Nickel and palladium complexes of pyridine-phosphine ligands: synthesis, characterization, and ethene oligomerization

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Chapter 2

Nickel and Palladium Complexes of Pyridine-Phosphine Ligands as Ethene Oligomerization Catalysts

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Nickel and Palladium Complexes of Pyridine-Phosphine Ligands as Ethene Oligomerization Catalysts

Summary
Pyridine-phosphine ligands 1–5 have been used to prepare neutral nickel dichloride complexes, neutral methylpalladium chloride complexes, and cationic methylpalladium complexes. The ligands consist of a diphenylphosphine and a pyridine moiety, and differ in the backbone connecting those donor groups. Nickel complexes 9–13 are paramagnetic complexes, and they were characterized by elemental analysis, high resolution mass spectrometry, and, for 10 and 12, single crystal X-ray diffraction. Neutral palladium complexes 14–18 were fully characterized. Single crystal X-ray diffraction was performed on complexes 15 and 16, and variable temperature NMR demonstrated that 16 exhibits slow flipping of the metallacycle. Cationic palladium species 19–23 were obtained from the neutral complexes after chloride abstraction. Like its neutral precursor, 21 showed slow ring flipping. The nickel species were evaluated as ethene oligomerization catalysts after activation with MAO. All complexes were highly active, with TOFs between 24·10³ and 85·10³ (mol C₂H₄)·(mol Ni·h)⁻¹. Butenes were the major product in all cases, forming 76 to 96 mole percent of the product. Selectivities for 1-butene were between 10 and 40 %. The cationic palladium species showed a very low productivity for ethene oligomerization, with TOFs ≤16 (mol C₂H₄)·(mol Pd·h)⁻¹ and 38 to 88 mole percent butenes as the main product.

Introduction
The development of metal complexes based on bidentate ligands with a phosphorus and a nitrogen donor atom (P,N ligands) is an important part of the field of transition metal catalysis.¹,² This class of ligands is particularly interesting because of the different trans-effect, as a result of different donor and acceptor properties of the two coordinating groups in the ligand. Despite extensive research, the influence of a ligand on catalytic properties of a transition metal complex is still very hard to predict.³ We wanted to investigate the effect of systematic changes of the backbone in a series of closely related ligands, and study the effect of changes in chelating properties when metal complexes bearing these ligands are used in catalysis.

The oligomerization of ethene is one of the most important industrial processes to obtain linear α-olefins. Nickel and palladium complexes with P,N ligands have been used in the
oligomerization and polymerization of ethene.⁴,⁵ An advantage of those ligands can be the improved thermal stability in catalysis, as nickel complexes with P,N ligands showed much higher thermal stability than related N,N ligand complexes.⁶,⁷ This might overcome the problem of fast catalyst deactivation at high temperatures that diimine based catalysts suffer from.⁸ A drawback of P,N ligands can be the reduced activity as a consequence of the different trans-effect of the two donor atoms,⁷,⁹ in polyketone synthesis the symmetric P,P and N,N ligands give much faster catalysts than P,N ligands,¹⁰ but the SHOP catalyst for instance contains an asymmetric P,O ligand that gives high rates.¹¹ Among the different types of P,N-ligands tested in nickel or palladium-catalyzed ethene oligomerization are pyridine-phosphines and phosphinites,¹²⁻¹⁹ oxazolinephosphines and -phosphinites,¹⁸⁻²² iminophosphoranes,²³ amido- and iminophosphines,²⁴⁻²⁶ iminopyrrolylphosphines,²⁷ pyrazolephosphines,²⁸ quinolinephosphines,²⁹,³⁰ and pyridinephospholes.³¹ We are particularly interested in pyridine-phosphine ligands.¹

In this article, we present the synthesis and characterization of neutral nickel complexes 9–13, neutral palladium compounds 14–18, and cationic palladium species 19–23. The metal centers in these complexes are coordinated by pyridine-phosphine ligands 1–5. The so far unreported synthesis for 4 and the modified syntheses of 1 and 5 are presented as well. Also, we evaluate the nickel complexes (using MAO activation) and the cationic palladium complexes as catalyst precursors in the oligomerization of ethene.

Results and discussion

We studied ligands 1–5 (see chart 1) and their neutral nickel complexes and neutral and cationic palladium complexes. They were chosen for their similar donor groups but different geometry. The ligands all consist of a diphenylphosphine moiety and a 2-pyridyl group, and differ in the backbone connecting those parts of the molecule. Compounds 1–3 have respectively one, two, or three methylene groups as the backbone. Ligand 4 has a two-carbon bridge between the 2-pyridyl and the phosphine, but integrated in a phenylene ring. The two-carbon spacer in 5 is aliphatic as in 2, but integrated in a substituted ring system which makes it much more rigid.
**Ligand synthesis**

The ligands 1, 2, 3, and 3 have first been reported over three decades ago. Their original syntheses involved the labile \([2\text{-pyridyl}]\text{-(CH}_2\text{)}_n\text{-Cl}\) species, which were made to react with diphenylphosphide. Different synthetic procedures for 1 and 2 have appeared since, mainly to circumvent the use of the labile intermediates. Synthesis of 2-[[diphenylphosphino)methyl]pyridine (1) has been carried out by lithiation of picoline and subsequent reaction with chlorodiphenylphosphine, either direct or via a more stable intermediate in a two-step process. We developed a new, one-pot procedure starting from commercial reagents for the synthesis of the ligand, see scheme 1. Triphenylphosphine was added to a solution of sodium in liquid ammonia at \(-78\) °C, resulting in P–C cleavage to give sodium diphenylphosphide and phenylsodium, the latter giving sodium amide and benzene. The formation of one equivalent of sodium amide allows the direct use of the stable 2-[chloromethyl]pyridine hydrochloride (6-HCl). When this is added to the reaction mixture, it is deprotected in situ at low temperatures. The resulting 2-[chloromethyl]pyridine (6) reacts with diphenylphosphide to give the product. After workup and purification, 1 was obtained as a white solid in 65% isolated yield. The yield is the highest reported for the pure product from commercial reagents.

![Scheme 1](chart.png)

**Scheme 1.** One-pot synthesis of ligand 1

Alternative published syntheses for 2-[[diphenylphosphino]ethyl]pyridine (2) include metal, acid, base, or fluoride mediated phosphination of 2-vinylpyridine. In our opinion, the acid catalyzed hydrophosphination of 2-vinylpyridine is the most convenient method.
procedure, because of the ease of multigram preparation from commercial starting compounds.

For the synthesis of 2-[3-diphenylphosphino]propyl]pyridine [3], we found that 2-[3-chloropropyl]pyridine\(^{39}\) was sufficiently stable to synthesize conveniently the ligand via the original procedure.\(^{32}\)

Several groups have reported the use of 2-[2-(diphenylphosphino)phenyl]pyridine [4]\(^ {40}\) but, to the best of our knowledge, full synthetic and analytical data were never reported. The synthesis of the ligand oxide, 2-[2-(diphenylphosphinoyl)phenyl]pyridine, has been reported,\(^ {41}\) but it involved several steps and moderate yields. We synthesized ligand 4 starting from 2-(2-fluorophenyl]pyridine [7],\(^ {42}\) see scheme 2. Following a procedure for a similar compound,\(^ {43}\) we obtained 4 in 63\% yield.

\[
\begin{align*}
\text{F} & \quad \text{KPPPh}_2, \text{18-crown-6} \\
7 & \text{THF, r.t., 24h.} \\
\rightarrow & \\
\text{PPh}_2 & \quad \text{THF, r.t., 24h.} \\
4, 63\% & \\
\end{align*}
\]

\textbf{Scheme 2.} Synthesis of ligand 4

The ligand 2-[[1S,2R,3R,4S]-3-diphenylphosphino]-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]pyridine [5] was developed in the group of Knochel.\(^ {44}\) The synthesis involved hydrophosphination of 2-[[1R,4R]-1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl]pyridine [8] with diphenylphospine oxide to give the oxide of the ligand, which was reduced in a second step. Use of diphenylphospine in the hydrophosphination led to a mixture of 5 and its oxide, as the product is partially oxidized by DMSO, which was used as the solvent. We found that the use of THF as solvent prevents this oxidation. Thus, the product could be obtained in one step from 8 in 68\% yield, see scheme 3. The yield was somewhat lower than the reported two-step process (76\% overall yield).

\[
\begin{align*}
\text{HPPPh}_2, \text{tBuOK} & \quad \text{THF, 60 °C, 16h.} \\
8 & \\
\rightarrow & \\
\text{PPh}_2 & \\
5, 68\% & \\
\end{align*}
\]

\textbf{Scheme 3.} Synthesis of ligand 5
Synthesis and characterization of nickel complexes

We obtained nickel dichloride complexes of the ligands by reaction with \((\text{DME})\text{NiCl}_2\) [DME = 1,2-dimethoxyethane], see scheme 4. All complexes were paramagnetic, as evidenced by their magnetic moment in solution. They were characterized by elemental analysis, high resolution mass spectrometry, and, for \(10\) and \(12\), single crystal X-ray diffraction.

All complexes showed a characteristic purple color in dichloromethane solution. In the solid state, however, only \(10\) and \(13\) were purple. The other solids were very dark purple to black \((9)\), orange \((11)\), or light brown \((12)\).

Very recently, the group of Braunstein also reported on complex \(9\).\(^{14}\) They used a slightly different synthetic procedure (\(\text{NiCl}_2\) as precursor, methanol as solvent, and one hour reaction time) and obtained the product as a gray powder. Also the magnetic moment in \(\text{CD}_2\text{Cl}_2\) solution of \(2.2\ \mu_\text{B}\) differed from the value of \(2.61\ \mu_\text{B}\) we found. This indicates that a slightly different species formed in our case compared to theirs. Satisfactory elemental analysis was obtained and the high resolution mass spectrum (Fast Atom Bombardment [FAB] ionization) showed the peak for the \([\text{[ligand]}\text{NiCl}]^+\) ion. Loss of one chlorine atom is a consequence of the ionization technique employed; the ionization of the complex by proton addition is immediately followed by loss of HCl.

The formation of a slightly different complex when using different conditions is further illustrated when the nickel complex of ligand \(2\) is considered. Braunstein \textit{et al.} also reported the formation of a related dimeric species \([10]\)', see chart 2.\(^{14}\) Although the dimeric species was not observed in the mass spectrum, the crystal structure unambiguously proved the binuclear nature of the complex in the solid state.
Chart 2. Complex 10⁺ as reported by Braunstein et al.¹⁴

Figure 1. Displacement ellipsoid plot of 10 in the crystal, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.
Table 1. Selected angles (in °) and bond lengths (in Å) in complex 10

<table>
<thead>
<tr>
<th></th>
<th>P1–Ni1–N1</th>
<th>Ni1–N1–C1</th>
<th>Ni1–P1</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1–Ni1–C1</td>
<td>110.81(2)</td>
<td>119.64(13)</td>
<td>2.3018(5)</td>
</tr>
<tr>
<td>P1–Ni1–C2</td>
<td>108.41(2)</td>
<td>113.96(12)</td>
<td>2.0240(13)</td>
</tr>
<tr>
<td>N1–Ni1–C1</td>
<td>100.46(4)</td>
<td>110.30(10)</td>
<td>2.2230(5)</td>
</tr>
<tr>
<td>N1–Ni1–C2</td>
<td>111.19(5)</td>
<td>104.61(5)</td>
<td>2.2196(6)</td>
</tr>
<tr>
<td>Cl1–Ni1–Cl2</td>
<td>124.33(2)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

We obtained single crystals of 10 suitable for X-ray diffraction. The structure is shown in figure 1 and selected angles and bond lengths are given in table 1. This shows that 10 has a mononuclear structure. The tetracoordinated nickel center has a distorted tetrahedral surrounding, in contrast to the pentacoordinated metal centers in 10', which are distorted square-pyramidal. Bond lengths around nickel are normal and similar to those in a tetrahedral surrounded nickel dichloride complex with a phosphinitopyridine ligand.14 The Cl1–Ni–Cl2 and the P–Ni–N angles in 10 are 124.33(2) and 98.36(4)° respectively, the other angles around the metal are less distorted from tetrahedral. The six-membered nickel chelate ring is in a 'screw-boat' conformation. X-ray crystal structures of nickel dichloride complexes have been reported with the tetracoordinated nickel having a square planar geometry with pyridine-phosphine15 and pyridine-phosphinite16 ligands, but these were shown to be tetrahedral in solution. The tetrahedral surrounding of nickel in the crystal structure of 10 is in agreement with the paramagnetic nature of the complex.15

The difference between 10 and 10' is further illustrated by the color of the solid (purple and green respectively) and the magnetic moment in CD2Cl2 solution (3.12 and 2.7 μB respectively). The difference in synthetic procedures was the same as mentioned above for complex 9. In both cases, satisfactory elemental analysis was obtained and the [ligand]NiCl4 peak was observed in the mass spectrum. The original report13 on complex 10 describes a red-violet complex with magnetic moment of 3.29 μB (presumably in the
solid state), obtained after reaction of the ligand with NiCl₂ in refluxing n-butanol for 20 minutes.

The complexes 9 and 11–13 are EPR silent, as can be expected for this type of complexes.⁴⁵ Compound 10, however, did give rise to a signal and the EPR spectrum is shown in figure 2. When the dichloromethane solution of the complex was cooled to liquid nitrogen temperature (necessary for the measurement), a color change from purple to green was observed. This color change was reversible. We cannot explain the EPR spectrum at present, but it is very likely that a different conformation of the species is formed compared to the solution structure at room temperature or the solid state structure.

![EPR spectrum of compound 10.](image)

**Figure 2.** EPR spectrum of compound 10. The signal marked with * is the results of a small amount of paramagnetic impurities in the cryostat Dewar.

Complexes 11–13 are all new compounds. Synthesis was straightforward and complexes with magnetic moments (in CD₂Cl₂) of 3.47 [11], 3.23 [12], and 3.11 μ_B [13] were obtained, indicative of distorted tetrahedral surrounding of the nickel center.⁴⁶ The high resolution mass spectra showed the expected peak of the [ligand]NiCl⁺ ion for all complexes. Elemental analyses were in agreement with the proposed structures. In addition to this, we obtained the crystal structure of 12. The structure is shown in figure 3 and selected angles and bond distances are presented in table 2.
**Figure 3.** Displacement ellipsoid plot of 12 in the crystal, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

**Table 2.** Selected angles (in °) and bond lengths (in Å) in complex 12

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (°)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1–Ni1–N1</td>
<td>89.75(4)</td>
<td>Ni1–N1–C1</td>
<td>127.68(10)</td>
</tr>
<tr>
<td>P1–Ni1–Cl1</td>
<td>106.39(15)</td>
<td>N1–C1–C6</td>
<td>121.21(13)</td>
</tr>
<tr>
<td>P1–Ni1–Cl2</td>
<td>109.78(16)</td>
<td>C1–C6–C7</td>
<td>125.53(12)</td>
</tr>
<tr>
<td>N1–Ni1–Cl1</td>
<td>102.54(3)</td>
<td>C6–C7–P1</td>
<td>120.33(10)</td>
</tr>
<tr>
<td>N1–Ni1–Cl2</td>
<td>108.68(3)</td>
<td>C7–P1–Ni1</td>
<td>102.26(5)</td>
</tr>
<tr>
<td>Cl1–Ni1–Cl2</td>
<td>131.54(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni1–P1</td>
<td>2.254(4)</td>
<td>N1–C1</td>
<td>1.358(7)</td>
</tr>
<tr>
<td>Ni1–N1</td>
<td>2.000(12)</td>
<td>P1–C7</td>
<td>1.817(2)</td>
</tr>
<tr>
<td>Ni1–Cl1</td>
<td>2.217(4)</td>
<td>C6–C7</td>
<td>1.414(2)</td>
</tr>
<tr>
<td>Ni1–Cl2</td>
<td>2.210(5)</td>
<td>C1–C6</td>
<td>1.497(2)</td>
</tr>
</tbody>
</table>
Just as in \textbf{10}, the nickel chelate ring in complex \textbf{12} has a ‘screw-boat’ conformation, with a distorted tetrahedral surrounding around the metal. The P–Ni–N angle of 89.75(4)° is relatively small, presumably due to the inflexibility of the backbone. As a consequence, the Cl1–Ni–Cl2 angle is relatively large (131.542(18)°). The others angles around nickel are less distorted from tetrahedral. The distances around nickel are normal and comparable to those in complex \textbf{10}. The torsion angle C7–C6–C1–N1 between the phenylene backbone and the pyridyl ring is 37.3(2)°.

**Bite angle calculations**

We calculated the natural bite angle ($\beta_n$)\textsuperscript{47,48} for complexes 1–5 when coordinated to nickel, values are given in table 3. As expected, ligand \textbf{1} exhibits the smallest bite angle, and this increases on increasing number of methylenes in the backbone (ligands \textbf{2} and \textbf{3}). The phenylene backbone in \textbf{4} results in a $\beta_n$ between those of \textbf{1} and \textbf{2}. The anti configuration of the pyridine and the diphenylphosphine groups in ligand \textbf{5} induce a rather large natural bite angle, being similar to that of \textbf{3}.

**Table 3.** Calculated natural bite angles ($\beta_n$) for complexes 9–13

<table>
<thead>
<tr>
<th>ligand</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta_n$ [°]</td>
<td>87.2</td>
<td>94.7</td>
<td>101.8</td>
<td>90.8</td>
<td>101.7</td>
</tr>
</tbody>
</table>

The difference between the calculated value of 94.7° for ligand \textbf{2} and the value in the crystal structure of complex \textbf{10} (98.36(4)°) can be ascribed to the electronic preference of the metal. The dummy metal used in the bite angle calculations does not have a preference, and $\beta_n$ is determined by ligand factors only.\textsuperscript{48} The tetrahedrally surrounded d\textsuperscript{5} metal center in \textbf{10}, on the other hand, prefers an angle of 109°. As a consequence of the ligand preferred bite angle and the steric of the chloride anions, the Cl–Ni–Cl angle is larger than this ideal angle, while P–Ni–N is smaller. The latter angle is still larger than the natural bite angle of the ligand, though. We have shown before that electronic preference of the metal can give a deviation from the natural bite angle of the ligand.\textsuperscript{49} In complex \textbf{12}, due to the inflexibility of the ligand, the P–Ni–N angle is determined by ligand preference. The found value of 89.75(4)° in \textbf{12} is therefore in good correlation with the calculated natural bite angle of 90.8° of ligand \textbf{4}. In ethene oligomerization, the active species is believed to be a nickel complex with a square planar surrounded metal center.\textsuperscript{44} This has an electronic preference
for a bite angle of 90°, and the deviation from the natural bite angle will therefore be much less than in the nickel dichloride complexes.

Scheme 5. Synthesis of neutral palladium complexes 14–18

Synthesis and characterization of neutral palladium complexes

Neutral methylpalladium chloride complexes were obtained from reaction of the ligand with [COD]Pd(CH₃)Cl [COD = 1,5-cyclooctadiene], see scheme 5. All compounds were obtained as white solids and were characterized by NMR, elemental analysis and high resolution mass spectrometry. In addition, single crystal X-ray diffraction was performed on complexes 15 and 16.

Elemental analyses for all neutral palladium complexes were in agreement with the proposed structures, and the [[ligand]Pd(CH₃)]⁺ ion was observed in high resolution mass spectrometry for all complexes. As is the case for the nickel complexes, loss of the chloride is a consequence of the FAB ionization.

In the NMR spectra, the ³¹P signal showed a shift of 38 to 50 ppm to higher value for the complexes, compared to the free ligands. The 1H NMR spectra showed a shift of the ortho-pyridyl protons of 0.6 to 1.2 ppm towards higher value. Furthermore, the ¹Jp,c coupling constants doubled for the aliphatic carbons and tripled for the aromatic ones upon complexation. These observations show that in solution the ligand is coordinated to the palladium atom, through both the pyridine and the phosphine. This corresponds to the solid state structures as obtained by X-ray diffraction (see below). As a consequence of the different trans influence of the two donor functionalities, the phosphine is expected to coordinate trans to chloride. This coordination mode is demonstrated by the coupling constant between the phosphorus and the Pd–CH₃ protons, which is small (2.5 to 3.1 Hz) for
14–17 and not observed for 18. Again, this is in agreement with the X-ray structures [see below].

![Figure 4](image.png)

**Figure 4.** Methylene region of the $^1$H NMR spectra of compound 16 at different temperatures (in °C), recorded in CDCl$_3$ except spectra marked with * which are recorded in Cl$_2$DCDCl$_2$.

The room temperature $^{13}$C and $^1$H NMR spectra in CDCl$_3$ of compound 16 contained broad peaks, indicative of hindered flipping of the seven-membered palladium chelate ring. When this flipping is slow on the NMR timescale, the two protons at each methylene carbon of the ligand backbone and the protons and carbons of the two phenyl rings become inequivalent. Hence, the signals of these nuclei become broad in the spectra. The signals of the methylene carbons in $^{13}$C-NMR are sharp. Also, the signals corresponding to the pyridyl and methyl in both $^1$H and $^{13}$C NMR are sharp, as is the phosphorus signal in $^{31}$P NMR. This shows that ring-flipping of the compound is the reason for the broad signals, and not an equilibrium between two different species. Variable temperature $^1$H NMR spectra of 16 are shown in figure 4. Upon cooling to −20 °C, the separate signals of the inequivalent protons are visible in the $^1$H NMR spectrum. In the aromatic region, a separate signal could be observed for one set of ortho-phenyl protons, while the signals of the other ortho and the meta and para protons overlapped. For the backbone, six multiplets are observed, each with an integral corresponding to one proton. One of the signals of the two CH$_2$-[2-pyridyl]
protons is shifted by 1.0 ppm towards higher value compared to the signal of the other proton or the chemical shift of those protons in the free ligand. This large difference can be explained by the relative short Pd⋯H distance of one of the protons in the crystal structure (see below). Apparently, there is an interaction between this proton and the metal, both in the solid state and in solution. This phenomenon has been observed before in a similar complex. At 80 °C, the ring-flipping was fast on NMR timescale and the proton spectrum (measured in Cl$_2$DCCDCI$_2$) showed three multiplets (each with an integral corresponding to two protons) for the methylene groups. The phenyl rings gave rise to a separate signal for the ortho protons (overlapping with the pyridyl-4 signal), while the meta and para signals overlapped. The $^{13}$C NMR spectrum at 25 °C in CDCl$_3$ showed some broad signals, and the signal for the ipso carbon could not be observed. At 80 °C in Cl$_2$DCCDCI$_2$, all carbon atoms gave rise to sharp signals.

The other neutral palladium complexes did not give rise to broad peaks in room temperature NMR spectra. In complex 18, the backbone of the ligand prohibits ring flipping and (also as a consequence of the chirality of the complex) the two phenyl rings are inequivalent. In the other complexes, the phenyl rings were equivalent in NMR spectra at ambient temperature.

![Figure 5](image.png)

**Figure 5.** Displacement ellipsoid plot of 15 in the crystal, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.
**Table 4.** Selected angles (in °) and bond lengths (in Å) in complex 15

<table>
<thead>
<tr>
<th></th>
<th>P1–Pd1–N1</th>
<th>Pd1–N1–C1</th>
<th>P1–Pd1–Cl1</th>
<th>N1–C1–C6</th>
<th>C1–C6–C7</th>
<th>N1–Pd1–C20</th>
<th>C7–P1–Pd1</th>
<th>Cl1–Pd1–C20</th>
<th>C6–C7</th>
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<tr>
<td></td>
<td>P1–Pd1–C20</td>
<td>86.88[9]</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd1–P1</td>
<td>2.1964[8]</td>
<td>N1–C1</td>
<td>1.358[3]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd1–Cl1</td>
<td>2.3837[7]</td>
<td>P1–C7</td>
<td>1.815[3]</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Single crystals of 15 suitable for X-ray diffraction were obtained. The crystal structure is shown in figure 5 and selected angles and bond lengths are summarized in table 4. Just as the nickel complex of this ligand, the palladium complex 15 has the metal chelate ring in a ‘screw-boat’ conformation. The metal has a distorted square planar surrounding. The five atoms of the palladium coordination plane have a dihedral angle of 21.87[11]° with the pyridyl ring. In comparison with palladium complexes of the same ligand with an alkoxy carbonyl group instead of a methyl group coordinated to the palladium, the P–Pd–Cl bond is a little more distorted from linear, the Pd–P distance is slightly shorter and the Pd–Cl bond slightly longer.52 Bond lengths and angles are similar to those in Pd(CH₃)Cl or PdCl₂ complexes of related pyridine–phosphine ligands.53
Figure 6. Displacement ellipsoid plots of 16 in the crystal, drawn at the 50% probability level. Aromatic hydrogen atoms and disordered solvent molecules are omitted for clarity.

Table 5. Selected angles (in °) and bond lengths (in Å) in complex 16

<table>
<thead>
<tr>
<th></th>
<th>94.86[5]</th>
<th>Pd1–N1–C1</th>
<th>125.37[16]</th>
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<td>P1–Pd1–N1</td>
<td>175.96[2]</td>
<td>N1–C1–C6</td>
<td>118.3[2]</td>
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<tr>
<td>P1–Pd1–Cl1</td>
<td>87.31[7]</td>
<td>C1–C6–C7</td>
<td>111.1[2]</td>
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<tr>
<td>N1–Pd1–Cl1</td>
<td>89.17[5]</td>
<td>C6–C7–C8</td>
<td>114.68[19]</td>
</tr>
<tr>
<td>N1–Pd1–C21</td>
<td>176.71[9]</td>
<td>C7–C8–P1</td>
<td>113.65[17]</td>
</tr>
<tr>
<td>Cl1–Pd1–C21</td>
<td>88.65[7]</td>
<td>C8–P1–Pd1</td>
<td>113.50[8]</td>
</tr>
<tr>
<td>P1–C8</td>
<td>1.839[2]</td>
<td>Pd1···H6B</td>
<td>2.81</td>
</tr>
</tbody>
</table>

The X-ray crystal structure of 16 is shown in figure 6 and selected angles and bond lengths are shown in table 5. The palladium has a distorted square planar surrounding. The flexibility of the backbone is demonstrated by the P–Pd–N bite angle of 94.86[5]°, which is not larger than that in complex 15, which has a shorter backbone. Also, the angles around
the metal are a little less distorted from square planar geometry. The most notable feature in the structure is a relatively short Pd⋯H distance: H6B is in a pseudo-axial position and has a distance of 2.81 Å to palladium. This is also reflected in the 1H NMR spectrum (see above). In complex 15, the shortest Pd⋯H distance is 3.39 Å. The structure of 16 can be compared with the PdCl₂ complex of a similar pyridine-phosphine ligand with a backbone consisting of three aliphatic carbons. In this structure, there also is a relatively short Pd⋯H distance of 2.72(3) Å.

![Scheme 6. Synthesis of cationic palladium complexes 19–23](image)

**Synthesis and characterization of cationic palladium complexes**

All neutral palladium complexes were pre-activated to give cationic complexes by reaction with NaBAR₄, [Ar⁺ = 3,5-di(trifluoromethyl)phenyl] and acetonitrile, see scheme 6. The products were obtained as white solids, and characterized by NMR, elemental analysis, and mass spectrometry. When using FAB ionization, the [[ligand]Pd(CH₂)]⁺ ion was observed with high resolution mass spectrometry for all complexes. Apparently, acetonitrile dissociates when using these ionization conditions. When the milder Field Desorption (FD) ionization was used, the [[ligand]Pd(CH₂)₂(C₂H₅CN)]⁺ ion was observed for complexes 19–22, but as a consequence of this ionization technique not in high resolution. For complex 23, acetonitrile did not remain coordinated even when this mild technique was used and the same species as when using FAB was observed. Elemental analyses were in agreement with the proposed structures for all complexes.

Compared to the neutral palladium complexes, the ³¹P chemical shift showed a shift of 1 to 3 ppm to higher value. The signals of the ortho-pyridyl protons showed a shift towards lower ppm value, although the chemical shift is still higher than that of the free ligand. The
coordinated acetonitrile molecule gives rise to a singlet. For the rest, the NMR spectra of the cationic complexes did not differ significantly from those of their neutral precursors. The $^{19}$F-NMR spectra showed a signal at $-63.0$ ppm, independent of the palladium cation, which shows the non-coordinating nature of the BAr$_+^-$ anion.

![Figure 7](image)

**Figure 7.** Methylene region of the $^1$H NMR spectra of compound 21 at different temperatures (in $^\circ$C), recorded in CD$_2$Cl$_2$ except spectra marked with * which are recorded in Cl$_2$DCCDCI$_2$.

In analogy to the neutral complex 16, complex 21 gave rise to broad signals in room temperature NMR spectra, see figure 7. The $^1$H NMR spectrum in CD$_2$Cl$_2$ showed broad signals for the backbone and phenyl protons, again as a consequence of hindered ring flipping. When the sample was cooled to $-40$ °C, the signals became sharp. Separate signals for the inequivalent ortho en meta-phenyl protons were visible, as were for the methylene protons. The signals of one of the (2-pyridyl)--CH$_2$ protons showed a difference in chemical shift from the other one and from the shift of the free ligand, like in 16. The difference of 0.7 ppm is somewhat smaller than that of the neutral complex, but still indicative of a Pd···H interaction. At 80 °C in Cl$_2$DCCDCI$_2$, the ring flipping was fast on the NMR timescale and only sharp peaks were observed in the $^1$H NMR spectrum. In the $^{13}$C NMR spectrum in CD$_2$Cl$_2$ at 25 °C, not all peaks could be observed and some were broad. At $-40$ °C, all peaks were observed as sharp signals and the phenyl carbons were inequivalent.
Nickel catalyzed ethene oligomerization

Nickel halide complexes bearing pyridine-phosphine ligands have been used as precursors in oligomerization of ethene.\textsuperscript{4,12-14,16,17} We tested the ability of complexes 9–13 to act as catalyst in this reaction after activation with MAO. Although the nickel halide complexes are only sparingly soluble in toluene, the species formed after activation are soluble. When a suspension of the nickel complex in toluene (with a little 1-hexene to stabilize the species formed) was treated with MAO in a Schlenk flask, the immediate dissolution of the complex was observed, together with a color change.

The results of the oligomerization are presented in table 6.

Table 6. Ethene oligomerization using 9–13 as catalyst precursor\textsuperscript{a}

<table>
<thead>
<tr>
<th>complex</th>
<th>productivity ((\text{g C}_2\text{H}_4 / \text{(mol Ni} \cdot \text{h)}))</th>
<th>TOF\textsuperscript{b}</th>
<th>product distribution (%)\textsuperscript{c}</th>
<th>1-butene (%)\textsuperscript{d}</th>
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<tr>
<td></td>
<td></td>
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<td>C4</td>
<td>C6</td>
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<tr>
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<td>(30 \cdot 10^3)</td>
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<tr>
<td>10</td>
<td>(196 \cdot 10^4)</td>
<td>(70 \cdot 10^3)</td>
<td>86</td>
<td>11</td>
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<tr>
<td>11</td>
<td>(240 \cdot 10^4)</td>
<td>(85 \cdot 10^3)</td>
<td>96</td>
<td>3</td>
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<tr>
<td>12</td>
<td>(218 \cdot 10^4)</td>
<td>(78 \cdot 10^3)</td>
<td>92</td>
<td>6</td>
</tr>
<tr>
<td>13</td>
<td>(68 \cdot 10^4)</td>
<td>(24 \cdot 10^3)</td>
<td>76</td>
<td>17</td>
</tr>
</tbody>
</table>

\textsuperscript{a}conditions: 10 \(\mu\)mol nickel complex, MAO activator \((\text{Al/Ni} = 230)\), 10 bar ethene, 1.0 mmol heptane [internal standard], toluene solvent, total volume: 25 mL, \(T\): 30 °C, time: 30 min. \textsuperscript{b}turnover frequency in \((\text{mol C}_2\text{H}_4) \cdot \text{(mol Ni-h)}^{-1}\). \textsuperscript{c}mol percentage of combined \(C_n\) products. \textsuperscript{d}as percentage of total C4 fraction.

All complexes form active species after activation, with butenes being the major catalysis product. Activities in general are high, and amongst the best reported for ethene oligomerization with nickel complexes bearing P,N ligands. From the amount of cooling, necessary to maintain the reaction temperature (against the exotherm of the reaction), it was clear that the catalysts were most active in the first five to ten minutes. In general, oligomerization activities seem to follow the same trend as the isomerization, with the catalysts giving most isomerization being the most active. Selectivity for C4 products can be as high as 96 percent. Complexes 9, 11, and 12 all have selectivity for butenes higher than 90\%, and can be considered dimerization catalysts rather than oligomerization catalysts. A significant amount of isomerization takes place, as can be seen from the relatively low amount of 1-butene. The other C4-products were \(cis\) and \(trans\) 2-butene. The GC traces
contained multiple peaks for the other fractions, showing that these fractions consist of a mixture of isomers as well.

The observed trends can be rationalized by considering the mechanism of isomerization and chain growth. Isomerization proceeds via β-hydrogen elimination and reinsertion. From the species formed after β-hydrogen elimination, chain transfer can take place. Thus, a high rate of isomerization results in a higher change of chain transfer. After chain transfer, a nickel hydride species is formed. Migratory insertion in this hydride is faster than in an alkylmetal complex (formed after every ethene insertion), leading to a higher productivity. Indeed, the catalyst precursors that give more isomerization have a higher productivity and a lower percentage of oligomers [as compared to dimers] formed, with the exception of complex 9. In complex 9, ethene insertion (and thus chain growth) is probably disfavored as a consequence of the small ligand bite angle, which disfavors migratory insertion.47,48

The catalytic behavior of complexes 9–11 shows a good correlation with their natural bite angle [see table 3]. With increasing value for the bite angle, both the productivity and amount of isomerization go up. The correlation between catalytic performance and the bite angle does not hold for complexes 12 and 13. This shows that the behavior in ethene oligomerization is not only dependent on the natural bite angle of the ligand, but also on factors as steric and electronic properties and ligand flexibility. Influence of the bite angle of diphosphine ligands on outcome of nickel catalyzed ethene oligomerization has been studied, but the dependence on βₙ is not uniform.54 Catalyst precursor 13, having a backbone which has a similar bite angle as complex 11 but that is very rigid, has the lowest rate of isomerization, accompanied with a relatively low productivity. Complex 12 behaves similar to complex 11, with only slightly more oligomers formed and slightly lower productivity.

The aromatic backbone in 12, more flat and electronically different from the aliphatic backbones, makes comparison with the other catalysts tested difficult. A paper by the group of Braunstein reports the use of a catalyst precursor similar to our complex 12, the only difference being a methyl group on the pyridyl-6 position of the ligand in their case.17 Surprisingly, this complex showed no activity towards ethene after activation with 400 or 800 equivalents of MAO, presumably due to decomposition as a result of free trimethylaluminum in the MAO used. When the complex was activated with EtAlCl₂, a maximum TOF of 56,000 was reached, with selectivities comparable to complex 12. The
catalytic performance of precursor 12 can also be compared with nickel complexes with phosphinooxazoline ligands. The ligands in these complexes have the same phenylene backbone and a diphenylphosphine donor, but the nitrogen donor atom is part of an oxazoline group instead of a pyridine. Under slightly different conditions than we used, these complexes gave systems that were two to four times less active and gave 45 to 90% butenes. Selectivity for 1-butene was higher than for 12, reaching a maximum of 30%.

The recent paper by the group of Braunstein that describes complexes 9 and 10 also deals with their oligomerization productivity. Although they tested more activation methods which sometimes gave better results, the conditions that compare best to our conditions are the activation with 200 equivalents of MAO in chlorobenzene as solvent. Under these conditions, they found turnover frequencies of 14,000 [9] and 17,300 [10], being lower than the activities we found. The selectivity for butenes was 64% for both catalyst precursors, while selectivity for 1-butene within that fraction was 19 and 16% respectively. The difference in catalytic behavior can partly be explained by the difference in geometry of the metal complexes (see above) and the differences in solvent, concentration, reactor, quality of MAO, and reaction time. But presumably the largest influence is the temperature of the reaction mixture. Braunstein reports that no cooling was applied to the reactor during the reaction and a temperature increase was observed as a consequence of reaction exotherm. We used an internal cooling spiral to maintain the temperature, and a maximum temperature increase of 5 °C was observed. The high temperature reached in the experiments without cooling explains the lower TOF due to catalyst deactivation and lower selectivity for 1-butene due to enhanced isomerization. The higher amounts of hexenes are probably a result of the higher catalyst concentration used. This results in a higher butenes concentration, which then reinserts to give hexenes or methylpentenes. It was reported that a significant amount of the C6 fraction was the result of butene reinsertion. At lower Ni/Al ratios, complexes 9 and 10 showed the same trends in productivity, product distribution, and selectivity as we observed for 9 and 10.

**Palladium-catalyzed ethene oligomerization**

Palladium complexes bearing pyridine-phosphine ligands have only sparingly been used as ethene oligomerization catalyst. The group of Rieger presented an active catalyst, whereas Liu reported the formation of negligible amounts of oligomers with complexes of
this kind.\textsuperscript{13} We tested our complexes for their ability to oligomerize ethene, results are presented in table 7.

**Table 7.** Ethene oligomerization using 19–23 as catalyst precursor$^a$

\[
\begin{array}{|c|c|c|c|c|c|c|c|c|}
\hline
\text{complex} & \text{TOF}$^{b}$ & \text{product distribution (%)}$^{c}$ \\
& & \text{C4} & \text{C5} & \text{C6} & \text{C7} & \text{C8} & \text{C9} & \text{C10} & \text{C10} \\
\hline
19 & 8 & 56 & 6 & 13 & 3 & 8 & 1 & 6 & 6 \\
20 & 6 & 85 & 11 & 2 & 1 & <1 & <1 & & \\
21 & 2.7 & 88 & 11 & 1 & <1 & <1 & & & \\
22 & 16 & 38 & 11 & 14 & 2 & 9 & 1 & 8 & 17 \\
23 & 1.4 & 78 & 22 & <1 & <1 & & & & \\
\hline
\end{array}
\]

$^a$conditions: 100 $\mu$mol palladium complex, 10 bar ethene, 0.10 mmol heptane [internal standard], toluene solvent, total volume: 25 mL, T: 30 °C, time: 120 min. $^b$turnover frequency in [mol C$_2$H$_4$]·(mol Pd-h)$^{-1}$. $^c$mol percentage of combined C$n$ products.

The table shows that the complexes have a very low productivity. Low or no activity has been described for other palladium complexes with P,N ligands,$^{6,26,27,29}$ although turnover frequencies of up to several hundreds per hour have also been reached with such systems.$^{7,20,24}$ A significant amount of oligomers with an odd number of carbons is formed. These originate from the first chain growing at the complex, which starts from the methylpalladium complex. After this first chain terminates, the next chain starts from a palladium hydride complex, producing only chains with an even number of carbons from then on. At very low TOF’s [like with complexes 21 and 23], the odd numbered chains still do not exceed one fifth of the total amount of oligomers formed. This shows that a large part of the growing chains eliminates after only one ethene insertion. The propene thus formed was evaporated together with the ethene at the end of the reaction and not included in the calculation of the turnover frequency. Complex 22 has a relatively high percentage of chains with an odd number of carbons, compared to the other complexes. This is consistent with the lower probability of chain termination, as evidenced by the formation of higher molecular weight products.

The difference between the very low productivity of our complexes and of those of Liu\textsuperscript{13} and the active catalyst of Rieger\textsuperscript{15} could be explained by the precursor used. The former systems make use of preactivated cationic complexes, where acetonitrile coordinates to palladium. It has been shown that acetonitrile binds much strongly to palladium than
ethene, and the nitrile adduct is an inactive species. The system of Rieber was activated in ether just before the oligomerization, thus circumventing the use of nitriles. Recently, a palladium complex with a P,N ligand was reported in which an axial Pd····H interaction resulted in the increased formation of olefins compared to dimers. In complex 21, the Pd····H interaction is clearly not enough to give a similar effect, as it produces the largest fraction of dimers of the complexes tested.

Conclusions
The pyridine-phosphine ligands 1–5 were used to make nickel and palladium complexes. The nickel dichloride complexes 9–13 are monomeric, paramagnetic species with a distorted tetrahedral structures. The differences in the structures of 9 and 10 compared to the nickel dichloride complexes of the same ligands recently reported is probably the result of differences in the synthetic procedures. The neutral methylpalladium chloride complexes 14–18 of the ligands all have a distorted square planar surrounding, with the chloride always trans to the phosphorus. In 16, a relatively short Pd····H distance is observed in the X-ray crystal structure and the NMR spectra of this complex.

When tested as catalyst precursors in the oligomerization of ethene, the cationic methylpalladium complexes 19–23 show a very low productivity to give mainly butenes as product. After MAO activation, the nickel complexes 9–13 show a high productivity with turnover frequencies between 24·10³ and 85·10³ mol ethene per mol nickel per hour, which is competitive with earlier reported nickel catalysts. The activity decreases over time and is highest in the first 5 to 10 minutes of the reaction, showing that the catalysts do not have a prolonged stability. Butenes are the main product, with maximum selectivities of 96 mol%. The 1-butene content within this fraction is between 10 and 40%. Comparison of the catalytic results of the different complexes show that within a series of highly related backbones (ligands 1–3), the productivity and isomerization increase with increasing bite angle. The results obtained with complexes of ligands 4 and 5 do not follow this trend, showing that other factors have a pronounced influence on the outcome of the catalysis as well. This complicates comparison of different catalysts.
Experimental part

General information

All reactions involving sensitive compounds were carried out under an atmosphere of purified dinitrogen using standard Schlenk and glovebox techniques. Solvents were dried and distilled under dinitrogen; acetonitrile, CH₂Cl₂, CD₃Cl, and CDCl₃ from CaH₂, toluene from sodium, Et₂O and THF from sodium / benzophenone, and pentane and hexanes from sodium / benzophenone / triglyme. Toluene and heptane in toluene solution used for nickel catalyzed oligomerization were stored over sodium / potassium alloy. 2-[2-(Diphenylphosphino)ethyl]pyridine (2), 2-[2-fluorophenyl]pyridine (7), 2-[1R,4R]-1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl]pyridine (8), [DME]NiCl₂, [COD]Pd(CH₃)Cl₂ and NaBAR₄ were synthesized according to the published procedures. All other chemicals were purchased from commercial suppliers and used as received. Silica 60 was used for column chromatography unless stated otherwise. Elemental analyses were carried out by Kolbe Mikroanalytisch Laboratorium, Mülheim an der Ruhr (Germany). Electron Ionization (EI) mass spectrometry (MS) was carried out on an Agilent Technologies 6890N/5973N GC-MS using an ionizing energy of 70 eV. Samples were dissolved in Et₂O or CH₂Cl₂. Fast Atom Bombardment (FAB) and Field Desorption (FD) high resolution mass spectrometry (HRMS) were carried out at the Department of Mass Spectrometry at the University of Amsterdam using a JEOL JMS SX/SX102A four-sector mass spectrometer, coupled to a JEOL MS-MP9021D/UPD system program. For FAB, samples were loaded in a matrix solution (3-nitrobenzyl alcohol) on to a stainless steel probe and bombarded with xenon atoms with an energy of 3KeV. During the high resolution FAB-MS measurements a resolving power of 10000 (10% valley definition) was used. For FD, 10 µm tungsten wire FD emitters containing carbon microneedles with an average length of 30 µm were used. The samples were dissolved in CH₂Cl₂ and then loaded onto the emitters with the dipping technique. An emitter current of 0-30 mA was used to desorb the samples. The ion source was generally at room temperature. NMR spectra were recorded on a Varian Mercury 300 operating at 300.1 (¹H), 75.5 (¹³C), 121.5 (¹⁹P), and 282.4 (¹⁹F) MHz or a Varian Inova 500 operating at 499.8 (¹H) and 125.7 (¹³C) MHz, at ambient temperature unless stated otherwise. Signals are referenced to TMS (¹H and ¹³C), 85% H₃PO₄ (¹⁹P), and CCl₃F (¹⁹F) as external standards at 0 ppm, except when CD₃DCCDCl₃ was the solvent, in which case signals are referenced to
residual solvent signal at 6.00 (1H) and 73.78 (13C) ppm. Magnetic moments were determined in CD2Cl2 solution with 5% cyclohexane as reference by the Evans NMR method. Experimental X-band EPR spectra were recorded on a Bruker EMX Plus spectrometer with a spectrometer frequency of 9.378347 GHz in CH2Cl2 at 20 K. The addition of ~0.1 M [n-Bu4N]PF6 to the solution improved the quality of the glass. Solution-phase GC analysis was performed on an Interscience Thermo Focus GC equipped with a flame ionization detector and a 10 m Restek RTX-5 column with a 0.18 mm internal diameter, using helium as carrier gas at 0.2 mL/min. Gas-phase GC analysis was performed on an Interscience Compact GC equipped with a thermal conductivity detector and a 10 m Porabond Q column with a 0.32 mm internal diameter operated isothermally at 60 °C, using helium as carrier gas at 60 kPa. Oligomerization reactions were performed in a stainless steel 180 mL autoclave, equipped with a glass liner, a thermocouple, an internal cooling spiral, a magnetic stirrer, and a gas inlet via a 40 mL injection chamber.

X-ray crystal structure determinations

X-ray reflections were measured with Mo-Kα radiation (λ = 0.71073 Å) on a Nonius Kappa CCD diffractometer with rotating anode at a temperature of 150 K up to a resolution of [sin θ/λ]max = 0.65 Å⁻¹. The structures were solved with Direct Methods (program SHELXS-8640 for 10, 12, and 15; SIR-9741 for 16) Refinement was performed with SHELXL-9740 against F² of all reflections. Non hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were introduced in calculated positions and refined with a riding model. The crystal of 16 contained large voids (114 Å³ / unit cell) filled with disordered solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the routine SQUEEZE of the program PLATON42 resulting in 31 electrons / unit cell. Geometry calculations and checking for higher symmetry was performed with the PLATON42 program. Further details about the crystal structure determinations are given in table 8.
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<td>C_{20}H_{21}CINPPd</td>
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a-derived parameters do not contain the contribution of the disordered solvent.

**Computational details**

Natural bite angle calculations were performed using the Cache WorkSystem (Fujitsu Ltd) Pro Version 7.5.0.85, using the MM2 program without changing parameters. The Ni–P distance parameter amounts to 2.20 Å, the Ni–N distance to 1.91 Å.

**2-[[diphenylphosphino]methyl]pyridine [1]**

To a solution of sodium (841 mg, 36.6 mmol, 2.0 equiv) in liquid ammonia (250 mL) was added triphenylphosphine (4.79 g, 18.3 mmol, 1.0 equiv) at −78 °C. The mixture was stirred at that temperature for 4 hours, after which the deep blue solution had become yellow.
Then, 2-(chloromethyl)pyridine hydrochloride (6-HCl) [3.00 g, 18.3 mmol, 1.0 equiv] was added at −78 °C and the mixture was stirred at −33 °C. THF [40 mL] was added, and the ammonia was evaporated overnight. The resulting mixture was refluxed for one hour, water [5 mL] was added and the THF was evaporated. CH₂Cl₂ was added and the organic layer was washed with water, saturated aqueous NaHCO₃ and water again. Purification by column chromatography using Et₂O as the eluents yielded the product as a white solid (3.47 g, 12.5 mmol, 68%).

mp 47 °C

¹H NMR δ (500MHz, CDCl₃) ppm: 8.51 [d, J = 4.6 Hz, 1H, py-H6], 7.49–7.43 [m, 5H, py-H4 + Ph-H2], 7.33–7.28 [m, 4H, Ph-H3 + -H4], 7.07–7.05 [m, 1H, py-H5], 6.99 [d, J = 7.8 Hz, 1H, py-H3], 3.65 [s, 2H, CH₂].

¹³C{¹H} NMR δ (125 MHz, CDCl₃) ppm: 158.3 [d, J = 8.0 Hz, py-C2], 149.6 [s, py-C6], 138.4 [d, J = 15.2 Hz, Ph-C1], 136.6 [s, CH], 133.1 [d, J = 19.0 Hz, CH], 129.0 [s, CH], 128.7 [d, J = 6.8 Hz, CH], 123.9 [d, J = 5.9 Hz, CH], 121.3 [d, J = 2.1 Hz, CH], 39.1 [d, J = 16.5 Hz, CH₂].

³¹P{¹H} NMR δ (121 MHz, CDCl₃) ppm: −9.6.

Anal. Calcd. for Cᵢ₉HᵰNP: C, 77.96; H, 5.82; N, 5.05. Found: C, 78.11; H, 5.94, N, 4.85.

MS [El] m/z (rel. intensity): 277 [85] [M]+, 200 [19] [M–Ph]+, 185 [23] [PPh₃]⁺, 183 [100] [PPh₂–2H]+, 168 [94].

2-[3-(diphenylphosphino)propyl]pyridine (3)

The compound was prepared according to the published procedure.³² Full NMR characterization was never reported.

¹H NMR δ (500MHz, CDCl₃) ppm: 8.52 [dd, J = 5.3, 1.7 Hz, 1H, py-H6], 7.61 [dt, J = 7.7, 1.7 Hz, 1H, py-H4], 7.44–7.38 [m, 4H, Ph-H2], 7.34–7.30 [m, 6H, Ph-H3 + -H4], 7.15–7.12 [m, 2H, py-H3 + -H5], 2.96 [t, J = 7.6 Hz, 2H, py-CH₃], 2.14–2.09 [m, 2H, P–CH₂], 1.95–1.88 [m, 2H, P–CH₂–CH₂]

¹³C{¹H} NMR δ (75 MHz, CDCl₃) ppm: 161.7 [s, py-C2], 149.5 [s, py-C6], 138.9 [d, J = 12.2 Hz, Ph-C1], 136.6 [s, CH], 133.0 [d, J = 18.3 Hz, CH], 128.7 [d, J = 3.7 Hz, CH], 128.6 [s, CH], 123.1 [s, CH], 121.3 [s, CH], 39.8 [d, J = 12.2 Hz, py-CH₃], 27.8 [d, J = 12.2 Hz, P–CH₂–CH₂], 26.4 [d, J = 17.1 Hz, P–CH₃]

³¹P{¹H} NMR δ (121 MHz, CDCl₃) ppm: −15.4
2-[2-(diphenylphosphino)phenyl]pyridine (4)
To solution of 2-[2-fluorophenyl]pyridine (7) (505 mg, 2.92 mmol, 1.0 equiv) and 18-crown-6
(1.00 g, 3.79 mmol, 1.3 equiv) in THF (25 mL) was slowly added a 0.5 M solution of
potassium diphenylphosphide (7.0 mL, 3.50 mmol, 1.2 equiv) in THF at 0°C. The mixture was
stirred at room temperature for 24 h, after which water (10 mL) was added and it was
concentrated in vacuo. Et₂O (60 mL) was added and the organic phase was washed with
water twice, dried, and concentrated in vacuo. Purification on a basic alumina 90 column
(PE to PE:EtOAc = 9:1 as the eluens) yielded the product as a light yellow solid (628 mg,
1.85 mmol, 63%).
mp 86 °C
^1H NMR δ (500 MHz, CDCl₃) ppm: 8.55 [d, J = 4.9 Hz, 1H, py-H6], 7.62 [dd, J = 7.6, 0.7 Hz, 1H,
phenylene-H6], 7.61–7.58 [m, 1H, py-H4], 7.45 [dt, J = 7.6, 1.1 Hz, 1H, phenylene-H5], 7.42
[d, J = 7.9 Hz, 1H, py-H3], 7.34–7.26 [m, 11H, phenylene-H4 + Ph-H2 + -H3 + -H4], 7.16 [dd,
J = 7.1, 4.9 Hz, 1H, py-H5], 7.11 [ddd, J = 7.7, 4.0, 0.6 Hz, 1H, phenylene-H3]
^13C(^1H) NMR δ (125 MHz, CDCl₃) ppm: 159.0 [d, J = 2.8 Hz, py-C2], 148.8 [s, py-C6], 146.1 [d,
J = 24.2 Hz, C₇], 138.3 [d, J = 11.1 Hz, C₈], 136.4 [d, J = 17.7 Hz, Ph-C1], 135.7 [s, CH], 134.7
[s, CH], 134.0 [d, J = 20.0 Hz, CH], 129.8 [d, J = 4.5 Hz, CH], 128.9 [s, CH], 128.5 [s, CH], 128.4 [s, CH], 124.3 [d, J = 4.8 Hz, CH], 122.0 [s, CH]
^31P(^1H) NMR δ (121 MHz, CDCl₃) ppm: -10.1
MS (EI) m/z [rel. intensity]: 339 [9] [M]⁺, 262 [100] [M–Ph]⁺, 185 [21] [M–2Ph]⁺

2-[[1S,2S,3R,4S]-3-(diphenylphosphino)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]pyridine (5)
To a solution of 2-[[1R,4R]-1,7,7-Trimethylbicyclo[2.2.1]hept-2-en-2-yl]pyridine (8) (1.01 g,
4.74 mmol, 1.0 equiv) and diphenylphosphine (0.82 mL, 4.74 mmol, 1.0 equiv) in THF (25
mL) was added t-BuOK (106 mg, 0.95 mmol, 0.2 equiv), after which the solution turned
orange. After stirring at 60 °C for 16 hours, water [5 mL] was added, and the mixture was
concentrated. Et₂O was added, and the organic layer was washed with water 3 times and
evaporated. Purification using column chromatography [eluens PE : EtOAc = 9:1] yielded the
product as a viscous oil (1.29 g, 3.22 mmol, 68%). Analysis was consistent with literature
data.⁴⁴
2-[[diphenylphosphino]methyl]pyridine nickel dichloride (9)

A mixture of 2-[[diphenylphosphino]methyl]pyridine (1) [220 mg, 0.79 mmol, 1.0 equiv], [DME]NiCl₂ [174 mg, 0.79 mmol, 1.0 equiv] and CH₂Cl₂ [15 mL] was stirred for 20 hours. It was filtered through a path of celite, washed with CH₂Cl₂ and concentrated in vacuo. Et₂O [15 mL] was added, and the mixture was put in a sonification bath for 30 minutes. The solids were filtered off, washed with Et₂O and dried in vacuo to yield the product as a very dark purple solid [280 mg, 0.69 mmol, 87%].

mp 208 °C (dec.)

Anal. Calcd. for C₁₉H₁₈Cl₂NiP: C, 53.13; H, 3.96; N, 3.44. Found: C, 53.26; H, 4.08, N, 3.34

HRMS [FAB] m/z: calcd. for C₁₉H₁₈Cl₂NiP [M–Cl]⁺: 370.0062; found: 370.0063

\( \mu_{\text{eff}} = 2.61 \mu_\text{B} \)

2-[[2-(diphenylphosphino)ethyl]pyridine nickel dichloride (10)

A mixture of 2-[[2-(diphenylphosphino)ethyl]pyridine (2) [500 mg, 1.72 mmol, 1.0 equiv], [DME]NiCl₂ [377 mg, 1.72 mmol, 1.0 equiv] and CH₂Cl₂ [15 mL] was stirred for 16 hours. It was filtered through a path of celite, washed with CH₂Cl₂ and concentrated in vacuo. Washing with hexanes 4 times yielded the product as a purple solid [697 mg, 1.66 mmol, 96%].

Crystals suitable for X-ray diffraction were obtained by layering a CH₂Cl₂ solution of the product with hexanes.

mp 203 °C (dec.)

Anal. Calcd. for C₁₉H₁₈Cl₂NiP: C, 54.21; H, 4.31; N, 3.33. Found: C, 54.06; H, 4.25, N, 3.26

HRMS [FAB] m/z: calcd. for C₁₉H₁₈Cl₂NiP [M–Cl]⁺:384.0219 ; found: 384.0210

\( \mu_{\text{eff}} = 3.12 \mu_\text{B} \)

2-[[3-(diphenylphosphino)propyl]pyridine nickel dichloride (11)

A mixture of 2-[[3-(diphenylphosphino)propyl]pyridine (3) [200 mg, 0.65 mmol, 1.0 equiv], [DME]NiCl₂ [144 mg, 0.65 mmol, 1.0 equiv] and CH₂Cl₂ [20 mL] was stirred for 24 hours. It was filtered through a path of celite, washed with CH₂Cl₂ and concentrated to a volume of 5 mL. This was slowly dropped to 75 mL of vigorously stirred Et₂O. The solids were filtered off, washed with Et₂O and dried in vacuo to yield the product as an orange solid [224 mg, 0.52 mmol, 79%].

mp 143 °C (dec.)
Anal. Calcd. for C\textsubscript{20}H\textsubscript{20}Cl\textsubscript{2}NNiP: C, 55.23; H, 4.63; N, 3.22. Found: C, 55.35; H, 4.61, N, 3.20
HRMS (FAB) m/z: calcd. for C\textsubscript{20}H\textsubscript{20}ClNNiP [M–Cl]: 398.0375; found: 398.0361
\( \mu_{\text{eff}} = 3.47 \mu_B \)

2-\{2-\{diphenylphosphino\}phenyl\}pyridine nickel dichloride (12)
A mixture of 2-\{2-\{diphenylphosphino\}phenyl\}pyridine (4) (100 mg, 0.29 mmol, 1.0 equiv), [DME]NiCl\textsubscript{2} (65 mg, 0.29 mmol, 1.0 equiv) and CH\textsubscript{2}Cl\textsubscript{2} (10 mL) was stirred for 24 hours. It was filtered through a path of celite, washed with CH\textsubscript{2}Cl\textsubscript{2} and concentrated to a volume of 10 mL. This was slowly dropped to 75 mL of vigorously stirred Et\textsubscript{2}O. The solids were filtered off, washed with Et\textsubscript{2}O and dried in vacuo to yield the product as a light brown solid (104 mg, 0.22 mmol, 76%).
mp 268 °C (dec.)
Anal. Calcd. for C\textsubscript{23}H\textsubscript{21}Cl\textsubscript{2}NNiP: C, 58.90; H, 3.87; N, 2.99. Found: C, 59.08; H, 3.84, N, 2.92
HRMS (FAB) m/z: calcd. for C\textsubscript{23}H\textsubscript{21}ClNNiP [M–Cl]: 432.0219; found: 432.0200
\( \mu_{\text{eff}} = 3.23 \mu_B \)

2-\{1S,2R,3R,4S\}-3-\{diphenylphosphino\}-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylpyridine nickel dichloride (13)
A mixture of 2-\{1S,2R,3R,4S\}-3-\{diphenylphosphino\}-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylpyridine (5) (115 mg, 0.29 mmol, 1.0 equiv), [DME]NiCl\textsubscript{2} (63 mg, 0.28 mmol, 1.0 equiv) and CH\textsubscript{2}Cl\textsubscript{2} (6 mL) was stirred for 24 hours. It was filtered through a path of celite, washed with CH\textsubscript{2}Cl\textsubscript{2} and concentrated to approximately 5 mL, after which the product was precipitated with 30 mL Et\textsubscript{2}O. It was filtrated off and washed with Et\textsubscript{2}O. Drying in vacuo yielded the product as a purple solid (104 mg, 0.20 mmol, 68%).
mp 298 °C (dec.)
Anal. Calcd. for C\textsubscript{25}H\textsubscript{24}Cl\textsubscript{2}NNiP: C, 61.29; H, 5.71; N, 2.65. Found: C, 61.20; H, 5.67; N, 2.49
HRMS (FAB) m/z: calcd. for C\textsubscript{25}H\textsubscript{24}ClNNiP [M–Cl]: 492.1158; found: 492.1163
\( \mu_{\text{eff}} = 3.11 \mu_B \)

2-\{diphenylphosphino\}methylpyridine methylpalladium chloride (14)
2-\{diphenylphosphino\}methylpyridine (1) (71 mg, 0.26 mmol, 1.0 equiv) and [COD]Pd(CH\textsubscript{3})Cl (68 mg, 0.26 mmol, 1.0 equiv) were dissolved in CH\textsubscript{2}Cl\textsubscript{2} (5 mL) and the mixture was stirred for 16 hours. Then, it was concentrated in vacuo to approximately 0.5 mL, after which 5 mL
Et₂O was added under vigorous stirring. The white precipitate was filtrated off and washed with Et₂O. Drying in vacuo yielded the product as a white solid (92 mg, 0.21 mmol, 83%).

¹H NMR δ [500MHz, CDCl₃] ppm: 9.42 [dd, J = 5.5, 1.5 Hz, 1H, py-H6], 7.73 [tt, J = 7.5, 1.5 Hz, 1H, py-H4], 7.68–7.63 (m, 4H, Ph-H2), 7.52–7.48 (m, 2H, Ph-H4), 7.47–7.42 (m, 4H, Ph-H3), 7.42–7.40 (m, 1H, py-H5), 7.30–7.27 (m, 1H, py-H3), 4.03 [d, J = 12 Hz, 2H, CH₂], 0.78 [d, J = 2.5 Hz, 3H, CH₃]

¹³C[¹H] NMR δ [75 MHz, CDCl₃] ppm: 157.3 [d, J = 4.6 Hz, py-C2], 151.3 [s, py-C6], 138.6 [s, CH], 133.2 [d, J = 12.2 Hz, CH], 131.7 [d, J = 2.5 Hz, CH], 129.5 [d, J = 51.0 Hz, Ph-C1], 129.3 [d, J = 11.4 Hz, CH], 123.4 [s, CH], 123.2 [d, J = 9.7 Hz, CH], 43.1 [d, J = 30.0 Hz, CH₂], −5.2 [s, CH₃]

³¹P[¹H] NMR δ [121 MHz, CDCl₃] ppm: 41.6

Anal. Calcd. for C₁₅H₁₃ClNPPd: C, 52.56; H, 4.41; N, 3.23. Found: C, 52.45; H, 4.30; N, 3.18

HRMS (FAB) m/z: calcd. for C₁₅H₁₃NPPd [M−Cl]⁺: 398.0298; found: 398.0294

2-[2-(diphenylphosphino)ethyl]pyridine methylpalladium chloride [15]

2-[2-(diphenylphosphino)ethyl]pyridine [2] (300 mg, 1.03 mmol, 1.1 equiv) and [COD]Pd(CH₃)Cl [273 mg, 1.03 mmol, 1.0 equiv] were dissolved in CH₂Cl₂ [20 mL] and the mixture was stirred for 16 hours. Then, it was concentrated in vacuo to approximately 2 mL, after which the product was precipitated with 20 mL Et₂O under vigorous stirring. It was filtrated off and washed with Et₂O. Drying in vacuo yielded the product as a white solid (390 mg, 0.87 mmol, 84%).

mp 231 °C (dec.)

¹H NMR δ [500MHz, CDCl₃] ppm: 9.54 [dd, J = 5.5, 1.2 Hz, 1H, py-H6], 7.71–7.63 (m, 5H, py-H4 + Ph-H2), 7.48–7.38 (m, 6H, Ph-H3 + -H4), 7.25–7.22 (m, 1H, py-H5), 7.16 [d, J = 7.6 Hz, 1H, py-H3], 3.21–3.12 (m, 2H, py–CH₂), 2.33–2.27 (m, 2H, P–CH₂), 0.67 [d, J = 3.1 Hz, 3H, CH₃]

¹³C[¹H] NMR δ [125 MHz, CDCl₃] ppm: 159.5 [s, py-C2], 153.8 [d, J = 1.7 Hz, py-C6], 138.5 [s, CH], 133.6 [d, J = 11.5 Hz, CH], 131.6 [d, J = 51.3 Hz, Ph-C1], 131.2 [d, J = 2.3 Hz, CH], 129.0 [d, J = 10.4 Hz, CH], 124.6 [s, CH], 123.2 [s, CH], 34.3 [d, J = 5.2 Hz, py–CH₂], 26.1 [d, J = 29.4 Hz, P–CH₂], −0.7 [s, CH₃]

³¹P[¹H] NMR δ [121 MHz, CDCl₃] ppm: 36.3


HRMS (FAB) m/z: calcd. for C₂₂H₁₉NPPd [M−Cl]⁺: 412.0455; found: 412.0457
2-[(3-diphenyl(3-phosphino)propyl)pyridine methyl]palladium chloride (16)

2-[(3-diphenyl(3-phosphino)propyl)pyridine (3) [102 mg, 0.33 mmol, 1.0 equiv] and (COD)Pd(CH$_3$)Cl [89 mg, 0.33 mmol, 1.0 equiv] were dissolved in CH$_2$Cl$_2$ [5 mL] and the mixture was stirred for 16 hours. Then, it was concentrated in vacuo to approximately 0.5 mL, after which 5 mL Et$_2$O was added under vigorous stirring. The white precipitate was filtrated off and washed with Et$_2$O. Drying in vacuo yielded the product as a white solid [131 mg, 0.28 mmol, 85%].

Crystals suitable for X-ray diffraction were obtained by layering a CH$_2$Cl$_2$ solution of the product with Et$_2$O.

mp 208 °C (dec.)

$^1$H NMR $\delta$ (500 MHz, CDCl$_3$, 25 °C) ppm: 9.11 (d, $J = 5.5$ Hz, 1H, py-H6), 7.80–7.58 (bs, 4H, Ph-H2) 7.72 (t, $J = 7.5$ Hz, 1H, py-H4), 7.56–7.40 (bs, 6H, Ph-H3 + -H4), 7.31–7.28 (m, 1H, py-H5), 7.20 (d, $J = 7.5$ Hz, 1H, py-H3), 4.2–2.6 (bs, 2H, py-CH$_2$), 2.1–1.8 (bs, 2H, P-CH$_2$), 1.9–1.6 (bs, 2H, P-CH$_2$-CH$_2$), 0.73 (d, $J = 3.0$ Hz, 3H, CH$_3$)

$^1$H NMR $\delta$ (500 MHz, CDCl$_3$, -20 °C) ppm: 9.08 (d, $J = 5.5$ Hz, 1H, py-H6), 7.91–7.87 (m, 2H, Ph$^a$-H2), 7.76 (dt, $J = 7.5, 1.5$ Hz, 1H, py-H4), 7.61–7.38 (m, 8H, Ph$^b$-H2 + Ph-H3 + -H4), 7.35–7.32 (m, 1H, py-H5), 7.24 (d, $J = 7.5$ Hz, 1H, py-H3), 3.99–3.91 (m, 1H, py-CH$_2$), 2.93–2.90 (m, 1H, py-CH$_3$), 2.16–2.09 (m, 1H, P-CH$_2$H), 2.00–1.85 (m, 1H, P-CH$_2$H), 1.80–1.73 (m, 1H, P-CH$_2$-CH$_2$), 1.59–1.50 (m, 1H, P-CH$_2$-CH$_2$), 0.67 (d, $J = 3.0$ Hz, 3H, CH$_3$)

$^1$H NMR $\delta$ (500 MHz, Cl$_2$DCCDCl$_3$, 80 °C) ppm: 9.13 (d, $J = 5.3$ Hz, 1H, py-H6), 7.79–7.70 (m, 5H, py-H4 + Ph-H2), 7.56–7.48 (m, 6H, Ph-H3 + -H4), 7.35–7.31 (m, 1H, py-H5), 7.23 (d, $J = 7.7$ Hz, 1H, py-H3), 3.55–3.48 (m, 2H, py-CH$_2$), 2.00–1.93 (m, 2H, P-CH$_2$), 1.87–1.78 (m, 2H, P-CH$_2$-CH$_2$), 0.74 (d, $J = 3.0$ Hz, 3H, CH$_3$)

$^{13}$C($^1$H) NMR $\delta$ (125 MHz, CDCl$_3$, 25 °C) ppm: 159.8 (s, py-C2), 152.3 (s, py-C6), 138.3 (s, CH), 135–132 (bs, CH), 131.1 (bs, CH), 129.0 (d, $J = 10.6$ Hz, CH), 123.8 (s, CH), 123.1 (s, CH), 36.6 (d, $J = 8.2$ Hz, py-CH$_2$), 26.3 (d, $J = 27.8$ Hz, P-CH$_2$), 24.5 (s, P-CH$_2$-CH$_2$), -0.5 (d, $J = 2.7$ Hz, CH$_3$) the signal for the Ph-C1 carbon atom was not observed

$^{13}$C($^1$H) NMR $\delta$ (125 MHz, Cl$_2$DCCDCl$_3$, 80 °C) ppm: 159.5 (s, py-C2), 152.0 (s, py-C6), 137.8 (s, CH), 133.0 (d, $J = 11.0$ Hz, CH), 130.6 (d, $J = 2.5$ Hz, CH), 130.3 (d, $J = 48.1$ Hz, Ph-C1), 128.6 (d, $J = 10.6$ Hz, CH), 123.3 (s, CH), 122.5 (s, CH), 36.2 (d, $J = 8.4$ Hz, py-CH$_2$), 26.2 (d, $J = 27.4$ Hz, P-CH$_3$), 24.1 (s, P-CH$_2$-CH$_2$), -1.2 (d, $J = 3.4$ Hz, CH$_3$)

$^{31}$P($^1$H) NMR $\delta$ (121 MHz, CDCl$_3$, 25 °C) ppm: 23.1
Anal. Calcd. for $C_2H_3ClNPd$: C, 54.56; H, 5.02; N, 3.03. Found: C, 54.37; H, 4.96; N, 2.88
HRMS (FAB) m/z: calcd. for $C_2H_3ClNPd \ [M-Cl]^+$: 426.0612; found: 426.0609

2-[2-(diphenylphosphino)phenyl]pyridine methylpalladium chloride (17)

2-[2-(diphenylphosphino)phenyl]pyridine (4) (128 mg, 0.377 mmol, 1.0 equiv) and [COD]Pd(CH₃)Cl (100 mg, 0.377 mmol, 1.0 equiv) were dissolved in CH₂Cl₂ (10 mL) and the mixture was stirred for 16 hours. Then, it was concentrated in vacuo to approximately 1 mL, after which 10 mL Et₂O was added under vigorous stirring. The white precipitate was filtrated off and washed with Et₂O. Drying in vacuo yielded the product as a white solid (170 mg, 0.343 mmol, 91%).

mp 213 °C (dec.)

$^1$H NMR δ [500MHz, CDCl₃] ppm: 9.53–9.51 [m, 1H, py-H₆], 7.64 [dt, J = 7.8, 1.7 Hz, 1H, py-H₄], 7.61–7.53 [m, 2H, phenylene-H₅ + -H₆], 7.45–7.38 [m, 3H, phenylene-H₄ + Ph-H₄], 7.37–7.32 [m, 8H, Ph-H₂ + -H₃], 7.27 [d, J = 7.8 Hz, 1H, py-H₃], 7.25–7.22 [m, 1H, py-H₅], 7.12–7.07, [m, 1H, phenylene-H₃], 0.75 [d, J = 2.7 Hz, 3H, CH₃]

$^{13}$C($^1$H) NMR δ [125 MHz, CDCl₃] ppm: 155.6 [d, J = 5.5 Hz, py-C2], 152.6 [s, py-C6], 142.9 [d, J = 13.5 Hz, phenylene-C1], 138.6 [s, CH], 134.5 [d, J = 11.8 Hz, CH], 132.2 [d, J = 8.4 Hz, CH], 131.8 [d, J = 4.2 Hz, CH], 131.5 [d, J = 2.1 Hz, CH], 131.4 [d, J = 2.5 Hz, CH], 129.7 [d, J = 7.6 Hz, CH], 128.8 [d, J = 11.0 Hz, CH], 127.5 [d, J = 44.3 Hz, C₆], 127.3 [d, J = 51.9 Hz, C₆], 125.5 [s, CH], 124.1 [s, CH], 1.2 [s, CH₃]

$^{31}$P($^1$H) NMR δ [121 MHz, CDCl₃] ppm: 39.2

Anal. Calcd. for $C_{23}H_{21}ClNPd$: C, 58.08; H, 4.27; N, 2.82. Found: C, 57.89; H, 4.17; N, 2.72
HRMS (FAB) m/z: calcd. for $C_{23}H_{21}ClNPd \ [M-Cl]^+$: 460.0456; found: 460.0458

2-[(1S,2S,3R,4S)-3-(diphenylphosphino)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]pyridine methylpalladium chloride (18)

2-[(1S,2R,3R,4S)-3-(diphenylphosphino)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]pyridine (5) (133 mg, 0.33 mmol, 1.0 equiv) and [COD]Pd(CH₃)Cl (88 mg, 0.33 mmol, 1.0 equiv) were dissolved in CH₂Cl₂ (5 mL) and the mixture was stirred for 16 hours. It was concentrated in vacuo to approximately 0.5 mL, after which 5 mL Et₂O was added under vigorous stirring. The white precipitate was filtrated off and washed with Et₂O. Drying in vacuo yielded the product as a white solid (143 mg, 0.26 mmol, 77%).

mp 181 °C (dec.)
$^1$H NMR $\delta$ (500MHz, CDCl$_3$) ppm: 9.53 [dd, $J = 5.6, 1.2$ Hz, 1H, py-H6], 7.83-7.77 [m, 2H, Ph$_2$-H2], 7.76-7.68 [m, 3H, py-H4 + Ph$_2$-H2], 7.48-7.37 [m, 7H, py-H3 + Ph-H3 + -H4], 7.23-7.19 [m, 1H, py-H5], 3.85 [dd, $J = 24.2, 9.6$ Hz, 1H, H2], 2.24 [ddd, $J = 13.9, 9.3, 5.1$ Hz, 1H, H6], 2.17 [dd, $J = 6.7, 3.5$ Hz, 1H, H6'], 2.07-2.02 [m, 1H, H3], 1.97 [ddd, $J = 22.0, 11.6, 5.4$ Hz, 1H, H4], 1.67-1.60 [m, 1H, H5], 1.35-1.29 [m, 1H, H5'], 1.12 [s, 3H, CH$_3$], 0.98 [d, $J = 1.2$ Hz, 3H, CH$_3$], 0.75 [s, 3H, CH$_3$], 0.17 [s, 3H, Pd-CH$_3$]  

$^{13}$C($^1$H) NMR $\delta$ (125 MHz, CDCl$_3$) ppm: 161.6 [s, py-C2], 154.8 [s, py-C6], 137.2 [s, CH], 136.8 [bs, CH], 133.4 [d, $J = 49.4$ Hz, Ph$_2$-C1], 132.8 [d, $J = 10.6$ Hz, CH], 131.4 [d, $J = 2.5$ Hz, CH], 130.7 [d, $J = 2.1$ Hz, CH], 129.2 [d, $J = 48.1$ Hz, Ph$_2$-C1], 129.0 [d, $J = 10.1$ Hz, CH], 128.1 [d, $J = 11.0$ Hz, CH], 122.1 [s, CH], 122.0 [s, CH], 56.7 [d, $J = 4.7$ Hz, CH], 50.2 [s, C$_2$], 47.7 [d, $J = 7.6$ Hz, C$_2$], 46.7 [d, $J = 6.3$ Hz, CH], 46.1 [d, $J = 24.1$ Hz, C3], 32.8 [d, $J = 8.0$ Hz, CH$_2$], 28.2 [s, CH$_2$], 20.8 [s, CH$_3$], 19.5 [s, CH$_3$], 14.7 [s, CH$_3$], 0.9 [d, $J = 3.4$ Hz, Pd-CH$_3$]  

$^{31}$P($^1$H) NMR $\delta$ (121 MHz, CDCl$_3$) ppm: 41.3  

Anal. Calcd. for C$_{28}$H$_{33}$ClNPPd: C, 60.44; H, 5.98; N, 2.52. Found: C, 60.35; H, 5.91; N, 2.46  

HRMS [FAB] m/z: calcd. for C$_{28}$H$_{33}$NPPd [M+Cl]$^+$: 520.1397; found: 520.1387  

2-[[diphenylphosphinomethyl]pyridine methylpalladium(acetonitrile) tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (19)  

To a mixture of 2-[[diphenylphosphino)methyl]pyridine palladium methylchloride [14] [188 mg, 0.433 mmol, 1.0 equiv] and sodium tetrakis[3,5-trifluoromethyl]phenyl]borate [384 mg, 0.433 mmol, 1.0 equiv] were added CH$_2$CN [5 mL] and CH$_3$Cl$_2$ [25 mL] and the mixture was stirred for 16 hours. It was cannula filtrated, evaporated to dryness and co-evaporated with 5 mL pentane to yield the product as a white solid [529 mg, 0.406 mmol, 94%].  

$^1$H NMR $\delta$ (500MHz, CD$_2$Cl$_2$) ppm: 8.77 [bs, 1H, py-H6], 7.88-7.84 [m, 1H, py-H4], 7.80-7.75 [m, 8H, Ar'-H2], 7.69-7.63 [m, 4H, Ph-H2], 7.62-7.57 [m, 6H, Ph-H4 + Ar'-H4], 7.56-7.51 [m, 5H, py-H5 + Ph-H3], 7.39-7.36 [m, 1H, py-H3], 4.16 [d, $J = 12.5$ Hz, 2H, CH$_2$], 2.33 [s, 3H, NCCCH$_2$], 0.72 [s, 3H, Pd-CH$_3$]  

$^{13}$C($^1$H) NMR $\delta$ (125 MHz, CD$_2$Cl$_2$) ppm: 162.4 [q, $J = 49.8$ Hz, Ar'-C1], 157.7 [s, py-C2], 150.2 [s, py-C6], 140.4 [s, CH], 135.5 [bs, Ar'-C2], 135.4 [overlapping with Bar' signal, Ph-C1], 133.5 [d, $J = 12.2$ Hz, CH], 133.0 [s, CH], 130.1 [d, $J = 11.4$ Hz, CH], 129.5 [quartet of multiplets, $J = 31.6$ Hz, Ar'-C3], 125.2 [q, $J = 272.4$, CF$_2$], 124.9 [d, $J = 8.3$ Hz, CH], 124.6 [s, CH], 120.6 [s, NCCCH$_2$], 118.1 [m, Ar'-C4], 43.5 [d, $J = 88.5$ Hz, CH$_2$], 3.4 [s, NCCCH$_3$], -3.6 [s, Pd-CH$_3$]
$^{31}$P($^1$H) NMR δ (121 MHz, CD$_2$Cl$_2$) ppm: 43.1
$^{19}$F($^1$H) NMR δ (282 MHz, CD$_2$Cl$_2$) ppm: -63.0
Anal. Calcd. for C$_{33}$H$_{32}$BF$_2$N$_2$Pd: C, 49.24; H, 2.76; N, 2.13. Found: C, 49.38; H, 2.81; N, 2.12
HRMS (FAB) m/z: calcd. for C$_{33}$H$_{32}$BF$_2$N$_2$Pd [M–BF$_2$N$_2$Pd]$: 412.0455; Found: 412.0454
MS (FD) m/z: 453 [M–BF$_2$N$_2$Pd]$^+$

2-[2-(diphenylphosphino)ethyl]pyridine methylpalladium(acetonitrile) tetrakis[3,5-bis(trifluoromethyl)phenyl]borate [20]
To a mixture of 2-[2-(diphenylphosphino)ethyl]pyridine palladium methylchloride (15) [381 mg, 0.850 mmol, 1.0 equiv] and sodium tetrakis[3,5-trifluoromethyl]phenylborate (753 mg, 0.850 mmol, 1.0 equiv) were added CH$_2$CN (4 mL) and CH$_2$Cl$_2$ (20 mL) and the mixture was stirred for 16 hours. It was cannula filtrated, evaporated to dryness and co-evaporated with 2 times 5 mL pentane to yield the product as a white solid (1.11 g, 0.845 mmol, 99%).

$^1$H NMR δ [500MHz, CD$_2$Cl$_2$] ppm: 8.66–8.64 (m, 1H, py-H6), 7.83 [dt, J = 7.6, 1.7 Hz, 2H, Ph-H4], 7.76–7.73 (m, 9H, py-H4 + Ar’-H2), 7.69–7.64 (m, 4H, Ph-H2), 7.58 (s, 4H, Ar’-H4), 7.54–7.49 (m, 4H, Ph-H3), 7.38–7.34 (m, 2H, py-H3 + -H5), 3.27–3.18 (m, 2H, py-CH$_2$), 2.42–2.37 (m, 2H, P–CH$_2$), 2.31 (s, 3H, NCCCH$_3$), 0.55 [d, J = 2.0 Hz, Pd–CH$_2$]

$^{13}$C($^1$H) NMR δ (125 MHz, CD$_2$Cl$_2$) ppm: 162.4 [q, J = 49.8 Hz, Ar’-C1], 160.3 (s, py-C2), 151.6 (s, py-C6), 140.3 (s, CH), 135.5 (bs, Ar’-C2), 133.8 (d, J = 11.8 Hz, CH), 132.5 [d, J = 2.9 Hz, CH], 130 [overlapping with other signals, Ph-C1], 129.8 [d, J = 11.4 Hz, CH], 129.5 [quartet of multiplets, J = 31.6 Hz, Ar’-C3], 126.5 [s, CH], 125.2 [q, J = 272.4, CF$_3$], 120.0 (s, NCCCH$_3$), 118.1 (m, Ar’-C4), 34.4 [d, J = 3.4 Hz, py-CH$_2$], 25.9, [d, J = 32.9 Hz, P–CH$_2$], 3.2 (s, NCCCH$_3$), -0.1 (s, Pd–CH$_3$)

$^{31}$P($^1$H) NMR δ (121 MHz, CD$_2$Cl$_2$) ppm: 39.3
$^{19}$F($^1$H) NMR δ (282 MHz, CD$_2$Cl$_2$) ppm: -63.0
Anal. Calcd. for C$_{33}$H$_{32}$BF$_2$N$_2$Pd: C, 49.24; H, 2.76; N, 2.13. Found: C, 49.38; H, 2.81; N, 2.12
HRMS (FAB) m/z: calcd. for C$_{33}$H$_{32}$BF$_2$N$_2$Pd [M–BF$_2$N$_2$Pd]$: 412.0455; Found: 412.0454
MS (FD) m/z: 453 [M–BF$_2$N$_2$Pd]$^+$

2-[3-(diphenylphosphino)propyl]pyridine methylpalladium(acetonitrile) tetrakis[3,5-bis(trifluoromethyl)phenyl]borate [21]
To a mixture of 2-[3-(diphenylphosphino)propyl]pyridine palladium methylchloride (16) [173 mg, 0.374 mmol, 1.0 equiv] and sodium tetrakis[3,5-trifluoromethyl]phenylborate (332
mg, 0.374 mmol, 1.0 equiv) were added CH₂CN (3 mL) and CH₂Cl₂ (15 mL) and the mixture was stirred for 16 hours. It was cannula filtrated, evaporated to dryness and co-evaporated with 5 mL pentane to yield the product as a white solid (481 mg, 0.363 mmol, 97%).

¹H NMR δ (500 MHz, CD₂Cl₂, 25 °C) ppm: 8.57 [ddd, J = 5.5, 1.7, 0.8 Hz, 1H, py-H6], 7.89 [dt, J = 7.7, 1.7 Hz, 1H, py-H4], 7.90–7.46 [m, 22H, Ph-H2 + -H3 + -H4 + Ar'-H2 + -H4], 7.40 [ddd, J = 7.7, 5.5, 1.4 Hz, 1H, py-H5], 7.38 [ddd, J = 7.7, 1.4, 0.8 Hz, 1H, py-H3], 3.9–2.8 [bs, 2H, py–CH₃], 2.23 [s, 3H, NCCH₃], 2.1–1.6 [bs, 4H, P–CH₂–CH₂], 0.59 [d, J = 2.2 Hz, 3H, Pd–CH₃]

¹H NMR δ (500 MHz, CD₂Cl₂, –40 °C) ppm: 8.56 [d, J = 4.9 Hz, 1H, py-H6], 7.83–7.73 [m, 11H, py-H4 + Ph²-H2 + Ar⁻-H2], 7.65–7.61 [m, 2H, Ph²-H2], 7.60–7.54 [m, 6H, Ph²-H3 + Ar⁻-H4], 7.51–7.46 [m, 2H, Ph-H4], 7.44–7.36 [m, 3H, py-H5 + Ph²-H3], 7.32 [d, J = 7.8 Hz, 1H, py-H3], 3.70–3.61 [m, 1H, py-CH₃], 3.01–2.96 [m, 1H, py-CH₇], 2.23 [s, 3H, NCCH₃], 2.15–2.08 [m, 1H, P-CH₇], 2.00–1.87 [m, 1H, P-CH₂-CH₇], 1.76–1.68 [m, 1H, P-CH₇-CH₃], 0.49 [d, J = 1.9 Hz, 3H, Pd-CH₃]

¹C{¹H} NMR δ (125 MHz, CD₂Cl₂, 25 °C) ppm: 162.4 [q, J = 49.8 Hz, Ar'-C1], 160.7 [s, py-C2], 150.2 [s, py-C6], 140.1 [s, CH], 135.5 [bs, Ar'-C2], 132.6–132.1 [bs, CH], 129.8 [d, J = 11.0 Hz, CH], 129.5 [quartet of multiplets, J = 31.6 Hz, Ar'-C3], 125.7 [s, CH], 125.2 [q, J = 272.4, CF₃], 124.3 [s, CH], 119.6 [s, NCCH₃], 118.1 [m, Ar'-C4], 36.8 [d, J = 8.0 Hz, py-CH₃], 26.2 [d, J = 31.2 Hz, P-CH₃], 24.4 [s, P-CH₂-CH₃], 3.2 [s, NCCH₃], -0.4 [s, Pd-CH₃] signals for some carbons could not be observed

¹C{¹H} NMR δ (125 MHz, CD₂Cl₂, –40 °C) ppm: 161.7 [q, J = 49.8 Hz, Ar'-C1], 159.7 [s, py-C2], 149.8 [s, py-C6], 139.4 [s, CH], 134.9–134.5 [m, CH + Ar'-C2], 132.3 [d, J = 2.2 Hz, CH], 131.4 [d, J = 10.1 Hz, CH], 131.0 [d, J = 2.2 Hz, CH], 130.4 [d, J = 55.7 Hz, Ph²-C1], 129.4 [d, J = 11.4 Hz, CH], 129.0 [d, J = 11.0 Hz, CH], 128.6 [quartet of multiplets, J = 31.6 Hz, Ar'-C3], 125.1 [s, CH], 125 [overlapping with other signals, Ph²-C1], 124.4 [q, J = 272.4, CF₃], 123.7 [s, CH], 119.1 [d, J = 12.7 Hz, NCCH₃], 117.5 [m, Ar'-C4], 36.1 [d, J = 8.0 Hz, py-CH₃], 25.0 [d, J = 30.8 Hz, P-CH₃], 23.7 [s, P-CH₂-CH₃], 3.3 [s, NCCH₃], -1.1 [d, J = 3.2 Hz, Pd-CH₃]

³¹P{¹H} NMR δ (121 MHz, CD₂Cl₂, 25 °C) ppm: 25.3

¹⁹F{¹H} NMR δ (282 MHz, CD₂Cl₂, 25 °C) ppm: -63.0
2-[2-(diphenylphosphino)phenyl]pyridine methylpalladium(acetonitrile) tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (22)

To a mixture of 2-[2-(diphenylphosphino)phenyl]pyridine palladium methylchloride [17] (164 mg, 0.330 mmol, 1.0 equiv) and sodium tetrakis[3,5-trifluoromethyl]phenyl]borate [293 mg, 0.330 mmol, 1.0 equiv] were added CH₃CN (4 mL) and CH₂Cl₂ (20 mL) and the mixture was stirred for 16 hours. It was cannula filtrated, evaporated to dryness and co-evaporated with 5 mL pentane to yield the product as a white solid (362 mg, 0.265 mmol, 80%).

$^1$H NMR δ (500MHz, CD₂Cl₂) ppm: 8.64 [d, J = 5.1 Hz, 1H, py-H6], 7.80–7.72 [m, 9H, py-H4 + Ar'-H2], 7.72–7.67 [m, 2H, phenylene-H5 + -H6], 7.59 [s, 4H, Ar'-H4], 7.56–7.50 [m, 3H, phenylene-H4 + Ph-H4], 7.48 [d, J = 8.1 Hz, 1H, py-H3], 7.45–7.40 [m, 4H, Ph-H3], 7.35–7.29 [m, 5H, py-H5 + Ph-H2], 7.19 [dd, J = 10.7, 8.1 Hz, 1H, phenylene-H3], 2.30 [s, 3H, NCCH₃], 0.63 [d, J = 1.5 Hz, 3H, Pd–CH₃]

$^{13}$C($^1$H) NMR δ (125 MHz, CD₂Cl₂) ppm: 162.4 [q, J = 49.8 Hz, Ar'-C1], 156.1 [d, J = 5.0 Hz, py-C2], 150.3 [s, py-C6], 142.5 [d, J = 12.7 Hz, phenylene-C1], 140.5 [s, CH], 135.5 [bs, Ar'-C2], 134.7 [d, J = 12.2 Hz, CH], 132.9 [s, CH], 132.7 [s, CH], 131.0 [d, J = 8.4 Hz, CH], 129.7 [d, J = 12.2 Hz, CH], 129.5 [quartet of multiplets, J = 31.6 Hz, Ar'-C3], 127.4 [s, CH], 125.5 [d, J = 48.5 Hz, C₉], 125.4 [d, J = 57.4 Hz, C₉], 125.3 [s, CH], 125.2 [q, J = 272.4, CF3], 119.9 [s, NCCH₃], 118.1 [m, Ar'-C4], 3.3 [s, Pd–CH₃], 2.0 [s, NCCH₃] signals for two aromatic CH carbons could not be observed due to overlap with other signals

$^{31}$P($^1$H) NMR δ (121 MHz, CD₂Cl₂) ppm: 40.2

$^{19}$F($^1$H) NMR δ (282 MHz, CD₂Cl₂) ppm: -63.0

Anal. Calcd. for C₉₉H₃₈BF₉₅N₂PPd: C, 51.03; H, 2.66; N, 2.05. Found: C, 51.07; H, 2.69; N, 2.01

HRMS (FAB) m/z: calcd. for C₉₉H₃₈BF₉₅N₂PPd [M–BAR'₄–CH₃CN]⁺: 460.0456; Found: 460.0454

MS (FD) m/z: 501 [M–BAR'₄]⁺

2-[[1S,2S,3R,4S]-3-(diphenylphosphino)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]pyridine methylpalladium(acetonitrile) tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (23)

To a mixture of 2-[[1S,2S,3R,4S]-3-(diphenylphosphino)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]pyridine palladium methylchloride [18] (167 mg, 0.300 mmol, 1.0 equiv) and sodium
tetrakis[[3,5-trifluoromethyl]phenyl]borate (266 mg, 0.300 mmol, 1.0 equiv) were added CH$_3$CN (3 mL) and CH$_2$Cl$_2$ (15 mL) and the mixture was stirred for 24 hours. It was cannula filtrated, evaporated to dryness and co-evaporated with 5 mL pentane to yield the product as an off-white solid (325 mg, 0.288 mmol, 76%).

$^1$H NMR $\delta$ (500MHz, CD$_2$Cl$_2$) ppm: 9.24–9.18 [m, 1H, py-H6], 7.83 [dt, $J = 7.8$, 1.5 Hz, 1H, py-H4], 7.78–7.68 [m, 10 H, Ph$_2$-H2 + Ar'-H2], 7.66–7.61 [m, Ph$_2$-H2], 7.58 [s, 4H, Ar'-H4], 7.56–7.45 [m, 7H, py-H3 + Ph-H3 + -H4], 7.35–7.32 [m, 1H, py-H5], 3.62–3.57 [m, H2], 2.22–2.10 [m, 6H, H3 + H6 + NCCH3], 2.00–1.93 [m, 1H, H4], 1.70–1.64 [m, 1H, H5], 1.37–1.23 [m, 1H, H5'], 1.12 [s, 3H, CH$_3$], 0.89 [s, 3H, CH$_3$], 0.76 [s, 3H, CH$_3$], 0.15 [s, 3H, Pd–CH$_3$]

$^{13}$C($^1$H) NMR $\delta$ (125 MHz, CD$_2$Cl$_2$) ppm: 162.5 [s, py-C2], 162.4 [q, $J = 49.8$ Hz, Ar'-C1], 154.1 [s, py-C6], 138.6 [s, CH], 137.1 [d, $J = 11.8$ Hz, CH], 135.5 [bs, Ar'-C2], 133.0 [d, $J = 15.1$ Hz, CH], 132.6 [s, CH], 132 [overlapping with other signals, Ph-C1], 131.7 [s, CH], 129.7 [d, $J = 10.1$ Hz, CH], 129.5 [quartet of multiplets, $J = 31.6$ Hz, Ar'-C3], 129.0 [d, $J = 11.4$ Hz, CH], 125.2 [q, $J = 272.4$, CF$_3$], 123.5 [s, CH], 122.8 [s, CH], 118.2 [s, NCCH$_3$], 118.1 [m, Ar'-C4], 57.4 [s, CH], 50.8 [s, C$_6$], 48.3 [d, $J = 7.2$ Hz, C$_6$], 47.1 [d, $J = 5.5$ Hz, CH], 46.6 [d, $J = 25.3$ Hz, C3], 33.1 [d, $J = 8.9$ Hz, CH$_3$], 28.4 [s, CH$_3$], 20.9 [s, CH$_3$], 19.7 [s, CH$_3$], 15.2 [s, CH$_3$], 2.8 [s, NCCH$_3$], 1.4 [s, Pd–CH$_3$]

$^{31}$P($^1$H) NMR $\delta$ (121 MHz, CD$_2$Cl$_2$) ppm: 42.7

$^{19}$F($^1$H) NMR $\delta$ (282 MHz, CD$_2$Cl$_2$) ppm: −63.0

Anal. Calcd. for C$_{49}$H$_{45}$BF$_{12}$N$_2$P$_2$: C, 52.25; H, 3.39; N, 1.97. Found: C, 52.38; H, 3.42; N, 1.87

HRMS (FAB) m/z: calcd. for C$_{49}$H$_{45}$BF$_{12}$N$_2$P$_2$ [M–Ar'$_4$–CH$_3$CN]$^+$: 520.1397; Found: 520.1391

MS (FD) m/z: 6 [M–Ar'$_4$–CH$_3$CN]$^+

**General procedure for the nickel-catalyzed oligomerization**

The autoclave was heated to 140 °C under vacuum for 1 h and cooled under dinitrogen atmosphere. A solution or suspension of the catalyst precursor (10 μmol) in toluene (18.5 mL) was introduced in the reaction chamber and the autoclave was purged with 10 bar of ethene 3 times and brought to 10 bar ethene pressure. After 10 min, the reaction chamber was closed. The injection chamber was vented and 1.5 mL MAO in toluene solution (10 % w/w, total Al 2.3 mmol) and 5.0 mL of a solution of heptane in toluene (0.20 M, total internal standard 1.0 mmol) were introduced under dinitrogen atmosphere. Then, it was purged with 10 bar of ethene 3 times and brought to 10 bar ethene pressure. After 10 minutes, the injection chamber was closed, the autoclave was disconnected from all lines, and the
autoclave was weighed. The autoclave was reconnected, the pressure in the reaction chamber was lowered to −8 bar and the connection between the reaction chamber and the injection chamber was opened, causing the immediate introduction of the MAO and internal standard solution in the reaction chamber. During the run, a constant ethene pressure of 10 bar was applied and the temperature was controlled at 30 °C through the internal cooling spiral against the exotherm of the reaction. After the run, the autoclave was closed and the autoclave was disconnected from all lines and weighed. A sample for gas-phase GC analysis was taken and the autoclave was vented and opened. 50 mL iced cold 2M hydrochloric acid was added to the reaction mixture and it was stirred vigorously in an iced bath before samples for liquid-phase GC analysis were taken. Ethene consumption was calculated from the increase in weight of the autoclave. Total amount of butenes was calculated from the difference between total ethene consumption and the amount of other oligomers formed.

**General procedure for the palladium-catalyzed oligomerization**

The autoclave was charged with the catalyst-precursor [100 µmol], closed, brought under dinitrogen atmosphere, and warmed to 30 °C. Then, 25 mL of a solution of heptane in toluene [0.0040 M, total internal standard 0.10 mmol] was introduced and the autoclave was purged with 10 bar of ethene 3 times and brought under 10 bar ethene pressure. After the run, the autoclave was vented and opened. 50 mL iced cold 2M hydrochloric acid was added to the reaction mixture and it was stirred vigorously in an iced bath. A sample of the organic phase was cooled to −70 °C and evacuated 3 times to remove ethene before liquid-phase GC analysis was performed.

**References**


