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

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Chapter 5

Nickel and Palladium Complexes of New Pyridine-Phosphine Ligands and Their Use in Ethene Oligomerization

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Nickel and Palladium Complexes of New Pyridine-Phosphine Ligands and Their Use in Ethene Oligomerization

Summary
New pyridine-phosphine ligands of general structure 2-[(2-([diarylphosphino]ethyl)pyridine were developed. The phosphorus substituents in these bidentates are 2-tolyl, 2-anisyl, and mesityl. The ligands could be conveniently synthesized in good yields. The nickel dichloride complexes of the ligands are paramagnetic. The metal centers have a distorted tetrahedral surrounding, as was evident from the crystal structures and the magnetic moments in solution. The neutral methylpalladium chloride and the cationic methylpalladium complexes have a distorted square planar surrounding around the metal center. For the complexes of two of the ligands, a steric interaction of a ligand-proton with the palladium atom was observed in the crystal structures and in solution. These interactions probably were related to hindered flipping of the six-membered metallocycle, which was observed in VT-NMR measurements. The complexes of the mesityl substituted ligand show neither hindered flipping of the metal chelate ring nor a sign of Pd-H interactions. The nickel complexes form active catalysts for the oligomerization of ethene after MAO activation. The bulky 2-tolyl and mesityl groups suppress isomerization of the growing chain, reflected in a high 1-butene selectivity. For the complex made from the ligand with the most bulky (mesityl) substituents, this selectivity was 90%. The anisyl substituents induced a different catalytic behavior of the corresponding nickel complex. Selectivity for 1-butene was lower but the productivity was higher, with a turnover frequency of $65\cdot10^3 \text{ (mol C}_2\text{H}_4\text{)}\text{-mol Ni-h)}^{-1}$. The cationic palladium complexes showed a very low activity in ethene oligomerization. Butenes were the major product, but significant amounts of higher olefins were formed as well.

Introduction
The oligomerization of ethene is an important industrial reaction, and megatons of $\alpha$-olefins are produced yearly in this way. Depending on the chain-length of the alkene, they are used for the production of various products. The most important ones are linear low-density polyethylene (LLDPE) [C4–C10], poly-$\alpha$-olefins [C4, C10], plasticizers [C6–C10], lubricants [C8–C10], lube oil additives [C12–C18], and surfactants [C12–C20]. In order to understand better the behavior of oligomerization catalysts and possibly improve their performance, much research is still devoted to the formation of olefins from
Amongst many transition metal complexes, nickel and –to a lesser extent–
palladium complexes of P,N ligands (bidentate ligands with a phosphorus and a nitrogen
donor atom) have been studied in this reaction. The development and application of P,N
ligands is a significant field of homogeneous catalysis, and this ligand type has proven its
value in many reactions. We were particularly interested in pyridine-phosphine ligands.
The chemistry of this class of ligand has been reviewed, and has been studied in nickel and
palladium-catalyzed ethene oligomerization.

In this chapter, we present the development and study of pyridine-phosphine ligands [1] and
their neutral nickel [4], neutral palladium [5], and cationic palladium [6] complexes.
Complexes 4 (with MAO activation) and 6 were also evaluated for their potential as ethene
oligomerization catalysts.

Results and discussion

In this study we used P,N-ligands 1a–c, with a pyridine and a diarylphosphine donor group,
connected by a 1,2-ethanediyl bridge. They differ in the aryl groups at the phosphine, which
are 2-tolyl, 2-anisyl and mesityl for a, b, and c, respectively.

Ligand synthesis

\[
\begin{align*}
\text{Ar}_2\text{P(O)}\text{H} \quad &\xrightarrow{\text{tBuOK, THF, 60 }^\circ\text{C, 16 h.}} \quad \text{PhSiH}_3 \\
\text{2} &\quad \text{3a: 80\%} \\
&\quad \text{3b: 72\%} \\
&\quad \text{3c: 62\%} \\

\text{Reflux 16 h.} &\quad \text{1a: 95\%} \\
&\quad \text{1b: 93\%} \\
&\quad \text{1c: 100\%}
\end{align*}
\]

Scheme 1. Synthesis of ligands 1.

The ligands were synthesized in 2 steps as depicted in scheme 1. Base-catalyzed
hydrophosphination of 2-vinylypyridine (2) with diarylphosphine oxides gave 2-[2-
{diarylphosphinoyl}ethyl]pyridine compounds 3 in moderate to good yields. The secondary
phosphine oxides used in this reaction can conveniently be prepared by reaction of
arylithium or Grignard reagents with diethylphosphite.\textsuperscript{11,12} In the second step, phosphine oxides 3 were reduced using phenylsilane and the 2-[2-(diarylphosphino)ethyl]pyridine ligands 1 were obtained in excellent yields. In the solid state, they are stable in air. In solution under aerobic conditions, they are slowly oxidized to phosphine oxides 3.

**Synthesis and characterization of nickel complexes**

The nickel dichloride complexes 4 were obtained from reaction of the ligands with [DME]NiCl\textsubscript{2} [DME = 1,2-dimethoxyethane], see scheme 2. After the reaction, the products were filtered through a path of celite to remove any unreacted [DME]NiCl\textsubscript{2}. The solids obtained after evaporation of the solvent were washed with ether to remove any remaining free ligand, and this yielded the complexes 4 in pure form. All complexes exhibit a characteristic purple color in CH\textsubscript{2}Cl\textsubscript{2} solution; in the solid state 4a and 4c are purple as well, while 4b is a brown solid.

![Scheme 2: Synthesis of nickel complexes 4.](image)

The nickel complexes are paramagnetic, as evidenced by their magnetic moments in CD\textsubscript{2}Cl\textsubscript{2} solution of 3.85 (4a), 3.30 (4b), and 3.30 \(\mu_B\) (4c). These values are indicative of a distorted tetrahedral surrounding of the nickel.\textsuperscript{13} Using high resolution mass spectrometry, the [ligand]NiCl\textsuperscript{2} ion was observed for all complexes. The loss of one chloride is a consequence of the fast atom bombardment (FAB) ionization technique used. Ionization of the complexes is accomplished by proton addition, which is immediately followed by loss of HCl and this results in the formation of the observed ion. Elemental analyses for the nickel complexes were in agreement with the proposed structures. Compounds 4 were EPR-silent, as can be expected for this type of complexes.\textsuperscript{14} In addition to the above mentioned characterization, we performed single crystal X-ray structure determinations on complexes 4a and 4c.
**Figure 1.** Displacement ellipsoid plot of 4a 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 4a.

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>P1–Ni1–N1</td>
<td>96.90(4)</td>
<td>Ni1–N1–C1</td>
<td>123.50(11)</td>
</tr>
<tr>
<td>P1–Ni1–Cl1</td>
<td>103.407(17)</td>
<td>N1–C1–C6</td>
<td>118.14(14)</td>
</tr>
<tr>
<td>P1–Ni1–Cl2</td>
<td>113.147(18)</td>
<td>C1–C6–C7</td>
<td>112.00(14)</td>
</tr>
<tr>
<td>N1–Ni1–Cl1</td>
<td>104.18(4)</td>
<td>C6–C7–P1</td>
<td>110.53(11)</td>
</tr>
<tr>
<td>N1–Ni1–Cl2</td>
<td>104.63(4)</td>
<td>C7–P1–Ni1</td>
<td>103.50(5)</td>
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<td>Cl1–Ni1–Cl2</td>
<td>129.513(19)</td>
<td></td>
<td></td>
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<tr>
<td>Ni1–P1</td>
<td>2.3036(4)</td>
<td>N1–C1</td>
<td>1.358(2)</td>
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<tr>
<td>Ni1–N1</td>
<td>2.0121(14)</td>
<td>P1–C7</td>
<td>1.8349(16)</td>
</tr>
<tr>
<td>Ni1–Cl1</td>
<td>2.2261(5)</td>
<td>C6–C7</td>
<td>1.549(2)</td>
</tr>
<tr>
<td>Ni1–Cl2</td>
<td>2.2151(5)</td>
<td>C1–C6</td>
<td>1.509(2)</td>
</tr>
</tbody>
</table>

The X-ray crystal structure of complex 4a is shown in figure 1 and selected bond angles and distances are presented in table 1. In agreement with the magnetic moment in solution, the nickel has a distorted tetrahedral surrounding. As a result of the small bite angle of the ligand and the steric repulsion of the chlorides, the P–Ni–N angle is somewhat smaller than the ideal value of 109°, while the Cl–Ni–Cl angle is larger. The other angles around nickel
are less distorted from tetrahedral. The other angles and the bond distances are in the normal range and do not require specification. The structure is similar to the related nickel dichloride complex \( \text{7} \) [see chart 1].

![Chart 1.](image)

**Figure 2.** Displacement ellipsoid plot of \( \text{4c} \) 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 4c

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (°)</th>
<th>Length (Å)</th>
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</thead>
<tbody>
<tr>
<td>P1-N1-N1</td>
<td>98.83(16)</td>
<td>1.361(7)</td>
</tr>
<tr>
<td>P1-N1-Cl1</td>
<td>124.71(8)</td>
<td>2.305(2)</td>
</tr>
<tr>
<td>N1-C1-Cl6</td>
<td>120.8(5)</td>
<td>1.999(5)</td>
</tr>
<tr>
<td>P1-N1-Cl2</td>
<td>96.89(7)</td>
<td>2.2158(18)</td>
</tr>
<tr>
<td>N1-Cl1</td>
<td>115.67(16)</td>
<td>2.244(2)</td>
</tr>
<tr>
<td>C6-C7-P1</td>
<td>119.0(5)</td>
<td>1.331(9)</td>
</tr>
<tr>
<td>C7-P1-N1</td>
<td>117.39(7)</td>
<td>1.517(9)</td>
</tr>
</tbody>
</table>

The X-ray crystal structure of 4c is shown in figure 2 and selected bond distances and angles are presented in table 2. Just as in 4a, the metal has a distorted tetrahedral surrounding, and this is in agreement with the paramagnetic nature of the complex in solution. The structure is similar to that of 4a, although the P–Ni–N and Cl–Ni–Cl bonds are less distorted from perfect tetrahedral.

Synthesis and characterization of neutral palladium complexes

The methylpalladium chloride complexes 5 were obtained by reaction of the ligands with [COD]Pd(CH₃)Cl [COD = 1,5-cyclooctadiene], see scheme 3. Precipitation of the product with diethyl ether separated the metal complexes from free COD and the pure complexes 5 were obtained in high yields.

The products were characterized by NMR, mass spectrometry, elemental analyses, and, for 5a and 5b, single crystal X-ray structure determination. In high resolution mass spectrometry, the [(ligand)Pd(CH₃)]⁺ ion was observed for all complexes. Just as is the case with the nickel complexes mentioned above, loss of the chloride if a consequence of the FAB ionization technique used. Elemental analyses were in agreement with the proposed structures.

The coordination of the phosphine to palladium was indicated by a shift towards higher ppm value in the ³¹P NMR spectra, compared to the spectra of the free ligands. The shift of the signal for the ortho-pyridine protons towards higher value showed the coordination of the pyridine ligand. Based on the larger trans influence of the phosphorus compared to the nitrogen, it is expected that the methyl coordinates cis with respect to the phosphine. This coordination mode was indeed observed, as shown by the small coupling ³J_P-H constant [3 to 4.5 Hz] between the phosphorus nucleus and the palladium-methyl protons. These solution phase observations are in agreement with the solid state structures of 5a and 5b obtained by single crystal X-ray structure determinations, see below.
Figure 3. Aromatic (top) and methylene (bottom) region of the $^1$H NMR spectra of compound 5a at different temperatures (in °C) recorded in CDCl$_3$. The arrows indicate the signals for the *ortho*-aryl protons.
Figure 4. Aromatic (top) and methylene (bottom) region of the $^1$H NMR spectra of compound 5b at different temperatures ($\text{in } ^\circ\text{C}$) recorded in CDCl$_3$. The arrows indicate the signals for the ortho-aryl protons.

For complex 5c, only sharp peaks were observed in NMR spectra at ambient temperature. In the room temperature $^1$H and $^{13}$C NMR spectra (recorded in CDCl$_3$) of 5a and 5b, on the contrary, broad peaks were observed. This is caused by hindered flipping of the six-
membered palladium chelate ring, making the interconversion slow on the NMR timescale. Because of this slow interconversion, the two aryl groups and the protons at each methylene become inequivalent. The signals for the methylene carbons appear sharp in room temperature spectra, as do the signals for the pyridine group and the phosphorus. This shows that ring-flipping is the reason for the broad signals, and not a slow equilibrium between two different species. When the proton spectra were recorded at −50 °C, all peaks appeared sharp. As a consequence of the slow ring-flipping at this temperature, several nuclei became inequivalent and thus, separate peaks were observed in the $^1$H NMR spectra for the aryl protons, the aryl methyl [for 5a] or methoxy [for 5b] group, and the protons at each methylene group. Especially notable is the large chemical shift difference for the protons at the aryl-6 position. The two signals for these protons are observed at 8.84 and 6.76 ppm [5a] and 8.66 and 6.55 ppm [5b]. This can be explained by an interaction of one of these protons with the palladium atom. This is also shown by relative short Pd···H distances in the crystal structures of the complexes (see below). At 60 °C, the flipping of the chelate ring was fast on the NMR timescale, and as a consequence only sharp peaks were visible in the NMR spectra. The aryl groups and the protons at each methylene were equivalent. The aromatic and methylene regions of the variable temperature $^1$H NMR spectra for 5a and 5b are shown in figures 3 and 4, respectively.

![Chart 2](image)

We have recently reported on the palladium complexes 8–10 (see chart 2), which are related to complexes 5. Complex 10 also exhibited broad signals in room temperature NMR spectra as a consequence of slow flipping of the metallocycle. In the crystal structure and NMR spectra, a Pd···H interaction was observed as well. Complexes 8 and 9 did not exhibit hindered flipping of the palladium chelate ring, nor did they show indications of short Pd···H distances. As the slow ring flipping is only observed for complexes that have an interaction of a proton with the axial position of the palladium, we believe there might be a
relation between these phenomena. The interaction of a proton with the axial position of the palladium atom could cause steric hindrance, resulting in the observed hindered ring flipping.

Figure 5. Displacement ellipsoid plot of 5a in the crystal, drawn at the 50% probability level. Hydrogen atoms (except H13) and disordered solvent molecules are omitted for clarity.

Table 3. Selected angles (in °) and bond lengths (in Å) in complex 5a.

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>P1–Pd1–N1</td>
<td>89.77(4)</td>
<td>Pd1–N1–C1</td>
<td>123.02(11)</td>
</tr>
<tr>
<td>P1–Pd1–Cl1</td>
<td>178.675(15)</td>
<td>N1–C1–C6</td>
<td>117.72(15)</td>
</tr>
<tr>
<td>P1–Pd1–C22</td>
<td>88.97(6)</td>
<td>C1–C6–C7</td>
<td>112.11(14)</td>
</tr>
<tr>
<td>N1–Pd1–Cl1</td>
<td>91.08(4)</td>
<td>C6–C7–P1</td>
<td>114.02(12)</td>
</tr>
<tr>
<td>N1–Pd1–C22</td>
<td>177.57(7)</td>
<td>C7–P1–Pd1</td>
<td>108.74(6)</td>
</tr>
<tr>
<td>Cl1–Pd1–C22</td>
<td>90.13(6)</td>
<td>C13–H13···Pd1</td>
<td>123</td>
</tr>
<tr>
<td>Pd1–P1</td>
<td>2.2305(6)</td>
<td>N1–C1</td>
<td>1.352(2)</td>
</tr>
<tr>
<td>Pd1–N1</td>
<td>2.1687(14)</td>
<td>C1–C6</td>
<td>1.505(2)</td>
</tr>
<tr>
<td>Pd1–Cl1</td>
<td>2.3796(6)</td>
<td>P1–C7</td>
<td>1.8493(17)</td>
</tr>
<tr>
<td>Pd1–C22</td>
<td>2.0487(17)</td>
<td>C6–C7</td>
<td>1.536(2)</td>
</tr>
<tr>
<td>Pd1···H13</td>
<td>2.77</td>
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<td></td>
</tr>
</tbody>
</table>
We obtained the single crystal X-ray crystal structure of complex 5a. The structure is shown in figure 5 and selected bond lengths and angles are given in table 3. The complex is in a 'boat' conformation and has a square planar surrounded metal center. The methyl group is coordinated cis with respect to the phosphorus atom, which is in accordance with the NMR studies [see above]. The bond angles around palladium show that the complex is only slightly distorted from perfect square planarity. The most notable feature of the structure is the relative short Pd--H13 distance of 2.77 Å. The hydrogen atom is in a pseudo-axial position and shows an interaction with palladium, as was also revealed in the NMR spectra of the complex in solution [see above]. In the solid state structure of the related palladium complex 9 [see chart 2], the shortest corresponding Pd--H distance was 3.09 Å.⁹

\[ 
\]

**Figure 6.** Displacement ellipsoid plot of 5b in the crystal, drawn at the 50% probability level. Hydrogen atoms (except H13) and disordered solvent molecules are omitted for clarity.
Table 4. Selected angles (in °) and bond lengths (in Å) in complex 5b.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (°)</th>
<th>Bond Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P2–Pd1–N1</td>
<td>92.22(4)</td>
<td>Pd1–N1–C1 123.03(13)</td>
</tr>
<tr>
<td>P2–Pd1–Cl1</td>
<td>175.035(17)</td>
<td>N1–C1–C6 117.86(16)</td>
</tr>
<tr>
<td>P2–Pd1–C22</td>
<td>88.68(7)</td>
<td>C1–C6–C7 112.94(15)</td>
</tr>
<tr>
<td>N1–Pd1–Cl1</td>
<td>89.45(4)</td>
<td>C6–C7–P2 113.13(13)</td>
</tr>
<tr>
<td>N1–Pd1–C22</td>
<td>176.44(8)</td>
<td>C7–P2–Pd1 108.69(6)</td>
</tr>
<tr>
<td>Cl1–Pd1–C22</td>
<td>89.94(7)</td>
<td>C13–H13...Pd1 119</td>
</tr>
</tbody>
</table>

We have also obtained the crystal structure of 5b, it is shown in figure 6 and selected bond lengths and angles are given in table 4. The structure is similar to that of 5a, the metallocycle has a 'boat' conformation and has a slightly distorted square planar surrounding of the palladium atom, with a cis orientation of the phosphorus atom and the methyl group. The oxygen atoms have no interaction with the palladium atom, as shown by the shortest Pd...O distance of 3.5845(18) Å. One ortho-aryl proton does show an interaction with palladium: H13 is in a pseudo-axial position of the metal, with a short Pd...H13 distance of 2.92 Å. These findings were corroborated by the NMR studies in the solution phase (see above).

Synthesis and characterization of cationic palladium complexes

We obtained the cationic palladium complexes 6 from reaction of their neutral precursors with NaBAR'₂ [Ar' = 3,5-di(trifluoromethyl)phenyl], see scheme 4. After work-up, the pure products were obtained as white solids in high yields. In the high resolution mass spectra (using FAB ionization), the [[ligand]Pd(CH₃)]⁺ species were observed. Under the ionization conditions used the acetonitrile molecule dissociated. When the milder field desorption (FD) ionization technique was used, acetonitrile did not dissociate and the [[ligand]Pd(CH₃)(CH₃CN)]⁺ species were observed for all complexes. As a consequence of the FD technique, this could not be done at high resolution.

In analogy with their neutral precursors, complexes 6a and 6b exhibited slow flipping of the six-membered metallocycle, as indicated by the appearance of broad signals in room temperature $^1$H NMR spectra (measured in CD$_2$Cl$_2$). When the samples were cooled to $\sim$40 °C, the signals became even broader and sharp separate signals for inequivalent aromatic or methylene protons could not be observed. Due to practical limitations, we did not cool the samples to a temperature at which the separate signals could be observed. When the temperature was raised, the signals became sharper. At 80 °C (in CDCl$_3$/CDCl$_2$ solution), all peaks in the spectra of compounds 6a and 6b appeared sharp.

Complex 6c did not show broad signals at room temperature, and the aryl groups and methylene protons were equivalent. This shows that ring-flipping of this complex is fast on the NMR timescale at ambient temperature, just like that of its precursor 5c.

**Nickel catalyzed ethene oligomerization**

Nickel complexes of pyridine-phosphine ligands have been applied successfully in the oligomerization of ethene. We studied the behavior of nickel complexes 4 as catalyst precursors in this reaction. The complexes were activated by MAO, and catalytic runs were performed in toluene at 30 °C for 30 minutes. The results of the catalytic studies are summarized in table 5. For comparison, the results we have previously obtained with complex 7 (see chart 1) are included as well.
Table 5. Ethene oligomerization using 4a–c and 7 as catalyst precursor<sup>a</sup>

<table>
<thead>
<tr>
<th>complex</th>
<th>productivity [g C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;/ (mol Ni · h)]</th>
<th>TOF&lt;sup&gt;b&lt;/sup&gt;</th>
<th>product distribution [%]&lt;sup&gt;c&lt;/sup&gt;</th>
<th>1-butene [%]&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>46·10&lt;sup&gt;3&lt;/sup&gt;</td>
<td>16·10&lt;sup&gt;3&lt;/sup&gt;</td>
<td>C4 78 7 5 4 6 &gt;C10</td>
<td>76</td>
</tr>
<tr>
<td>4b</td>
<td>82·10&lt;sup&gt;3&lt;/sup&gt;</td>
<td>65·10&lt;sup&gt;3&lt;/sup&gt;</td>
<td>C6 95 4 &lt;1 &lt;1</td>
<td>46</td>
</tr>
<tr>
<td>4c</td>
<td>38·10&lt;sup&gt;3&lt;/sup&gt;</td>
<td>14·10&lt;sup&gt;3&lt;/sup&gt;</td>
<td>C8 93 7 &lt;1 &lt;1</td>
<td>90</td>
</tr>
<tr>
<td>7</td>
<td>196·10&lt;sup&gt;3&lt;/sup&gt;</td>
<td>70·10&lt;sup&gt;3&lt;/sup&gt;</td>
<td>C10 86 11 3 &lt;1 &lt;1</td>
<td>18</td>
</tr>
</tbody>
</table>

<sup>a</sup>conditions: 10 μmol nickel complex, MAO activator [Al/Ni = 230], 10 bar ethene, 1.0 mmol heptane (internal standard), toluene solvent, total volume: 25 mL, T: 30 °C, time: 30 min. <sup>b</sup>turnover frequency in (mol C<sub>2</sub>H<sub>4</sub>):(mol Ni-h)<sup>-1</sup>. <sup>c</sup>mol percentage of combined Cn products. <sup>d</sup>as percentage of total C4 fraction.

As can be seen from the table, complexes 4 form active catalysts after MAO activation. They were most active during the first 5 to 10 minutes of a run, as evident from the amount of cooling necessary to maintain the desired temperature of the exothermic reaction. Butenes are the main products in all cases, with a maximum selectivity of 95% for 4b. Complex 4a produces a significant amount of higher olefins, while 4b and 4c can be regarded as dimerization catalysts. The influence of the different aromatic P-substituents is apparent from the different catalytic behavior of complexes 4a–c and 7. Whereas the selectivity for 1-butene within the butenes fraction is low for complex 7, which has phenyl substituents at phosphorus, the larger aromatic groups in 4 cause the formation of a higher percentage of 1-butene. Especially 4c shows a high selectivity of 90%. Apparently the bulky mesityl substituents prevent isomerization of the growing oligomer chain. This can be rationalized by considering the fact that a branched alkyl chain, formed after isomerization, requires more space around the metal center than a linear chain, which can bend away from this center. The formation of branched alkyl chains is therefore disfavored in the case of the bulky mesityl substituents at phosphorus. This is accompanied by a decrease in activity, as compared to the catalytic behavior of phenyl substituted 7.

The 2-tolyl substituents in 4a cause a similar, but less strong effect as 4c. This explains the 1-butene selectivity and activity of this complex. Catalyst precursor 4b deviates from this trend. The electronic properties of this complex are expected to be similar to those of 4c, and the electronic properties cannot explain the lower 1-butene selectivity and higher activity of 4b. Possibly, an interaction of the methoxy oxygen atoms causes the different catalytic behavior. No Pd····O interaction was observed in the crystal structure of palladium complex 5b, but this might be different for the catalytically active, cationic species formed from 4b. A different behavior in ethene oligomerization for a palladium complex of an anisyl
substituted ligand, as compared to complexes of related alkyl substituted ligands, has been observed before.\textsuperscript{15}

**Palladium-catalyzed ethene oligomerization**

Palladium complexes of P,N-ligands have been tested for ethene oligomerization activity much less frequently then their nickel counterparts. They have been reported to be active in ethene oligomerization,\textsuperscript{6,15,16} although no or very low activity in this reaction has often been observed as well with these complexes.\textsuperscript{7,9,10,17} Only one report describes an active catalyst containing a pyridine-phosphine ligand,\textsuperscript{6} whereas other systems showed no or very low activity.\textsuperscript{7,9,10} We tested complexes 6 for productivity in the oligomerization of ethene and the results are summarized in table 6.

**Table 6.** Ethene oligomerization using 6a–c as catalyst precursor\textsuperscript{a}

<table>
<thead>
<tr>
<th>complex</th>
<th>TOF\textsuperscript{b}</th>
<th>product distribution [%]\textsuperscript{c}</th>
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<tbody>
<tr>
<td></td>
<td>C4</td>
<td>C5</td>
</tr>
<tr>
<td>6a</td>
<td>6</td>
<td>47</td>
</tr>
<tr>
<td>6b</td>
<td>25</td>
<td>41</td>
</tr>
<tr>
<td>6c</td>
<td>8</td>
<td>63</td>
</tr>
</tbody>
</table>

\textsuperscript{a}conditions: 100 μmol palladium complex, 10 bar ethene, 0.10 mmol heptane (internal standard), toluene solvent, total volume: 25 mL, T: 30 °C, time: 120 min. \textsuperscript{b}turnover frequency in [mol C\textsubscript{2}H\textsubscript{4}]/[mol Pd-h]\textsuperscript{-1}. \textsuperscript{c}mol percentage of combined C\textsubscript{n} products.

As can be seen from the table, the complexes all have a very low productivity. Like their nickel counterparts, the complex containing ligand 1b forms the most active catalyst. Next to butenes, a significant amount of higher oligomers is formed as well. This is in contrast to the catalytic behavior of related complexes.\textsuperscript{9,10} The oligomers with an odd number of carbons in the chain originate from the first chain growing from the catalyst precursor, which starts from a methylpalladium species. After β-hydride elimination, a palladium hydride species is formed and only chains with an even number of carbons are formed henceforth. As a consequence, the catalyst with the highest turnover number (6b) has the lowest percentage of oligomers with an odd number of carbons.

**Conclusions**

The new pyridine-phosphine ligands 1 were used for the preparation of nickel and palladium complexes. The nickel complexes 4 all have a distorted tetrahedral surrounding of the metal center and are consequently paramagnetic. The neutral palladium complexes
5 have a distorted square planar surrounding around the metal. In complexes 5a and 5b, the flipping of the six-membered metalloccycle is hindered. This phenomenon is probably related to an interaction of a proton of the ligand with the axial position of the palladium atom. This could be explained by steric hindrance that hampers ring flipping, caused by Pd····H repulsion. The proximity of the two atoms was apparent from the crystal structures and low-temperature NMR spectra of the complexes. Complex 5c does not exhibit hindered flipping of the palladium chelate ring, nor any Pd····H interactions. The cationic palladium complexes 6 show similar coordination behavior as their neutral precursors, with square planar surrounded metal centers and hindered ring flipping for 6a and 6b.

After MAO activation the nickel complexes form active catalysts for the oligomerization of ethene. The bulky mesityl and 2-tolyl phosphorus substituents in 5a and 5c disfavor isomerization of the oligomer chain, as shown by a high 1-butene selectivity. This becomes evident from the comparison with the catalytic behavior of earlier reported complex 7, in which the corresponding substituents are phenyl groups. The higher 1-butene selectivity is accompanied by a lower productivity. The catalytic behavior of the complex formed after activation of 5b, containing the anisyl substituted ligand, is different from that of the other complexes. An interaction of the methoxy oxygen with the nickel center might be the reason for this. The cationic palladium complexes show a very low activity in ethene oligomerization. Selectivity for butenes is much lower than for their nickel counterparts, and significant amounts of higher oligomers are formed.

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, CDCl₃, and CDCl₅ 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. Phenylsilane and 2-vinylpyridine (2) were distilled under dinitrogen. Di-2-tolylphosphine oxide,¹¹ di-2-anisylphosphine oxide,¹² dimesitylphosphine oxide¹¹, [DME]NiCl₂,¹⁸ [COD]Pd(CH₃)Cl,¹⁹ and NaBAR⁺,²⁰ 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. Elemental analyses were carried out by Kolbe Mikroanalytisch Laboratorium, Mülheim an der Ruhr [Germany]. Electron Ionization (EI) mass spectrometry 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) mass spectrometry 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 [³¹P], 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 [³¹P], and CCl₄F₂ [¹⁹F] as external standards at 0 ppm, except when Cl₂DCCDCl₂ was the solvent, in that case signals are referenced to residual solvent signal at 6.00 [¹H] and 73.78 [¹³C] ppm. The following abbreviations are used: py = pyridyl, tol = tolyl, anis = anisyl, mes = mesityl, Ar′ = 3,5-di(trifluoromethyl)phenyl. 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 KappaCCD diffractometer with rotating anode. The structures were solved with Direct Methods (program SHELXS-97 for 4a; program SHELXS-86 for 4c and 5b) or automated Patterson methods (program DIRDIF-99 for 5a). Refinement was performed with SHELXL-97 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.

In 4a the methyl group at C14 was refined with two orientations.

The crystals of 5a and 5b contained a large void, respectively, (118 Å³ / unit cell for 5a; 285 Å³ / unit cell for 5b) filled with disordered solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the routine SQUEEZE of the program PLATON resulting in 34 electrons / unit cell for 5a and 35 electrons / unit cell for 5b.

Geometry calculations and checking for higher symmetry was performed with the PLATON program. Further details about the crystal structure determinations are given in table 7.
Table 7. Selected crystallographic data for complexes 4a, 4c, 5a, and 5b.

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<th>4a</th>
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<th>5b</th>
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<td>-0.61 / 0.77</td>
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</tbody>
</table>

*a*derived parameters do not contain the contribution of the disordered solvent.

2-[2-(di-2-toly|phosphinoyl|ethyl]pyridine (3a)

Di-2-tolylphosphate oxide [1.07 g, 4.63 mmol, 1.0 equiv] and 2-vinylpyridine [2] [487 mg, 4.63 mmol, 1.0 equiv] were dissolved in 25 mL THF. KOtBu [26 mg, 0.23 mmol, 0.05 equiv] was added and the mixture was stirred at 60°C for 16 hours. A little water was added, and the mixture was concentrated in vacuo. EtOAc was added and the solution was washed with water twice and with brine, dried over MgSO₄, and concentrated in vacuo to yield a colorless
oil. The product was precipitated by addition of Et₂O, filtrated, washed with Et₂O, and dried in vacuo to yield the product as a white solid (1.24 g, 3.69 mmol, 80%).

mp: 120 °C

¹H NMR δ (500 MHz, CDCl₃) ppm: 8.50–8.48 [m, 1H, py-H6], 7.80 [ddd, J = 12.8, 7.7, 1.0 Hz, 2H, tol-H6], 7.56 [dt, J = 7.7, 1.3 Hz, 1H, py-H4], 7.39–7.35 [m, 2H, tol-H4], 7.29–7.25 [m, 2H, tol-H5], 7.17–7.13 [m, 3H, py-H3 + tol-H3], 7.12–7.08 [m, 1H, py-H5], 3.16–3.10 [m, 2H, py-CH₂], 2.92–2.86 [m, 2H, P-CH₃], 2.30 [s, 6H, CH₃]

¹³C{¹H} NMR δ (125 MHz, CDCl₃) ppm: 160.6 [d, J = 14.3 Hz, py-C2], 149.4 [s, py-C6], 141.7 [d, J = 8.6 Hz, tol-C2], 136.6 [s, CH], 132.2 [d, J = 10.4 Hz, CH], 132.0 [s, CH], 131.9 [s, CH], 131.8 [s, CH], 131.4 [d, J = 95.5 Hz, tol-C1], 125.8 [d, J = 11.8 Hz, CH], 123.2 [s, CH], 121.5 [s, CH], 30.0 [d, J = 2.2 Hz, py-CH₃], 28.6 [d, J = 71.6 Hz, P-CH₃], 21.4 [d, J = 4.3 Hz, CH₃]

³¹P{¹H} NMR δ (121 MHz, CDCl₃) ppm: 34.6

Anal. Calcd. for C₂,H₂₃NOP: C, 75.21; H, 6.61; N, 4.18. Found: C, 75.06; H, 6.70; N, 4.06

HRMS (FAB) m/z: calcd. for C₂₂H₂₃NOP [M+H]+: 336.1517; Found: 336.1505

2-[2-(di-2-anisylphosphinoylethyl)pyridine (3b)

Di-2-anisylphosphate oxide [2.49 g, 9.49 mmol, 1.0 equiv] and 2-vinylpyridine [2] [1.00 mL, 9.49 mmol, 1.0 equiv] were dissolved in 50 mL THF. KOTBu [107 mg, 0.95 mmol, 0.1 equiv] was added and the mixture was stirred at 60°C for 16 hours after which unlocked ³¹P NMR showed full conversion. Water was added, and the mixture was concentrated in vacuo. It was redissolved in EtOAc and washed with water twice and with brine. After drying over MgSO₄ and concentration in vacuo, column chromatography [eluens 5% MeOH in CH₂Cl₂] yielded the product as a white solid (2.52 mg, 6.87 mmol, 72%).

mp: 67 °C

¹H NMR δ (500MHz, CDCl₃) ppm: 8.45 [d, J = 4.3 Hz, 1H, py-H6], 7.64 [ddd, J = 13.4, 7.5, 1.6 Hz, 2H, anis-H6], 7.52 [dt, J = 7.7, 1.5 Hz, 1H, py-H4], 7.46–7.42 [m, 2H, anis-H4], 7.14 [d, J = 7.7 Hz, 1H, py-H3], 7.09–7.05 [m, 1H, py-H5], 7.02–6.97 [m, 2H, anis-H5], 6.85 [dd, J = 8.3, 5.2 Hz, 2H, anis-H3], 3.70 [s, 6H, CH₃], 3.12–3.05 [m, 2H, py-CH₂], 3.05–2.97 [m, 2H, P-CH₂]

¹³C{¹H} NMR δ (75 MHz, CDCl₃) ppm: 161.5 [d, J = 15.3 Hz, py-C2], 160.7 [s, anis-C2], 149.1 [s, py-C6], 136.3 [s, CH], 134.1 [d, J = 6.5 Hz, CH], 133.5 [s, CH], 123.0 [s, CH], 121.2 [s, CH], 120.9 [d, J = 100.6 Hz, anis-C1], 120.7 [d, J = 11.3 Hz, CH], 110.9 [d, J = 5.9 Hz, CH], 55.5 [s, CH₃], 30.5 [s, py-CH₂], 29.2 [d, J = 74.4 Hz, P-CH₂]

³¹P{¹H} NMR δ (121 MHz, CDCl₃) ppm: 33.7
Anal. Calcd. for C_{12}H_{18}NO_3P: C, 68.66; H, 6.04; N, 3.81. Found: C, 68.52; H, 5.94, N, 3.72
HRMS (FAB) m/z: calcd. for C_{12}H_{18}NO_3P [M+H]^+: 368.1416; Found: 368.1417

2-{2-[dimesitylphosphino]ethyl}pyridine (3c)

Dimesitylphosphine oxide [425 mg, 1.48 mmol, 1.0 equiv] and 2-vinylpyridine [2] [0.156 mL, 1.48 mmol, 1.0 equiv] were dissolved in 10 mL THF. K0tBu [34 mg, 0.29 mmol, 0.2 equiv] was added and the mixture was stirred at 60°C for 16 hours, after which unlocked 31P NMR showed full conversion. Water was added, and the mixture was concentrated in vacuo. It was redissolved in EtOAc and washed with water twice and with brine. It was dried over MgSO₄ and concentrated in vacuo, after which column chromatography (eluens 5% MeOH in CH₃Cl₂) yielded the product as an off-white solid [361 mg, 0.92 mmol, 62%].

mp: 158 °C

1H NMR δ [300MHz, CDCl₃] ppm: 8.45 [d, J = 7.9 Hz, 1H, py-H₆], 7.52 [dt, J = 7.7, 1.8 Hz, 1H, py-H₄], 7.11 [d, J = 7.7 Hz, 1H, py-H₃], 7.06 [m, 1H, py-H5], 6.77 [d, J = 3.4 Hz, 4H, mes-H3], 3.08–2.96 [m, 2H, py-CH₂], 2.92–2.82 [m, 2H, P-CH₂], 2.37 [s, 12H, mes-2-CH₃], 2.22 [s, 6H, mes-4-CH₃]

13C[1H] NMR δ [75 MHz, CDCl₃] ppm: 161.1 [d, J = 15.2 Hz, py-C2], 149.2 [s, py-C6], 141.4 [d, J = 9.8, mes-C2], 140.8 [s, mes-C4], 136.8 [s, CH], 131.3 [d, J = 10.7 Hz, mes-C3], 130.2 [d, J = 94.4 Hz, mes-C1], 123.3 [s, CH], 121.5 [s, CH], 35.8 [d, J = 66.3 Hz, P-CH₂], 31.2 [s, py-CH₂], 23.2 [s, mes-2-CH₃], 21.1 [s, mes-4-CH₃]

31P[1H] NMR δ [121 MHz, CDCl₃] ppm: 41.8

Anal. Calcd. for C₃₂H₂₈N₅P: C, 76.70; H, 7.72; N, 3.58. Found: C, 76.61; H, 7.78, N, 3.93
HRMS (FAB) m/z: calcd. for C₃₂H₂₈N₅P [M+H]^+: 392.2143; Found: 392.2147

2-[2-[di-2-tolylphosphino]ethyl]pyridine (1a)

2-[2-[di-2-tolylphosphino]ethyl]pyridine [3a] [1.48 g, 4.41 mmol, 1.0 equiv] was dissolved in phenylsilane [8.0 mL, 65 mmol, 15 equiv] and the mixture was refluxed overnight, after which unlocked 31P NMR showed full conversion. The mixture was concentrated in vacuo and co-evaporated with 3 times 5 mL toluene. The product was purified using column chromatography using Et₂O as the eluens and a second column with CH₃Cl₂ as the eluens to yield the product as a yellowish oil [1.33 g, 4.18 mmol, 95%].

1H NMR δ [500MHz, CDCl₃] ppm: 8.50–8.48 [d, J = 4.4 Hz, 1H, py-H₆], 7.58 [dt, J = 7.7, 1.8 Hz, 1H, py-H₄], 7.29–7.26 [m, 2H, tol-H₄], 7.25–7.21 [m, 2H, tol-H₆], 7.19–7.14 [m, 4H, tol-
H3 + -H5), 7.14–7.09 [m, 2H, py-H3 + -H5], 2.97–2.92 (m, 2H, py-CH2), 2.48–2.44 (m, 2H, P-CH2), 2.45 [s, 6H, CH3]

13C(1H) NMR δ (125 MHz, CDCl3) ppm: 162.2 [d, J = 13.9 Hz, py-C2], 149.5 [s, py-C6], 142.5 [d, J = 25.2 Hz, tol-C2], 136.9 [d, J = 13.5 Hz, tol-C1], 136.5 [s, CH], 131.3 [s, CH], 130.2 [d, J = 4.6 Hz, CH], 128.6 [s, CH], 126.3 [s, CH], 122.8 [s, CH], 121.4 [s, CH], 34.7 [d, J = 18.6 Hz, py-CH2], 27.1 [d, J = 12.7 Hz, P-CH2], 21.4 [d, J = 21.1 Hz, CH3]

31P(1H) NMR δ (121 MHz, CDCl3) ppm: −35.8

Anal. Calcd. for C27H27NO7P: C, 78.97; H, 6.94; N, 4.39. Found: C, 78.88; H, 6.87, N, 4.31

MS [EI] m/z [rel. intensity]: 319 [8] [M]+, 228 [100] [M-tol]+, 106 [10] [M-P(tol)]+^

2-[2-[di-2-anisylphosphino]ethyl]pyridine (1b)

2-[2-[di-2-anisylphosphino]ethyl]pyridine [3b] (137 mg, 0.37 mmol, 1.0 equiv) was dissolved in phenylsilane (2.0 mL, 16.2 mmol, 43 equiv) and the mixture was refluxed overnight, after which unlocked 31P NMR showed full conversion. The mixture was concentrated and purified by column chromatography with CH2Cl2 → 5% MeOH / CH2Cl2 as the eluents to yield the product as a white solid (122 mg, 0.35 mmol, 93%).

mp: 47 °C

1H NMR δ (500 MHz, CDCl3) ppm: 8.53 [d, J = 4.7 Hz, 1H, py-H6], 7.58 [t, J = 7.6 Hz, 1H, py-H4], 7.34–7.30 (m, 2H, anis-H4), 7.21–7.16 (m, 3H, py-H3 + anis-H6), 7.12–7.09 (m, 1H, py-H5), 6.93 [t, J = 7.4 Hz, 2H, anis-H5], 6.87 (dd, J = 8.1, 4.1 Hz, 2H, anis-H3), 3.80 (s, 6H, CH3), 3.01–2.94 (m, 2H, py-CH2), 2.55–2.50 (m, 2H, P-CH2)

13C(1H) NMR δ (125 MHz, CDCl3) ppm: 162.7 [d, J = 13.6 Hz, py-C2], 161.7 [d, J = 13.5 Hz, anis-C2], 149.3 [s, py-C6], 136.4 [s, CH], 132.9 [d, J = 5.1 Hz, CH], 130.0 [s, CH], 125.7 [d, J = 15.2 Hz, anis-C1], 122.8 [s, CH], 121.1 [s, CH], 121.0 [d, J = 2.1 Hz, CH], 110.4 [s, CH], 55.7 [s, CH3], 35.2 [d, J = 18.6 Hz, py-CH2], 25.1 [d, J = 13.1 Hz, P-CH3]

31P(1H) NMR δ (121 MHz, CDCl3) ppm: −34.6

Anal. Calcd. for C27H27NO7P: C, 71.78; H, 6.31; N, 3.99. Found: C, 71.64; H, 6.27, N, 3.84


2-[2-[di-mesitylphosphino]ethyl]pyridine (1c)

2-[2-[di-mesitylphosphino]ethyl]pyridine [3c] (205 mg, 0.52 mmol, 1.0 equiv) was dissolved in phenylsilane (4 mL, 32 mmol, 62 equiv) and the mixture was refluxed overnight, after
which unlocked $^{31}$P NMR showed full conversion. The mixture was concentrated in vacuo and purified by column chromatography with CH$_2$Cl$_2$ $\rightarrow$ 5% MeOH / CH$_2$Cl$_2$ as the eluens. After co-evaporation with hexanes (5×5 mL), the product was obtained as a white solid (196 mg, 0.52 mmol, 100%).

mp: 83 °C

$^1$H NMR δ (500 MHz, CDCl$_3$) ppm: 8.51 [d, $J = 4.2$ Hz, 1H, py-H6], 7.56 [dt, $J = 7.7$, 1.8 Hz, 1H, py-H4], 7.11–7.06 [m, 2H, py-H3 + H5], 6.78 [d, $J = 2.1$ Hz, 2H, mes-H3], 2.94–2.89 [m, 2H, py-CH$_2$], 2.80–2.74 [m, 2H, P-CH$_3$], 2.31 [s, 12H, mes-2-CH$_3$], 2.24 [s, 6H, mes-4-CH$_3$]

$^{13}$C($^1$H) NMR δ (125 MHz, CDCl$_3$) ppm: 162.5 [d, $J = 16.8$ Hz, py-C2], 149.4 [s, py-C6], 142.1 [d, $J = 13.6$ Hz, mes-C2], 137.5 [s, mes-C4], 136.5 [s, CH], 133.1 [d, $J = 21.5$ Hz, mes-C1], 130.1 [d, $J = 3.0$ Hz, mes-C3], 122.7 [s, CH], 121.2 [s, CH], 36.1 [d, $J = 22.7$ Hz, py-CH$_2$], 31.2 [d, $J = 16.0$ Hz, P-CH$_3$], 23.4 [d, $J = 13.1$ Hz, mes-2-CH$_3$], 21.0 [s, mes-4-CH$_3$]

$^{31}$P($^1$H) NMR δ (121 MHz, CDCl$_3$) ppm: -20.8

Anal. Calcd. for C$_2$H$_{39}$NP: C, 79.97; H, 8.05; N, 3.73. Found: C, 80.11; H, 7.98, N, 3.65

MS (EI) m/z (rel. intensity): 375 [10] [M]$^+$, 360 [100] [M–CH$_3$], 256 [89] [M–mes]$^+$, 138 [25] [M–2mes+H]$^+$, 106 [37] [M–P(mes)]$^+$

2-[2-[di-2-tolylphosphino]ethyl]pyridine nickel dichloride (4a)

A mixture of 2-[2-[di-2-tolylphosphino]ethyl]pyridine [1a] (215 mg, 0.67 mmol, 1.0 equiv), [DME]NiCl$_2$ (148 mg, 0.67 mmol, 1.0 equiv), and CH$_2$Cl$_2$ (8 mL) was stirred for 16 hours. It was filtered through a path of celite, washed with CH$_2$Cl$_2$ and concentrated in vacuo. Et$_2$O (5 mL) was added, and the mixture was put in a sonication bath for 30 minutes. The solids were filtered off, washed with Et$_2$O and dried in vacuo to yield the product as a purple solid (175 mg, 0.39 mmol, 58%).

mp: 254 °C (dec.)

Anal. Calcd. for C$_2$H$_{39}$ClNNiP: C, 56.18; H, 4.94; N, 3.12. Found: C, 55.99; H, 4.90, N, 2.96

HRMS (FAB) m/z: calcd. for C$_2$H$_{39}$ClNNiP [M–Cl]$^+$: 412.0532; found: 412.0536

$\mu_{eff} = 3.85 \mu_B$

2-[2-[di-2-anisylphosphino]ethyl]pyridine nickel dichloride (4b)

A mixture of 2-[2-[di-2-anisylphosphino]ethyl]pyridine [1b] (114 mg, 0.32 mmol, 1.0 equiv), [DME]NiCl$_2$ (71 mg, 0.32 mmol, 1.0 equiv), and CH$_2$Cl$_2$ (5 mL) was stirred for 16 hours. It was filtered through a path of celite, washed with CH$_2$Cl$_2$ and concentrated in vacuo. Et$_2$O (5 mL)
was added, and the mixture was put in a sonication bath for 30 minutes. The solids were filtered off, washed with Et$_2$O and dried in vacuo to yield the product as a brown solid [134 mg, 0.28 mmol, 86%].

mp: 235 °C [dec.]
Anal. Calcd. for C$_2$H$_{32}$Cl$_2$NNiO$_2$P: C, 52.44; H, 4.61; N, 2.91. Found: C, 52.53; H, 4.72, N, 2.85
HRMS (FAB) m/z: calcd. for C$_2$H$_{32}$Cl$_2$NNiO$_2$P [M–Cl]$^+$: 444.0430; found: 444.0426
\[\mu_{eff} = 3.30 \mu_B\]

2-[2-(dimesitylphosphinoethyl)pyridine nickel dichloride (4c)
A mixture of 2-[2-(dimesitylphosphinoethyl)pyridine [1c] (42 mg, 0.11 mmol, 1.0 equiv), (DME)NiCl$_2$ (25 mg, 0.11 mmol, 1.0 equiv), and CH$_2$Cl$_2$ (3 ml) was stirred for 16 hours. It was filtered through a path of celite, washed with CH$_2$Cl$_2$ and concentrated in vacuo. Et$_2$O (3 mL) was added, and the mixture was put in a sonication bath for 30 minutes. The solids were filtered off, washed with Et$_2$O and dried in vacuo to yield the product as a purple solid [38 mg, 0.075 mmol, 67%].

mp: 240 °C [dec.]
Anal. Calcd. for C$_{26}$H$_{38}$Cl$_2$NNiP: C, 59.45; H, 5.99; N, 2.77. Found: C, 59.36; H, 5.91, N, 2.71
HRMS (FAB) m/z: calcd. for C$_{26}$H$_{38}$Cl$_2$NNiP [M–Cl]$^+$: 468.1158; found: 468.1168
\[\mu_{eff} = 3.30 \mu_B\]

2-[2-[di-2-tolylphosphinoethyl]pyridine methylpalladium chloride (5a)
2-[2-[di-2-tolylphosphinoethyl]pyridine [1a] (350 mg, 1.10 mmol, 1.0 equiv) and [COD]Pd(CH$_3$)Cl (291 mg, 1.10 mmol, 1.0 equiv) were dissolved in CH$_2$Cl$_2$ (20 mL) and the mixture was stirred for 16 hours. Then, it was concentrated in vacuo to approximately 2 mL, after which 20 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 [460 mg, 0.97 mmol, 88%].

mp: 227 °C [dec.]
$^1$H NMR δ (500MHz, CDCl$_3$, 25 °C) ppm: 9.30 (dd, $J = 5.4$, 1.0 Hz, 1H, py-H6), 7.90–7.66 (bs, 2H, tol-H6), 7.63 (d pst, $J = 7.7$, 1.7 Hz, 1H, py-H4), 7.40–7.34 (m, 2H, tol-H4), 7.32–7.26 (m, 2H, tol-H3), 7.24–7.20 (m, 1H, py-H5), 7.20–7.14 (m, 3H, py-H3 + tol-H5), 3.50–3.42 (m, 2H, py–CH$_3$), 2.51 (s, 6H, CH$_3$), 2.49–2.43 (m, 2H, P–CH$_2$), 0.39 (d, $J = 3.7$ Hz, 3H, CH$_3$)
$^1$H NMR $\delta$ (500MHz, CDCl$_3$, -50 °C) ppm: 9.21 [d, $J = 5.3$ Hz, 1H, py-H6], 8.86–8.82 [m, 1H, tol-H6], 7.71–7.67 [m, 1H, py-H4], 7.47–7.43 [m, 1H, tol-H4], 7.41–7.34 [m, 2H, tol'-H3 + -H4], 7.34–7.25 [m, 3H, py-H3 + tol-H3 + -H5], 7.23 [d, $J = 7.6$ Hz, 1H, py-H5], 7.11–7.04 [m, 1H, tol'-H5], 6.78–6.72 [m, 1H, tol'-H6], 3.73–3.36 [m, 1H, py-CHH], 3.36–3.24 [m, 1H, py-CHH], 2.84 [s, 3H, tol-CH$_3$], 2.71–2.63 [m, 1H, P-CHH], 2.21 [s, 3H, tol-CH$_3$], 2.20–2.12 [m, 1H, P-CHH], 0.23 [d, $J = 3.0$ Hz, 3H, Pd-CH$_3$]

$^1$H NMR $\delta$ (500MHz, CDCl$_3$, 60 °C) ppm: 9.37 [d, $J = 5.5$ Hz, 1H, py-H$\delta$], 7.77 [dd, $J = 13.5$, 7.8 Hz, 2H, tol-H6], 7.62 [d psr, $J = 7.6$, 1.5 Hz, 1H, py-H4], 7.38–7.34 [m, 2H, tol-H4], 7.30–7.26 [m, 2H, tol-H3], 7.24–7.21 [m, 1H, py-H5], 7.20–7.16 [m, 2H, tol-H5], 7.14 [d, $J = 7.6$ Hz, 1H, py-H3], 3.50–3.41 [m, 2H, py-CH$_2$], 2.53 [s, 6H, tol-CH$_3$], 2.49–2.45 [m, 2H, P-CH$_2$], 0.47 [d, $J = 3.7$ Hz, 3H, Pd-CH$_3$]

$^{13}$C($^1$H) NMR $\delta$ (125 MHz, CDCl$_3$, 25 °C) ppm: 159.2 [d, $J = 3.0$ Hz, py-C2], 152.7 [s, py-C6], 140.8 [d, $J = 6.3$ Hz, tol-C2], 138.5 [s, CH], 137.0–136.1 [bs, CH], 132.2 [d, $J = 7.6$ Hz, CH], 131.4 [s, CH], 129.7 [d, $J = 48.5$ Hz, tol-C1], 126.1 [d, $J = 12.7$ Hz, CH], 124.1 [s, CH], 123.3 [s, CH], 36.7 [d, $J = 6.8$ Hz, py-CH$_2$], 25.5 [d, $J = 29.1$ Hz, P-CH$_2$], 23.5 [d, $J = 5.9$ Hz, tol-CH$_3$], 0.0 [s, Pd-CH$_3$]

$^{31}$P($^1$H) NMR $\delta$ (121 MHz, CDCl$_3$, 25 °C) ppm: 40.3

Anal. Calcd. for C$_{22}$H$_{28}$ClNPPd: C, 55.48; H, 5.29; N, 2.94. Found: C, 55.56; H, 5.22; N, 2.82

HRMS (FAB) m/z: calcd. for C$_{22}$H$_{28}$NPPd [M–Cl]$^+$: 440.0768; found: 440.0756

2-[2-(di-2-anisylphosphino)ethyl]pyridine methylpalladium chloride (4b)

2-[2-(di-2-anisylphosphino)ethyl]pyridine (1b) [332 mg, 0.95 mmol, 1.0 equiv] and (COD)Pd(CH$_3$)Cl (250 mg, 0.95 mmol, 1.0 equiv) were dissolved in CH$_2$Cl$_2$ (15 mL) and the mixture was stirred for 16 hours. Then, it was concentrated in vacuo to approximately 1.5 mL, after which 15 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 (436 mg, 0.86 mmol, 91%).

$^1$H NMR $\delta$ (500MHz, CDCl$_3$, 25 °C) ppm: 9.35 [dd, $J = 5.5$, 1.1 Hz, 1H, py-H6], 7.64–7.60 [m, 1H, py-H4], 7.47–7.43 [m, 2H, anis-H4], 7.22–7.19 [m, 1H, py-H5], 7.14 [d, $J = 7.7$ Hz, 1H, py-H3], 6.96–6.92 [m, 4H, anis-H3 + -H5], 3.83 [s, 6H, anis-CH$_3$], 3.48–3.40 [m, 2H, py-CH$_2$], 2.41–2.38 [m, 2H, P-CH$_2$], 0.31 [d, $J = 3.5$ Hz, 3H, Pd-CH$_3$] the signal for anis-H6 was not observed
$^1$H NMR $\delta$ (500 MHz, CDCl$_3$, -50 °C) ppm: 9.22 (d, $J = 5.1$ Hz, 1H, py-H$_6$), 8.66 (dd, $J = 16.5$, 7.2 Hz, 1H, anis-H$_6$), 7.68–7.64 (m, 1H, py-H$_4$), 7.58–7.54 (m, 1H, anis-H$_4$), 7.43–7.39 (m, 1H, anis'-H$_4$), 7.24–7.20 (m, 2H, py-H$_3$ + -H$_5$), 7.10–7.07 (m, 1H, anis-H$_5$), 7.01–6.98 (m, 1H, anis'-H$_3$), 6.91 (d, $J = 7.8$ Hz, 1H, anis-H$_3$), 6.82–6.78 (m, 1H, anis'-H$_5$), 6.57–6.52 (dd, $J = 11.5$, 8.1 Hz, 1H, anis'-H$_6$), 4.00 (s, 3H, anis-CH$_3$), 3.80–3.69 (m, 1H, py-CH$_2$H), 3.68 (s, 3H, anis'-CH$_3$), 3.25–3.12 (m, 1H, py-CH$_2$H), 2.79–2.72 (m, 1H, P-CH$_2$H), 2.01–1.92 (m, 1H, P-CH$_3$H), 0.17 (d, $J = 3.5$ Hz, 3H, Pd-CH$_3$)

$^1$H NMR $\delta$ (500 MHz, CDCl$_3$, 60 °C) ppm: 9.40 (d, $J = 5.1$ Hz, 1H, py-H$_6$), 7.69–7.61 (m, 2H, anis-H$_6$), 7.61–7.56 (m, 1H, py-H$_4$), 7.44–7.39 (m, 2H, anis-H$_4$), 7.20–7.16 (m, 1H, py-H$_5$), 7.10 (d, $J = 7.7$ Hz, 1H, py-H$_3$), 6.95–6.90 (m, 4H, anis-H$_3$ + -H$_5$), 3.81 (s, 6H, anis-CH$_3$), 3.45–3.34 (m, 2H, Py-CH$_2$), 2.44–2.37 (m, 2H, P-CH$_2$), 0.35 (d, $J = 3.4$ Hz, 3H, Pd-CH$_3$)

$^{13}$C($^1$H) NMR $\delta$ (125 MHz, CDCl$_3$, 25 °C) ppm: 160.7 (d, $J = 2.1$ Hz, py-C$_2$), 160.1 (s, anis-C$_2$), 152.9 (s, py-C$_6$), 138.1 (s, CH), 138–136 (bs, CH), 132.9 (s, CH), 123.9 (s, CH), 122.8 (s, CH), 120.7 (d, $J = 12.2$ Hz, CH), 119.2 (d, $J = 51.9$ Hz, anis-C$_1$), 111.1 (d, $J = 4.2$ Hz, CH), 55.8 (s, anis-CH$_3$), 36.5 (d, $J = 7.2$ Hz, py-CH$_2$), 25.2 (d, $J = 33.3$ Hz, P-CH$_3$), -1.3 (s, Pd-CH$_3$)

$^{13}$C($^1$H) NMR $\delta$ (125 MHz, Cl$_2$DCCDCl$_2$, 80 °C) ppm: 160.4 (d, $J = 2.5$ Hz, py-C$_2$), 159.9 (s, anis-C$_2$), 152.6 (s, py-C$_6$), 137.6 (s, CH), 136.6 (d, $J = 15.2$ Hz, CH), 132.5 (s, CH), 123.5 (s, CH), 122.1 (s, CH), 120.4 (d, $J = 12.2$ Hz, CH), 119.2 (d, $J = 51.1$ Hz, anis-C$_1$), 111.2 (d, $J = 4.7$ Hz, CH), 55.5 (s, anis-CH$_3$), 36.0 (d, $J = 6.8$ Hz, py-CH$_2$), 24.9 (d, $J = 32.9$ Hz, P-CH$_2$), -1.9 (s, Pd-CH$_3$)

$^{31}$P($^1$H) NMR $\delta$ (121 MHz, CDCl$_3$, 25 °C) ppm: 37.5

Anal. Calcd. for C$_{25}$H$_{26}$ClN$_2$OPPd: C, 51.99; H, 4.96; N, 2.76. Found: C, 51.84; H, 5.08; N, 2.64

HRMS (FAB) m/z: calcd. for C$_{25}$H$_{26}$NO$_2$PPd [M-Cl]$^+$: 472.0667; found: 472.0661

2-[2-(dimesitylphosphino)ethyl]pyridine methylpalladium chloride (5c)

2-[2-(dimesitylphosphino)ethyl]pyridine (1c) (100 mg, 0.27 mmol, 1.0 equiv) and [COD]Pd(CH$_3$)$_2$Cl (71 mg, 0.27 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 3 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 (115 mg, 0.22 mmol, 81%).

$^1$H NMR $\delta$ (500 MHz, CDCl$_3$) ppm: 9.20 (dd, $J = 4.5$, 2.0 Hz, 1H, py-H$_6$), 7.62 (dt, $J = 7.5$, 2.0 Hz, 1H, py-H$_4$), 7.27–7.25 (m, 1H, py-H$_5$), 7.12 (d, $J = 7.5$ Hz, 1H, py-H$_3$), 6.82 (d, $J = 3.0$ Hz,
2-[2-(di-2-tolylphosphino)ethyl]pyridine methylpalladium(acetonitrile) tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (6a)

To a mixture of 2-[2-(di-2-tolylphosphino)ethyl]pyridine methylpalladium chloride (5a) (148 mg, 275 mmol, 1.0 equiv) and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBAR₄) (275 mg, 0.311 mmol, 1.0 equiv) were added CH₂CN (2 mL) and CH₂Cl₂ (10 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 (392 mg, 0.291 mmol, 94%).

¹H NMR δ (500 MHz, CD₂Cl₂, 25 ℃) ppm: 8.58 [bs, 1H, py-H6], 7.80–7.73 [m, 9H, py-H4 + Ar’-H2], 7.68–7.58 [bs, 2H, tol-H6], 7.58 [s, 4H, Ar’-H4], 7.47–7.42 [m, 2H, tol-H4], 7.38–7.29 [m, 4H, py-H3 + -H5 + tol-H5], 7.26–7.20 [m, 2H, tol-H3], 3.50–3.40 [m, 2H, py-CH₂], 2.58–2.42 [m, 8H, P–CH₃ + tol–CH₃], 2.29 [s, 3H, NCC₃H₉], 0.26 [s, 3H, Pd–CH₃]

¹H NMR δ (500 MHz, CDCl₃, 80 ℃) ppm: 8.63–8.57 [m, 1H, py-H6], 7.78–7.74 [m, 8H, Ar’-H2], 7.72 [t, J = 7.6 Hz, py-H4], 7.60 [dd, J = 14.4, 7.6 Hz, 2H, tol-H6], 7.57 [s, 4H, Ar’-H4], 7.48–7.44 [m, 2H, tol-H4], 7.37–7.33 [m, 2H, tol-H5], 7.29–7.22 [m, 4H, py-H3 + -H5 + tol-H3], 3.44–3.36 [m, 2H, py-CH₂], 2.55–2.47 [m, 2H, P–CH₃], 2.48 [s, 3H, tol-CH₃], 2.24 [s, 3H, NCC₃H₉], 0.39 [s, 3H, Pd–CH₃]

¹³C [¹H] NMR δ (125 MHz, CD₂Cl₂, 25 ℃) ppm: 162.4 [q, J = 49.8 Hz, Ar’-C1], 159.9 [s, py-C2], 150.6 [s, py-C6], 141.4 [d, J = 6.3 Hz, tol-C2], 140.2 [s, CH], 135.5 [bs, Ar’-C2], 132.9 [d, J = 8.0 Hz, CH], 132.5 [s, CH], 129.5 [quartet of multiplets, J = 31.6 Hz, Ar’-C3], 128.0 [d, J = 57.3 Hz, tol-C1], 126.7 [d, J = 12.7 Hz, CH], 126.1 [bs, CH], 125.2 [q, J = 272.4, CF₃], 124.4 [bs, CH], 119.7 [s, NCC₃H₉], 118.1 [m, Ar’-C4], 36.9 [s, Py-CH₂], 25.6 [d, J = 30.3 Hz, P–CH₃], 23.6 [d, J = 6.3 Hz, tol-CH₃], 3.2 [s, Pd–CH₃], 0.7 [s, NCC₃H₉]
$^{31}\text{P}[^{1}\text{H}]$ NMR $\delta$ (121 MHz, CD$_2$Cl$_2$) ppm: 42.7

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

Anal. Calcd. for C$_{33}$H$_{29}$BF$_2$N$_2$Pd: C, 50.00; H, 3.00; N, 2.08. Found: C, 49.94; H, 3.06; N, 2.10

HRMS [FAB] m/z: calcd. for C$_{33}$H$_{29}$NPPd [M−BAR']$^+$ : 440.0768; Found: 440.0765

MS (FD) m/z: 481 [M−BAR']$^+$

2-[2-[di-2-anisylphosphino]ethyl]pyridine methylpalladium(acetonitrile) tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (6b)

To a mixture of 2-[2-[di-2-anisylphosphino]ethyl]pyridine methylpalladium chloride (5b) (323 mg, 0.64 mmol, 1.0 equiv) and sodium tetraakis[3,5-trifluoromethyl]phenyl]borate (NaBAR')$_4$ (563 mg, 0.64 mmol, 1.0 equiv) were added CH$_3$CN (2 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 5 mL hexanes to yield the product as a white solid (762 mg, 0.55 mmol, 87%).

$^1\text{H}$ NMR $\delta$ (500MHz, CD$_2$Cl$_2$, 25 °C) ppm: 8.58 [d, J = 4.9 Hz, 1H, py-H6], 7.79–7.73 [m, 9H, py-H4 + Ar'-H2], 7.58 [s, 4H, Ar'-H4], 7.56–7.51 [m, 2H, anis-H4], 7.54–7.46 [bs, 2H, anis-H6], 7.33 [d, J = 7.8 Hz, 1H, py-H3], 7.32–7.28 [m, 1H, py-H5], 7.04–6.97 [m, 4H, anis-H3 + -H5], 3.85 [s, 3H, anis-CH$_3$], 3.46–3.39 [m, 2H, py-CH$_2$], 2.46–2.40 [m, 2H, P-CH$_2$], 2.29 [s, 3H, NCCCH$_3$], 0.15 [d, J = 4.2 Hz, 3H, Pd-CH$_3$].

$^1\text{H}$ NMR $\delta$ (500MHz, CD$_2$Cl$_2$, 25 °C) ppm: 8.61–8.55 [m, 1H, py-H6], 7.78–7.74 [m, 8H, Ar'-H2], 7.73 [dt, J = 7.7, 1.5 Hz, 1H, py-H4], 7.57 [s, 4H, Ar'-H4], 7.56–7.51 [m, 2H, anis-H4], 7.49 [dd, J = 14.8, 7.4 Hz, 2H, anis-H6], 7.29 [d, J = 7.7 Hz, 1H, py-H3], 7.27–7.23 [m, 1H, py-H5], 7.04–6.99 [m, 4H, anis-H3 + -H5], 3.84 [s, 6H, anis-CH$_3$], 3.43–3.34 [m, 2H, py-CH$_2$], 2.48–2.43 [m, 2H, P-CH$_2$], 2.24 [s, 3H, NCCCH$_3$], 0.27 [s, 3H, Pd-CH$_3$].

$^{13}\text{C}[^{1}\text{H}]$ NMR $\delta$ (125 MHz, CD$_2$Cl$_2$, 25 °C) ppm: 162.4 [q, J = 49.8 Hz, Ar'-C1], 161.5 [s, anis-C2], 160.6 [s, py-C2], 150.7 [s, py-C6], 139.9 [s, CH], 137.0 [s, CH], 135.5 [bs, Ar'-C2], 134.3 [s, CH], 129.5 [quartet of multiplets, J = 31.6 Hz, Ar'-C3], 125.9 [s, CH], 125.2 [q, J = 272.4, CF$_3$], 123.9 [s, CH], 121.3 [d, J = 12.7 Hz, CH], 119.6 [s, NCCCH$_3$], 118.1 [m, Ar'-C4], 117.3 [d, J = 56.4 Hz, anis-C1], 111.9 [d, J = 4.6 Hz, CH], 56.1 [s, anis-CH$_3$], 36.7 [d, J = 4.6 Hz, py-CH$_2$], 25.5 [d, J = 37.1 Hz, P-CH$_3$], 3.3 [s, NCCCH$_3$], −1.0 [s, Pd-CH$_3$].

$^{31}\text{P}[^{1}\text{H}]$ NMR $\delta$ (121 MHz, CD$_2$Cl$_2$) ppm: 39.7

$^{19}\text{F}[^{1}\text{H}]$ NMR $\delta$ (282 MHz, CD$_2$Cl$_2$) ppm: −63.0
2-[2-(dimesitylphosphino)ethyl]pyridine methylpalladium(acetonitrile) tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (6c)

To a mixture of 2-[2-(dimesitylphosphino)ethyl]pyridine methylpalladium chloride [5c] (161 mg, 0.302 mmol, 1.0 equiv) and sodium tetrakis[3,5-trifluoromethyl]phenyl]borate (NaBAR') (268 mg, 0.302 mmol, 1.0 equiv) were added CH₃CN (1 mL) and CH₂Cl₂ (10 mL) and the mixture was stirred for 16 hours. It was cannula filtrated, evaporated to dryness and co-evaporated with hexanes and pentane to yield the product as a white solid (353 mg, 0.252 mmol, 83%).

1H NMR δ (500MHz, CD₂Cl₂) ppm: 8.61 [d, J = 5.4 Hz, 1H, py-H6], 7.78–7.73 [m, 9H, py-H4 + Ar’-H2], 7.59 [s, 4H, Ar’-H4], 7.37–7.33 [m, 1H, py-H5], 7.30 [d, J = 7.6 Hz, py-H3], 6.91 [d, J = 3.4 Hz, 4H, mes-H3], 3.51–3.45 [m, 2H, py-CH₂], 2.57–2.54 [m, 2H, P-CH₃], 2.42 [s, 12H, mes-2-CH₃], 2.26 [s, 6H, mes-4-CH₃], 2.22 [s, 3H, NCCCH₃], 0.39 [d, J = 3.4 Hz, 3H, Pd-CH₃]

13C{1H} NMR δ (125 MHz, CD₂Cl₂) ppm: 162.4 [q, J = 49.8 Hz, Ar’-C1], 160.6 [s, py-C2], 150.5 [s, py-C6], 141.6 [s, mes-C2], 141.5 [s, mes-C4], 140.29 [s, CH], 135.5 [bs, Ar’-C2], 131.8 [d, J = 8.9 Hz, mes-C3], 129.5 [quartet of multiplets, J = 31.6 Hz, Ar’-C3], 128.0 [d, J = 42.5 Hz, mes-C1], 125.8 [s, CH], 125.2 [q, J = 272.4, CF₃], 124.4 [s, CH], 120.1 [s, NCCCH₃], 118.1 [m, Ar’-C4], 37.9 [d, J = 4.4 Hz, py-CH₂], 30.8 [d, J = 34.6 Hz, P-CH₃], 25.2 [d, J = 8.2 Hz, mes-2-CH₃], 21.0 [s, mes-4-CH₃], 3.4 [s, NCCCH₃], 2.1 [s, Pd-CH₃]

31P{1H} NMR δ (121 MHz, CD₂Cl₂) ppm: 14.7

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

HRMS (FAB) m/z: calcd. for C₂₇H₂₅NPPd [M–BAR’–CH₃CN]: 496.1396; Found: 496.1395

MS (FD) m/z: 537 [M–BAR’]⁺

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 icedcold 2M hydrochloric acid was added to the reaction mixture and it was stirred vigorously in an icebath 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 icedcold 2M hydrochloric acid was added to the reaction mixture and it was stirred vigorously in an icebath. 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**


