.8 mmol) in dry THF (150 mL) was activated by addition of a few drops of dibromoethane. To this mixture was added 2-bromobenzaldehyde-ethylene acetal (13.64 g, 59.6 mmol) in a dropwise fashion and the resulting reaction mixture was stirred for 1 hour. At a temperature of between -10 °C and 0 °C chlorodiphenylphosphine (10.7 mL, 59.6 mmol) was added dropwise. The mixture was stirred for 1 hour, the solution was hydrolyzed at -10 °C with 80 mL of a concentrated NH₄Cl solution and the product was extracted with toluene (3x 150 mL). The resulting solution was filtered over silica and the THF and toluene were evaporated in vacuo. The resulting light yellow oil was crystallised from methanol, yielding white crystals. Yield: 7.76 g (23.2 mmol, 39 %). ¹H NMR: δ 7.72-6.95 (m, 14 H), 6.44 (d, 1H, JHP = 4.8 Hz), 4.11-3.95 (m, H8+9, 4H). ¹³C NMR: δ 149.86 ,, 142.51  ,  141.93 , 137.37 , 136.76 , 136.64 , 101.97 (CHacetal), 65.64 (CH2 acetal). ³¹P-NMR (121.5 MHz, CDCl₃) δ -15.85.

(2-diphenylphosphanylbenzylidene)-iso-propylamine (5c)

To a solution of 2-diphenylphosphinebenzaldehyde-ethylenecacetal (1.0 g, 3.0 mmol) in dry THF (30 mL) was added an excess of concentrated HCl, and the solution was refluxed for 1.5 hours. The solution was washed with a concentrated Na₂CO₃ solution (3 x 25 mL) and dried on MgSO₄. To the resulting solution of 2-diphenylphosphine-benzaldehyde in THF was added an excess of isopropylamine and a catalytic amount of p-toluenesulphonic acid and this solution was refluxed for 2 hours in the presence of molsieves (3 Å). The resulting solution was washed with concentrated Na₂CO₃ solution (2 x 10 mL). After evaporation of the solvent a brown oil was collected, form which white crystals were obtained by crystallization from acetone. Yield: 0.63 g (1.9 mmol, 64 %). ¹H NMR: δ 8.88 (d, H7, 1H, JHP = 4.8 Hz), 7.99-6.83 (m, 14H), 3.39 (m, H8, 1H), 1.05 (d, H9, 6H, JHH = 6.0 Hz). ¹³C NMR: δ 156.89 (d, Cimine, JCP = 12.5 Hz), 139.76 , 139.44 , 137.23 , 136.87 , 136.54 , 136.26 , 134.08 , 133.93 , 132.87 , 129.85 , 128.76 , 128.50 , 127.46 , 61.21 (CH₃-prop), 23.82 (CH₃-i-prop) ³¹P-NMR (121.5 MHz, CDCl₃) δ -12.84.

(2-diphenylphosphanylbenzylidene)-tert-butylamine (5d)

The same procedure was used as for compound 5c, except that the product was obtained as a light yellow powder after evaporation of the solvent and didn’t need to be recrystallized. Yield: 73 % . ¹H NMR: δ 8.79 (d, H7, 1H, JHP = 3.0 Hz), 7.95-6.82 (m, 14H), 1.07 (s, H9, 9H) ¹³C NMR: δ 154.64 (d, Cimine, JCP = 12.4 Hz), 140.37 , 140.13 , 137.73 , 137.43 , 136.84 , 136.68 , 134.55 , 134.40 , 132.98 , 129.95 , 128.83 , 128.77 , 127.61 , 127.53 , 57.94 (CMe₃), 29.70 (C(CH₃)₃). ³¹P-NMR (121.5 MHz, CDCl₃) δ -16.55.

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8-bromoquinoline

To a solution of 8-aminoquinoline (5.0 g, 34.7 mmol) in water (75 mL) was added HBr (36 mL of a 33 % solution in acetic acid), ice (50 g) and NaNO₂ (2.5 g in 20 mL of water, 36.2 mmol). This darkened solution was the added dropwise to a solution of CuBr (8.0 g, 41.8 mmol) in HBr (100 mL of a 33 % solution in acetic acid) at 70 °C. Upon cooling a red precipitate was formed, which was filtered and washed with water. The precipitate was treated with a concentrated NaOH solution and extracted with diethyl ether. The ethereal layer was collected, the diethyl ether evaporated and the resulting brown oil was distilled in vacuo, resulting in a colorless oil. Yield: 2.22 g (10.7 mmol, 31 %).

H NMR: δ 8.91 (dd, H₈, 1H, 3J_H₈H₇ = 4.2 Hz, 4J_H₈H₆ = 1.5 Hz), 8.25 (dd, H₆, 1H, 3J_H₆H₇ = 7.9 Hz, 4J_H₆H₈ = 1.5 Hz), 8.04 (dd, H₂, 1H, 3J_H₂H₃ = 7.6 Hz, 4J_H₂H₄ = 1.5 Hz), 7.83 (dd, H₄, 1H, 3J_H₄H₃ = 8.1 Hz, 4J_H₄H₅ = 1.5 Hz), 7.52 (dd, H₇, 1H, 3J_H₇H₆ = 7.9 Hz, 4J_H₇H₈ = 4.2 Hz), 7.41 (ps, H₃, 1H, 3J_H₃H₁ = 7.8 Hz).

13C NMR: δ 160.61 (HCN_quinoline), 144.36 (C_qN), 137.05, 133.12, 129.51, 127.70, 126.83, 123.48, 121.72.

2-(-(2-(diphenylphosphino)phenyl)-oxazoline (6)

To a solution of 2-phenyl-2-oxazoline (3.68 g, 25 mmol) and tetramethylethylenediamine (4.5 mL, 30 mmol) in dry THF (100 mL) was added at -60 °C a 1.6 M solution of n-BuLi in hexanes (18.75 mL, 30 mmol). The solution turned a dark red instantaneously and soon after this a brownred suspension was formed. This suspension was stirred for 1.5 h at temperatures of between -45 and -60 °C before at a temperature of -45 °C chlorodiphenylphosphine (5.4 mL, 30 mmol) was added. The mixture turned a light yellow and later a dark red and was stirred overnight at room temperature. The mixture was quenched with a saturated ammonium chloride solution and the organic products were extracted with ether. The resulting solution was concentrated and purified by column chromatography (ether/hexanes mixtures). Yield: 1.72 g (5.2 mmol, 21 %).

H NMR: δ 7.85 (m, H₁, 1H), 7.25-7.46 (m, HAr, 12H), 6.89 (m, H₄, 1H), 4.07 (t, H₅, 2H, 3J_H₅H₄ = 9.9 Hz), 3.74 (t, H₆, 2H, 3J_H₆H₇ = 9.9 Hz).

13C NMR: δ 164.39 (d, C_imine, 3J_CP = 3.1 Hz), 138.98, 138.78, 137.87, 137.78, 134.02, 133.85, 133.70, 133.56, 133.55, 131.84, 131.69, 131.14, 130.29, 129.68, 129.66, 128.79, 128.59, 128.54, 128.49, 128.32, 128.26, 128.20, 128.13, 128.03, 127.87, 67.38 (O-C_oxazoline), 55.15 (N-C_oxazoline).

31P-NMR (121.5 MHz, CDCl₃) δ -4.29.

8-(diphenylphosphino)quinoline (7)

To a solution of 8-bromoquinoline (1.0 g, 4.8 mmol) in dry THF at -78 °C was added sec-butyl-lithium (3.7 mL of 1.3 M solution in hexane, 4.8 mmol) in a dropwise fashion. After 5 minutes at -78 °C, chlorodiphenylphosphine (1.16 g, 5.3 mmol) was added and the mixture was allowed to warm up to roomtemperature. The solution was neutralized with HCl-solution (3M), the THF
layer was collected and the solvent removed under reduced pressure. The resulting yellow oil was dissolved in dichloromethane and washed with brine. The dichloromethane solution was dried on MgSO$_4$, filtered and the dichloromethane was removed in vacuo, yielding a yellow oil. Yield: 1.05 g (3.6 mmol, 76 %). $^1$H NMR: $\delta$ 8.88 (d, H$_8$, 1H, $^3$J$_{HH}$ = 4.0 Hz), 8.17 (d, H$_6$, 1H, $^3$J$_{HH}$ = 8.2 Hz), 7.83 (d, H$_4$, 1H, $^3$J$_{HH}$ = 8.0 Hz), 7.44 (pt, H$_3$, 1H, $^3$J$_{HH}$ = 7.5 Hz), 7.40 (dd, H$_7$, 1H, $^3$J$_{HH}$ = 8.2 Hz, $^3$J$_{HH}$ = 4.0 Hz), 7.34 - 7.13 (m, 10H), 7.14 (dd, H$_2$, $^3$J$_{HH}$ = 7.0 Hz, $^3$J$_{HH}$ = 4.0 Hz). $^{13}$C NMR: $\delta$ 149.79 (HCN$_{quinoline}$), 138.40 , 138.22 , 137.52 , 137.36 , 136.12 , 134.29 , 134.22 , 134.06 , 128.70 , 128.46 , 128.33 , 128.27 , 126.50 , 121.34 . $^{31}$P-NMR (121.5 MHz, CDCl$_3$) $\delta$ -14.44.

4.4.3 Complex synthesis

For the atom labelling of the ligands for NMR see Chart 4.1. For the $^1$H NMR data of complexes 1-13 see Table 4.1. Pd(0)(dppe)(dmfu) was prepared according to an existing procedure.$^{25}$

**Pd(2,6-di(N-phenylcarbaldimino)pyridine)(dmfu) (10a)**

A solution of Pd(dba)$_2$ (0.57 g, 1 mmol), 1a (0.31 g, 1.1 mmol), and dmfu (0.16 g, 1.1 mmol) in 50 ml of dry acetone was stirred for 8 hours at room temperature. A brown solid formed, which was filtered and washed repeatedly with diethyl ether to remove dba. The resulting solid was dissolved in dichloromethane and filtered over Celite to remove traces of Pd(0). The resulting solution was concentrated, the product precipitated by addition of n-hexane, filtered and dried in vacuo. Yield 0.42 g of a brown powder, (78 %). $^1$H NMR: see Table 4.1. IR (cm$^{-1}$): v(C=C + C=O) = 1678 s; v(C=N) = 1581 w. d.p. ($^0$C): 154. Anal. Calc. for C$_{25}$H$_{23}$N$_3$O$_4$Pd: C 56.03, H 4.29, N 7.84. Found: C 55.59, H 4.09, N 7.59.

**Pd(2,6-di(N-4-methoxyphenylcarbaldimino)pyridine)(dmfu) (10b)**

The procedure was similar to that of 10a using 1b (0.37 g, 1.1 mmol) as a ligand. Yield: 0.48 g (75%) of a brown powder. d.p. ($^0$C): 154. Anal. Calc. for C$_{27}$H$_{27}$N$_3$O$_6$Pd: C, 54.46; H, 4.57; N, 7.05. Found: C, 53.90; H, 4.34; N 6.88. $^1$H NMR: owing to dynamic processes it was not possible to unambiguously attribute the signals. IR (cm$^{-1}$): v(C=C + C=O) = 1693 s; v(C=N) = 1558 w.
Pd(2-(N-2-propanecarbaldimino)pyridine)(dmf) (11c)

The procedure was similar to that of 10a using 2c (0.16 g; 1.1 mmol) as a ligand. Yield: 0.34 g (85%) as a yellow solid. Anal. Calc. for C_{15}H_{20}N_{2}O_{4}Pd: C, 42.06; H, 4.75; N, 10.51. Found: C, 42.35; H, 4.78; N, 10.32. $^1$H NMR: see Table 4.1. $^{13}$C NMR: δ 160.29 (C$_7$), 153.87 (C$_2$), 152.45 (C$_6$), 138.84 (C$_4$), 128.50 (C$_5$), 126.50 (C$_3$), 62.81 (CH$_3$ ester), 51.20 (CH$_3$-Py), 50.86 (CH$_3$-Py), 42.13 (HC=CH consumed), 41.14 (HC=CH consumed), 24.00 (CH$_3$-Py), 23.64 (CH$_3$-Py), the carbonyl signal was not observed. IR (cm$^{-1}$): ν(C=O) = 1671 s; ν(ON) = 1592 w.

Pd(2-(N-ß-butancarbadimino)pyridine)(dmf) (11d)

1.1 mmol of 2d (0.18 g) in 40 ml of acetone at 45 °C in the presence of 1.1 mmol (0.16 g) of dmf. 0.57 g (1.0 mmol) of Pd(dba)$_2$ was added by small portions within 2 hours, with the care of observing the disappearance of the purple color of the Pd(dba)$_2$ between every addition. The solvent was then removed under reduced pressure, the residual dissolved in dichloromethane and filtered through Celite. The product was precipitated by addition of diethyl ether. Yield: 0.244 g (58%). $^1$H NMR: see Table 4.1. $^{13}$C NMR: δ 175.14 + 174.38 (C=O), 157.74 (C$_7$), 154.77 (C$_2$), 152.18 (C$_6$), 138.81 (C$_4$), 128.38 (C$_5$), 126.93 (C$_3$), 61.33 (CH$_3$ ester), 51.20 + 50.83 (C t-Bu), 42.16 + 41.41 (CH alkene), 29.60 (CH$_3$ t-Bu). Anal. Calc. for C$_{16}$H$_{22}$N$_2$O$_4$Pd: C, 46.56; H, 5.37; N, 6.79. Found: C, 46.31; H, 5.40; N, 6.46. IR (cm$^{-1}$): ν(C=O) = 1685 s; ν(C=N) = 1591 w.

Pd(2-(N-dimethylaminocarbaldimino)-pyridine)(dmf) (11e)

The procedure was similar to that of 10a using 2e (0.16 g, 1.1 mmol), as a ligand except that the reaction required 16 hours to go to completion. Yield: 0.33 g (82%) as a yellow solid. Anal. Calc. for C$_{14}$H$_{19}$N$_2$O$_4$Pd: C, 42.06; H, 4.75; N, 10.51. Found: C, 42.35; H, 4.78; N, 10.32. $^1$H NMR: see Table 4.1. $^{13}$C NMR data could not be collected due to the low solubility and stability of the complex in deuterated NMR solvents. IR (cm$^{-1}$): ν(C=O) = 1674 w; ν(C=N) = 1596 w.

Pd(2-(N-butancarbadimino)pyridine)(dmf) (11f)

A solution of Pd(dba)$_2$ (0.57 g, 1 mmol), 2f (0.18 g, 1.1 mmol) and dmf (0.16 g, 1.1 mmol) in 50 ml of dry THF was stirred for 2 hours at 20 °C. A clear yellow solution was obtained, which was concentrated until a precipitate formed. The product was further precipitated by addition of diethyl ether. The solid was filtered, washed with diethyl ether and re-dissolved in dichloromethane and then filtered over Celite. The product was precipitated with n-hexane, filtered and dried in vacuo. 11f Yield: 0.32 g (77%) yellow powder. $^1$H NMR: see Table 4.1. $^{13}$C NMR data could not be collected due to the low solubility and stability of the complex in deuterated NMR solvents.
Pd(2-(N-2-ethanolcarbaldimino)-pyridine)(dmfu) (11g)

The procedure was similar to that of 11f, using 2g (0.17 g, 1.1 mmol) as a ligand. Yield: 0.30 g (75%) as a yellow powder. \(^1\)H NMR: see Table 4.1. \(^{13}\)C NMR: \(\delta\) 164.42 (C7), 152.62 (C6), 139.03 (C4), 128.81 (C5), 126.77 (C3), 66.24 (CH\(_3\)OH), 64.91 (CH\(_2\)OH), 62.05 (CH\(_2\)N), the carbonyl, C2 and the alkene signals were not observed.

Pd(2-(N-phenylacetimino)pyridine)(dmfu) (12a)

The procedure was similar to 11d. As a ligand 0.33 mmol (0.07 g) of 3a was used with 0.30 mmol (0.17 g) of Pd(dba)\(_2\) and 0.33 mmol (0.05 g) of dmfu. Yield: 0.05 g (35%) as a red powder. Anal. Calc. for C\(_{19}\)H\(_{20}\)N\(_2\)O\(_4\)Pd: C, 51.08; H, 4.48; N, 6.27. Found: C, 51.21; H, 4.40; N, 6.48. \(^1\)H NMR: see Table 4.1. \(^{13}\)C NMR data could not be collected due to the low solubility and stability of the complex in deuterated NMR solvents.

Pd(2-(N-4-methoxyphenylacetimino)pyridine)(dmfu) (12b)

The reaction was similar to 11d. As a ligand 0.33 mmol (0.07 g) of 3b was used with 0.30 mmol (0.17 g) of Pd(dba)\(_2\) and 0.33 mmol (0.05 g) of dmfu. Yield: 0.05 g (30%) of a brown powder. Anal. Calc. for C\(_{20}\)H\(_{22}\)N\(_2\)O\(_5\)Pd: C, 50.38; H, 4.65; N, 5.87. Found: C, 50.12; H, 4.22; N 5.68. \(^1\)H NMR: see Table 4.1. \(^{13}\)C NMR data could not be collected due to the low solubility and stability of the complex in deuterated NMR solvents. IR (cm\(^{-1}\)): \(\nu(C=\text{C} + C=\text{O}) = 1685-1666\) s; \(\nu(C=N) = 1590\) w.

Pd(2-(N-2-propaneacetimino)pyridine)(dmfu) (12c)

The reaction was similar to 11d. As a ligand 1.1 mmol (0.18 g) of 3c was used. Yield: 0.17 g (40%). Anal. Calc. for C\(_{16}\)H\(_{22}\)N\(_2\)O\(_4\)Pd: C, 46.56; H, 5.37; N, 6.79. Found: C, 46.62; H, 5.40; N, 6.46. \(^1\)H NMR: see Table 4.1. \(^{13}\)C NMR data could not be collected due to the low solubility and stability of the complex in deuterated NMR solvents. IR (cm\(^{-1}\)): \(\nu(C=\text{C} + C=\text{O}) = 1676\) s; \(\nu(C=N) = \text{not visible.}\)

Pd(2-(N-2-propanecarbaldimino)-6-methylpyridine) (dmfu) (13c)

The procedure was similar to that of 10a except as a ligand 4c (0.18 g, 1.1 mmol) was used. Yield: 0.04 g (35%) as a brown solid. Anal. Calc. for C\(_{16}\)H\(_{22}\)N\(_2\)O\(_4\)Pd: C, 46.56; H, 5.37; N, 6.79. Found: C, 47.03; H, 4.94; N, 6.80. \(^1\)H NMR: see Table 4.1. \(^{13}\)C NMR data could not be collected due to the low solubility and stability of the complex in deuterated NMR solvents. IR (cm\(^{-1}\)): \(\nu(C=\text{C} + C=\text{O}) = 1671\) s; \(\nu(C=N) = 1592\) w.
Pd((2-diphenylphosphanylbenzylidene)-isopropylamine)(dmfu) (14c)

The procedure was similar to that of 10a except that 36 h. were required for the reaction to go to completion. As a ligand was used (0.36 g, 1.1 mmol) of 5c. Yield: 0.22 g (38 %) as a yellow solid. \(^1\)H NMR: \(\delta 8.25\) (d, \(H_2\), 1H, \(^3\)J\(_{HP} = 3.6\) Hz), 7.57 - 6.99 (m, 14H), 4.12 (dd, \(H_{10-1\text{H}}\), 1H, \(^3\)J\(_{HH} = 10.1\) Hz, \(^3\)J\(_{HP} = 2.3\) Hz), 3.79 (ps, \(H_{11}, 1\text{H}\), \(^3\)J\(_{HH} = 10.1\) Hz, \(^3\)J\(_{HP} = 10.2\) Hz), 3.60 (m, \(H_8+\)

CHMe\(_2, 3\)H), 3.14 (s, \(H_{13}, 3\)H), 1.29 (d, \(H_{15+1\text{H}}\), 6H, \(^3\)J\(_{HH} = 10.2\) Hz), 3.79 (ps, \(H_b, 1\text{H}\), \(^3\)J\(_{HH} = 10.0\) Hz, \(^3\)J\(_{HP} = 10.0\) Hz), 3.54 (s, \(H_8\), 3H), 3.14 (s, \(H_{13}, 3\)H), 1.13 (s, \(H_{15}, 9\)H). \(^{13}\)C NMR: \(\delta 174.08\) (C=O), 160.71 (C=N), 138.45 , 138.21 , 134.69 , 134.55 , 134.51 , 134.25 , 133.95 , 133.69 , 133.45 , 131.31 , 131.23 , 130.18 , 130.08 , 129.97 , 128.62 , 128.51 , 128.40 , 67.45 (HCMe\(_2), 51.19\) (OCH\(_3\) dmfu), 50.89 (OCH\(_3\) dmfil), 47.38 (HC=CH dmftl), 47.26 (HC=CH dmfu), 22.16 (CH\(_3\)-Pr). \(^{31}\)P-NMR \(\delta 18.50\).

Pd((2-diphenylphosphanylbenzylidene)-tertbutylamine)(dmfu) (14d)

The procedure was similar to that of 10a. As a ligand was used (0.37 g, 1.1 mmol) of 5d. Yield: 0.300 g (51 %) as a yellow solid. \(^1\)H NMR: \(\delta 8.07\) (d, \(H_7\), 1H, \(^3\)J\(_{HP} = 3.6\) Hz), 7.45 - 6.83 (m, 14H), 4.12 (dd, \(H_{10-1\text{H}}\), 1H, \(^3\)J\(_{HH} = 10.0\) Hz, \(^3\)J\(_{HP} = 2.6\) Hz), 3.69 (ps, \(H_{11}, 1\text{H}\), \(^3\)J\(_{HH} = 10.0\) Hz, \(^3\)J\(_{HP} = 10.0\) Hz), 3.54 (s, \(H_8\), 3H), 3.14 (s, \(H_{13}, 3\)H), 1.13 (s, \(H_{15}, 9\)H). \(^{13}\)C NMR: \(\delta 174.08\) (C=O), 160.71 (C=N), 138.45 , 138.21 , 134.69 , 134.55 , 134.51 , 134.25 , 133.95 , 133.69 , 132.66 , 131.02 , 130.05 , 129.92 , 128.51 , 128.46 , 128.38 , 128.32 , 127.05 , 63.23 (CMe\(_3), 50.59\) (OCH\(_3\) dmfu), 48.44 (HC=CH dmfu), 48.18 (HC=CH dmftl), 29.77 (CH\(_3\)-Bu). \(^{31}\)P-NMR \(\delta 24.46\). MW: 581.85 (calculated 581.06).

Pd(2-(-2-(diphenylphosphino)phenyl)-oxazoline)(dmfu) (15)

The procedure was similar to that of 10a except that 2.39 g of Pd(dba)\(_2\) (4.2 mmol), 1.72 g (5.2 mmol of 6 and 0.66 g (4.6 mmol) of dmfu was used. Yield: 1.60 g (2.75 mmol; 66 %). \(^1\)H NMR: \(\delta 8.11\) (m, \(H_1\), 1H), 7.07-7.70 (m, \(H_{Ar}, 13\)H), 4.40 (b, \(H_{alkene}, 2\)H), 4.18 (t, \(H_5, 2\)H, \(^3\)J\(_{HH} = 10.5\) Hz), 3.87 (t, \(H_6, 2\)H, \(^3\)J\(_{HH} = 10.5\) Hz), 3.12 (s, \(H_{ester}, 3\)H), 3.59 (s, \(H_{ester}, 3\)H). \(^{13}\)C NMR: \(\delta 173.99\) (C=O), 163.83 (C=N), 135.27 , 134.23 , 134.10 , 133.99 , 133.70 , 133.53 , 133.07 , 132.94 , 132.82 , 132.56 , 131.72 , 131.67 , 131.57 , 131.54 , 130.05 , 129.83 , 129.71 , 129.62 , 128.56 , 128.48 , 66.80 (O-C=H\(_2\) oxazoline), 59.20 (N-C\(_2\) oxazoline), 50.48 (OCH\(_3\) dmfu), 50.18 (OCH\(_3\) dmfil), 48.23 (HC=CH dmfu), 47.99 (HC=CH dmftl). \(^{31}\)P-NMR (121.5 MHz, CDCl\(_3\)): \(\delta 24.46\). MW: 581.85 (calculated 581.06).

Pd(8-diphenylphosphinequinoline)(dmfu) (16)

The procedure was similar to that of 10a, using 0.57 g of Pd(dba)\(_2\) (1.0 mmol), 0.34g (1.1 mmol of 7 and 0.16 g (1.1mmol) of dmfu. Yield: 0.41 g (73 %). \(^1\)H NMR: \(\delta 9.40\) (dd, \(H_1\), 1H, \(^3\)J\(_{HH} = 3.0\) Hz, \(J = 1.5\) Hz), 8.35 (d, \(H_3\), 1H, \(^3\)J\(_{HH} = 8.5\) Hz), 7.96 (d, 1H, \(^3\)J\(_{HH} = 6.5\) Hz), 7.66 - 7.26
(m, 12H), 4.51 (d, H_{13}, 1H, ^{3}J_{HH} = 10.3 \, Hz), 4.09 (p, H_{12}, 1H, ^{3}J_{HH} = 10.3 \, Hz, ^{3}J_{HP} = 10.3 \, Hz), 3.68 (s, H_{15}, 3H), 3.35 (s, H_{10}, 3H). ^{13}C \, NMR: \delta 174.72 (C=O), 173.40 (C=O), 155.76, 155.67, 151.78, 151.46, 138.38, 137.94, 136.93, 134.60, 134.08, 133.93, 133.67, 133.31, 133.05, 130.43, 129.95, 129.43, 129.07, 128.91, 128.88, 128.80, 127.74, 127.66, 123.14, 51.02 (OCH_3_{dmfu}), 50.47 (OCH_3_{dmfu}), 46.03 (HC=CH_{dmfu}), 45.84 (HC=CH_{dmfu}). ^{31}P-NMR (121.5 \, MHz, CDCl_3): \delta 15.43.

**Pd(bipyridine)(dmfu) (17)**

The procedure was similar to that of 10a, using 0.57 g of Pd(dba)_2 (1.0 mmol), 0.17 g of bipyridine (1.1 mmol) and 0.16 g (1.1mmol) of dmfu. Yield: 0.32 g (80 %). \(^{1}\)H NMR: \delta 8.73 (d, H_1, 2H, ^{3}J_{HH} = 4.6 \, Hz), 8.05 (d, H_4, 2H, ^{3}J_{HH} = 8.1 \, Hz), 7.92 (p, H_3, 2H, ^{3}J_{HH} = 8.1 \, Hz), 7.39 (p, H_2, 2H, ^{3}J_{HH} = 4.6 \, Hz), 3.94 (s, H_5, 2H), 3.63 (s, H_6, 6H).

### 4.4.4 Crystal structure determination of 12c

A red irregular prism single crystal of 12c was mounted on a glass fiber and X-ray diffraction data were collected on a Bruker-Siemens SMART AXS 1000 equipped with CCD detector, using graphite monochromated MoKα radiation (\(\lambda = 0.71069\) Å). Data collection details are: crystal to detector distance = 5.0 cm, 2424 frames collected (complete sphere mode), time per frame = 30 s, oscillation Δω = 0.30°. Crystal decay was negligible. Data reduction was performed up to d = 0.80 Å by the SAINT package and data were corrected for absorption effects by the SADABSS procedure (Tmax = 1.000, Tmin = 0.857). The phase problem was solved by direct methods and refined by full matrix least squares on all F^2 method and refined isotropically, except for methyl and CH2Cl2 hydrogens which were introduced in calculated positions. The Cambridge Crystallographic Database facility was used for the discussion of the structure. The final map was featureless. Data collection and refinement results are summarized in Table 4.4.
Table 4.4: Data collection and refinement results of 12e.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{16.50} H_{23} Cl N_{2} O_{4} Pd</td>
</tr>
<tr>
<td>Formula weight</td>
<td>455.22</td>
</tr>
<tr>
<td>Temperature</td>
<td>293(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71069 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P 21/c</td>
</tr>
<tr>
<td>a</td>
<td>13.629(2) Å</td>
</tr>
<tr>
<td>b</td>
<td>20.363(2) Å</td>
</tr>
<tr>
<td>c</td>
<td>14.169(2) Å</td>
</tr>
<tr>
<td>V</td>
<td>3925.5(9) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.541 Mg/m³</td>
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<tr>
<td>Absorption coefficient</td>
<td>1.103 mm⁻¹</td>
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<tr>
<td>F(000)</td>
<td>1848</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.5 x 0.3 x 0.3 mm³</td>
</tr>
<tr>
<td>Θ range for data collection</td>
<td>1.50 to 26.36°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-17≤h≤16, -25≤k≤25, -17≤l≤17</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>40678</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>8001 (R(int) = 0.0347)</td>
</tr>
<tr>
<td>Observed reflections [I &gt; 2σ(I)]</td>
<td>5907</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>8001 / 0 / 508</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>0.973</td>
</tr>
<tr>
<td>Final R indices [I &gt; 2σ(I)]</td>
<td>R1 = 0.0318, wR2 = 0.0835</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0494, wR2 = 0.0908</td>
</tr>
<tr>
<td>Largest final F maximum/minimum</td>
<td>0.955 / -0.766 e Å⁻³</td>
</tr>
</tbody>
</table>

4.4.5 Hydrogenation Experiments

The hydrogenation reactions were performed by dissolving, in a Schlenk tube, 0.04 mmol of the appropriate palladium complex in 40 ml of dry THF, under nitrogen atmosphere. Subsequently, the Schlenk tube was connected to a gas inlet and flushed with hydrogen. Immediately after this 4 mmol of 1-phenyl-1-propyne was added and the solution was then vigorously stirred at 25 °C; micro samples were withdrawn at regular intervals to monitor the reaction, and the samples were analyzed by means of a gas chromatograph.
4.5 References


SAINT: SAX, *Area Detector Integration*, Siemens Analytical Instruments INC., Madison, Wisconsin, USA.

SADABS: Siemens Area Detector Absorption Correction Software, Sheldrick G., 1996, University of Goettingen, Germany.


