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

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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 inversion 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 inversion. The nickel species were evaluated as ethene oligomerization catalysts after activation with MAO. All complexes were highly active, with TOFs between 24×10^3 and 85×10^3 (mol C_2H_4)·(mol Ni·h)$^{-1}$. Butenes were the major product in all cases, forming 76 to 96 mol % 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 C_2H_4)·(mol Pd·h)$^{-1}$ and 38 to 88 mol % 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] oxazoline-phosphines and -phosphinites,[18−22] iminophosphoranes,[23] ami-

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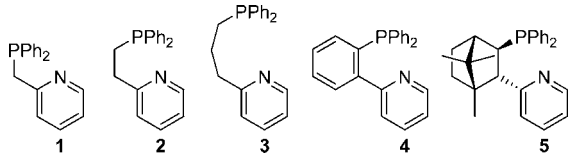
Chart 1. Ligands Used in This Study



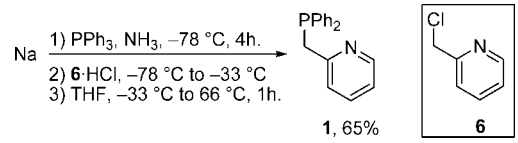
do- and iminophosphines,[24−26] iminopyrrolylphosphines,[27] pyrazolephosphines,[28] quinolinephosphines,[29,30] and pyridinephospholes.[31] We are particularly interested in pyridine−phosphine ligands.[1]

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 of **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.

Scheme 1. One-Pot Synthesis of Ligand 1



Ligand Synthesis. The ligands **1**,[32] **2**,[33] and **3**[32] were first reported over three decades ago. Their original syntheses involved the labile (2-pyridyl)−$(CH_2)_n$−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[34] or via a more stable intermediate in a two-step process.[14] 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 1 equiv 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.

Alternative published syntheses for 2-[2-(diphenylphosphino)ethyl]pyridine (**2**) include metal,[35] acid,[36] base,[37] or fluoride[38] mediated phosphination of 2-vinylpyridine. In our opinion, the acid-catalyzed hydrophosphination of 2-vinylpyridine[36] is the most convenient 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]

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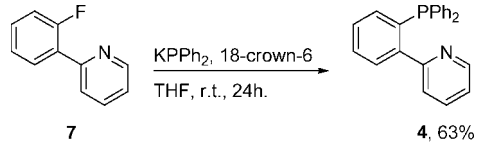
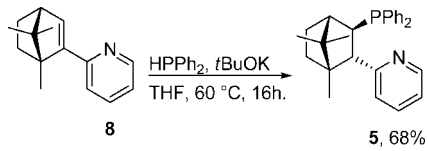
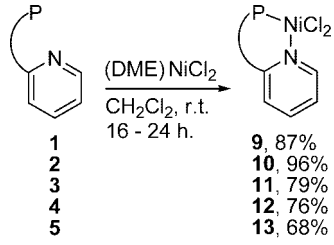
Scheme 2. Synthesis of Ligand 4



Scheme 3. Synthesis of Ligand 5



Scheme 4. Synthesis of Nickel Complexes 9−13

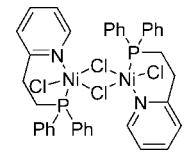


Several groups have reported the use of 2-[2-(diphenylphosphino)phenyl]pyridine (**4**),[40] but, to the best of our knowledge, full synthetic and analytical data were never reported. The synthesis of the ligand oxide, 2-[2-(diphenylphosphinoyl)phenyl]pyridine, has been reported,[41] but it involved 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.

The ligand 2-[(1*S*,2*R*,3*R*,4*S*)-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-[(1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl]pyridine (**8**) with diphenylphosphine oxide to give the oxide of the ligand, which was reduced in a second step. Use of diphenylphosphine 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).

Synthesis and Characterization of Nickel Complexes. We obtained nickel dichloride complexes of the ligands by reaction with (DME)$NiCl_2$ [DME = 1,2-dimethoxyethane]; see Scheme 4. All complexes were paramagnetic, as evidenced by their magnetic moment in solution. Satisfactory elemental analyses were obtained for all complexes. The high-resolution mass spectra showed the peak for the $[(ligand)NiCl]^+$ ion. Loss of one chlorine atom is a consequence of the ionization; proton addition is immediately followed by loss of HCl. For complexes **10** and **12**, single-crystal X-ray diffraction was performed. 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 deep purple (appearing almost black) (**9**), orange (**11**), or light brown (**12**).

Chart 2. Complex 10′ as Reported by Braunstein et al.[14]



Very recently, the group of Braunstein also reported on complex **9**.[14] They used a slightly different synthetic procedure ($NiCl_2$ as precursor, methanol as solvent, and 1 h reaction time) and obtained the product as a gray powder. Also the magnetic moment in CD_2Cl_2 solution of 2.2 μ_B differed from the value of 2.61 μ_B we found. This indicates that a slightly different species formed in our case compared to theirs.

The formation of a slightly different complex when using different conditions is further illustrated when the nickel complex of ligand **2** is considered. Braunstein 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.

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 geometry, 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, and the other angles around the metal are less distorted from tetrahedral. The six-membered nickel chelate ring is in a "twist-boat" conformation. X-ray crystal structures of nickel dichloride complexes have been reported with the tetracoordinated nickel having a square-planar geometry with pyridine−phosphine[16] and pyridine−phosphinite[19] ligands, but these were shown to be tetrahedral in solution. The tetrahedral geometry of nickel in the crystal structure of **10** is in agreement with the paramagnetic nature of the complex.[45]

The difference between **10** and **10′** is further illustrated by the color of the solid (purple and green, respectively) and the magnetic moment in CD_2Cl_2 solution (3.12 and 2.7 μ_B, respectively). The difference in synthetic procedures was the same as mentioned above for complex **9**. The original report[33] on complex **10** describes a red-violet complex with magnetic moment of 3.29 μ_B (presumably in the solid state), obtained after reaction of the ligand with $NiCl_2$ in refluxing *n*-butanol for 20 min.

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 (the EPR spectrum is given in the Supporting Information). 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

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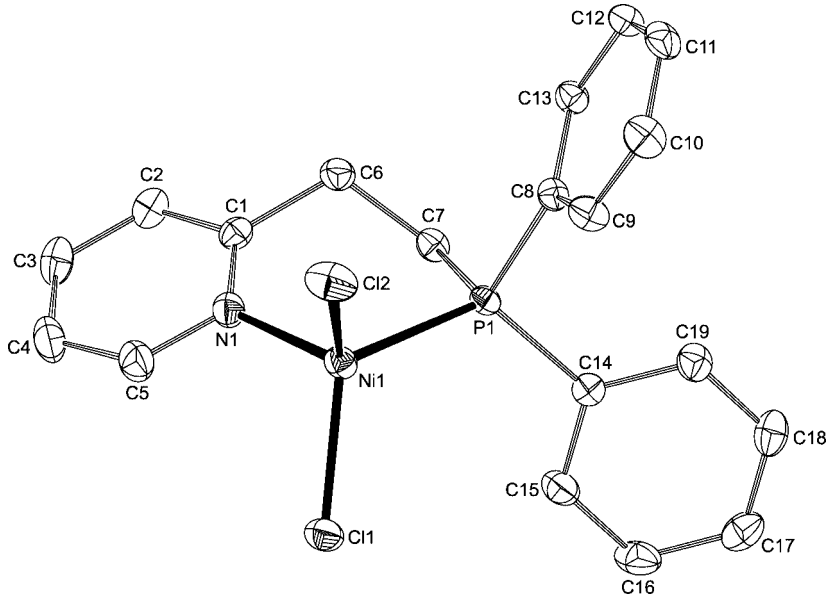

Figure 1. Displacement ellipsoid plot of **10** in the crystal, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 1. Selected Angles (deg) and Bond Lengths (Å) in Complex 10

P1−Ni1−N1	98.36(4)	Ni1−N1−C1	128.43(10)
P1−Ni1−Cl1	110.81(2)	N1−C1−C6	119.64(13)
P1−Ni1−Cl2	108.41(2)	C1−C6−C7	113.96(12)
N1−Ni1−Cl1	100.46(4)	C6−C7−P1	110.30(10)
N1−Ni1−Cl2	111.19(5)	C7−P1−Ni1	104.61(5)
Cl1−Ni1−Cl2	124.33(2)		
Ni1−P1	2.3018(5)	N1−C1	1.352(2)
Ni1−N1	2.0240(13)	P1−C7	1.8231(15)
Ni1−Cl1	2.2301(5)	C6−C7	1.543(2)
Ni1−Cl2	2.2196(6)	C1−C6	1.509(2)

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.

Complexes **11**−**13** are all new compounds. Synthesis was straightforward, and complexes with magnetic moments (in CD_2Cl_2) of 3.47 (**11**), 3.23 (**12**), and 3.11 μ_B (**13**) were obtained, indicative of distorted tetrahedral geometry of the nickel center.[46] We obtained the crystal structure of **12**. The structure is shown in Figure 2, and selected angles and bond distances are presented in Table 2.

Just as in **10**, the nickel chelate ring in complex **12** has a "twist-boat" conformation, with a distorted tetrahedral geometry 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 other angles around nickel are less distorted from tetrahedral. The distances around nickel are normal and comparable to those in complex **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 (β_n)[47,48] for complexes **1**−**5** when coordinated to nickel; values are given in Table 3. As expected, ligand **1** exhibits the smallest bite angle, and this increases on increasing the number of methylenes in the backbone (ligands **2** and **3**). The phenylene backbone in **4** results in a β_n between those of **1** and **2**. The *anti* configuration of the pyridine and the diphenylphosphine groups in ligand **5** induces a rather large natural bite angle, being similar to that of **3**.

The difference between the calculated value of 94.7° for ligand **2** and the value in the crystal structure of complex **10** (98.36(4)°) can be ascribed to the electronic preference of the metal. The dummy metal used in the bite angle calculations

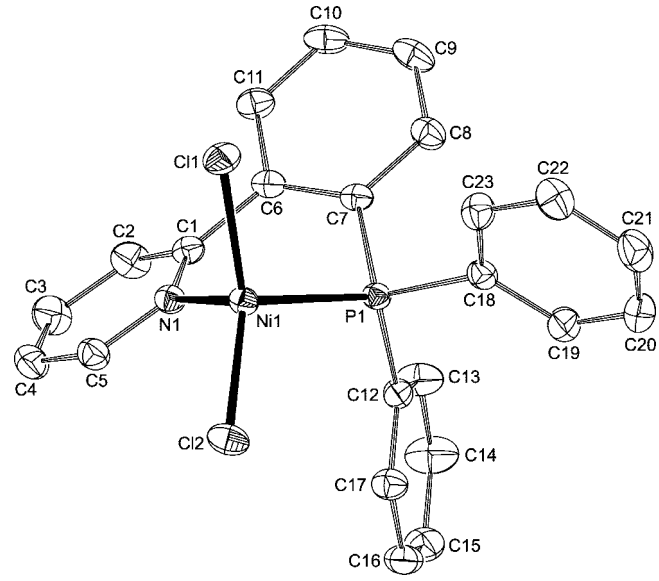

Figure 2. Displacement ellipsoid plot of **12** in the crystal, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 2. Selected Angles (deg) and Bond Lengths (Å) in Complex 12

P1−Ni1−N1	89.75(4)	Ni1−N1−C1	127.68(10)
P1−Ni1−Cl1	106.390(15)	N1−C1−C6	121.21(13)
P1−Ni1−Cl2	109.788(16)	C1−C6−C7	125.53(12)
N1−Ni1−Cl1	102.54(3)	C6−C7−P1	120.33(10)
N1−Ni1−Cl2	108.68(3)	C7−P1−Ni1	102.26(5)
Cl1−Ni1−Cl2	131.542(18)		
Ni1−P1	2.2548(4)	N1−C1	1.3587(18)
Ni1−N1	2.0001(12)	P1−C7	1.8172(14)
Ni1−Cl1	2.2170(4)	C6−C7	1.414(2)
Ni1−Cl2	2.2105(4)	C1−C6	1.497(2)

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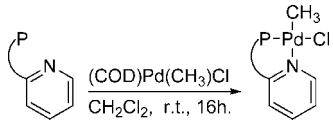
Table 3. Calculated Natural Bite angles (β_n) for Complexes 9−13

	ligand				
	1	**2**	**3**	**4**	**5**
β_n (deg)	87.2	94.7	101.8	90.8	101.7

Scheme 5. Synthesis of Neutral Palladium Complexes 14−18



1 → **14**, 84%
2 → **15**, 83%
3 → **16**, 85%
4 → **17**, 91%
5 → **18**, 77%

does not have a preference, and β_n is determined by ligand factors only.[48] The tetrahedrally surrounded d^8 metal center in **10**, on the other hand, prefers an angle of 109°. As a consequence of the ligand preferred bite angle and the sterics 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.[49] In complex **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 **12** is therefore in good correlation with the calculated natural bite angle of 90.8° of ligand **4**. In ethene oligomerization, the active species is believed to be a nickel complex with a square-planar-surrounded metal center.[50] 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.

Synthesis and Characterization of Neutral Palladium Complexes. Neutral methylpalladium chloride complexes were obtained from reaction of the ligand with (COD)Pd(CH_3)Cl [COD = 1,5-cyclooctadiene]; see Scheme 5. All compounds were obtained as white solids and were characterized by NMR, high-resolution mass spectrometry (showing the [(ligand)-Pd(CH_3)]$^+$ ion), and elemental analysis. In addition, single-crystal X-ray diffraction was performed on complexes **15** and **16**.

The NMR spectra showed the formation of the desired complexes. 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−CH_3 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).

The room-temperature ^{13}C and ^{1}H NMR spectra in $CDCl_3$ of compound **16** contained broad peaks, indicative of hindered inversion of the seven-membered palladium chelate ring. Variable-temperature ^{1}H NMR spectra of **16** are shown in Figure 3. Upon cooling to −20 °C, the separate signals of the inequivalent protons are visible in the ^{1}H NMR spectrum. One of the signals of the two CH_2−(2-pyridyl) protons is shifted by 1.0 ppm toward 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 relatively 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.[51] At 80 °C, the ring inversion was fast on the NMR time scale. 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 $Cl_2DCCDCl_2$, 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 inversion, 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.

Single crystals of **15** suitable for X-ray diffraction were obtained. The crystal structure is shown in Figure 4, and selected angles and bond lengths are summarized in Table 4. Just like the nickel complex of this ligand, the palladium complex **15** has the metal chelate ring in a "twist-boat" conformation. The metal has a distorted square-planar geometry. 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 alkoxycarbonyl 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(CH_3)Cl or $PdCl_2$ complexes of related pyridine−phosphine ligands.[53]

The X-ray crystal structure of **16** is shown in Figure 5, and selected angles and bond lengths are shown in Table 5. The palladium has a distorted square-planar geometry. 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 pseudoaxial position and has a distance of 2.81 Å to palladium. This is also reflected in the ^{1}H 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 $PdCl_2$ complex of a similar pyridine−phosphine ligand with a backbone consisting of three aliphatic carbons.[51] In this structure, there also is a relatively short Pd···H distance of 2.72(3) Å.

Synthesis and Characterization of Cationic Palladium Complexes. All neutral palladium complexes were preactivated to give cationic complexes by reaction with $NaBAr'_4$ [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.

In analogy to the neutral complex **16**, complex **21** gave rise to broad signals in room-temperature NMR spectra (the variable-temperature ^{1}H NMR spectra are given in the Supporting Information). When the sample was cooled to −40 °C, the

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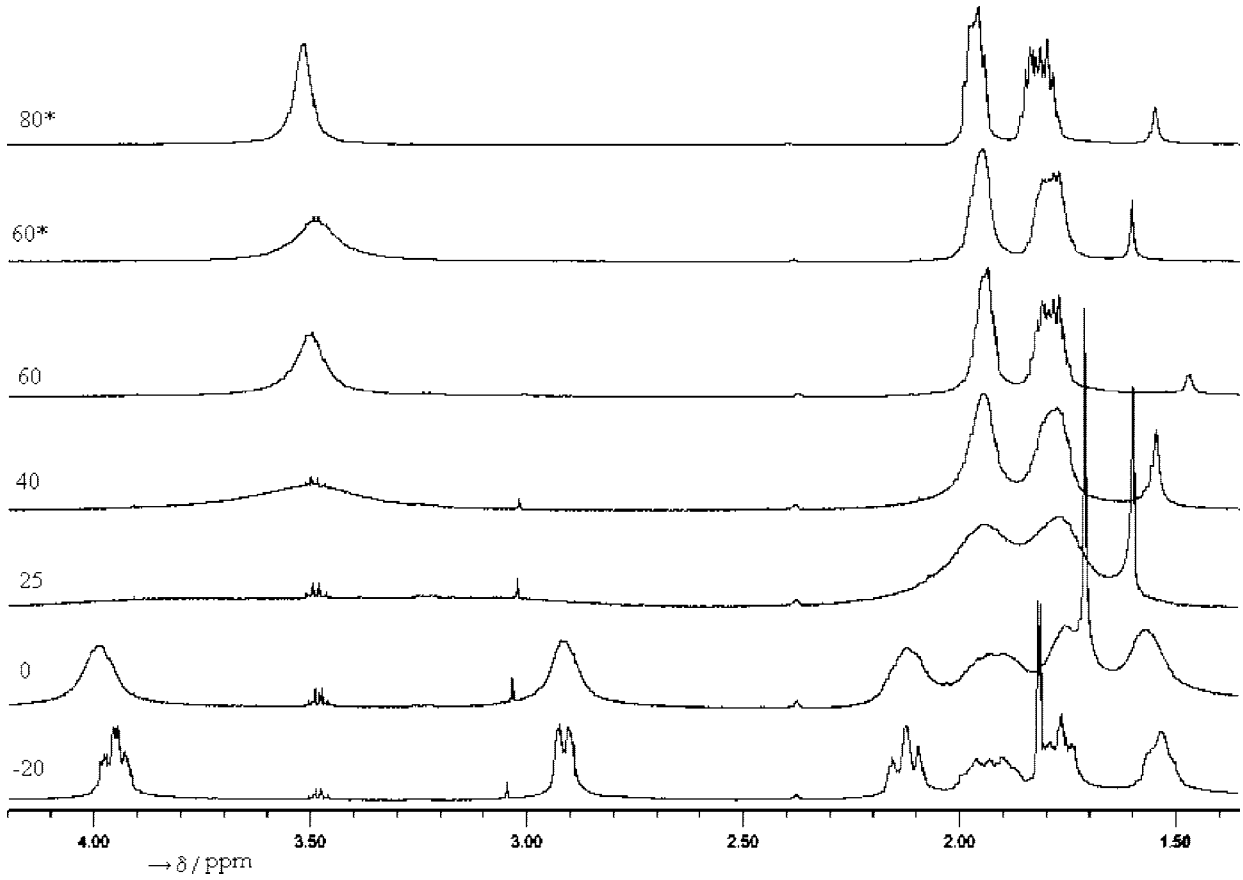


Figure 3. Methylene region of the ^{1}H NMR spectra of compound **16** at different temperatures (in °C), recorded in $CDCl_3$ except spectra marked with *, which are recorded in $Cl_2DCCDCl_2$.

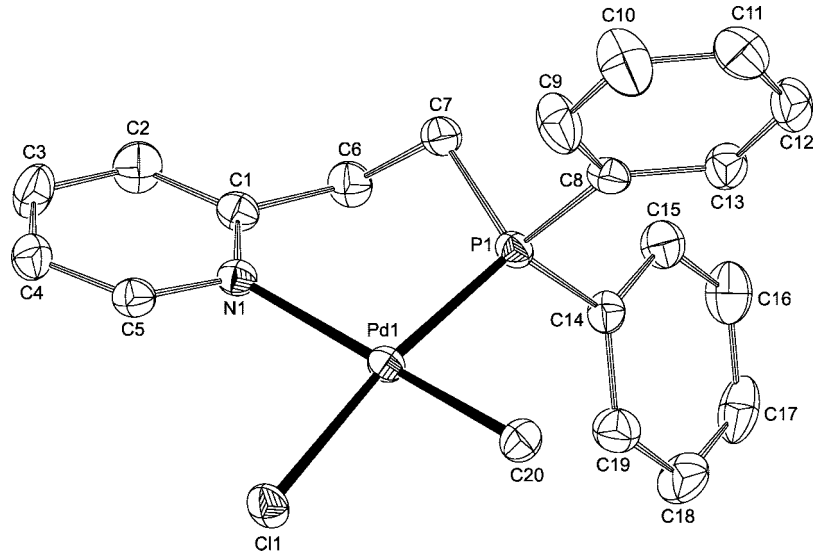


Figure 4. Displacement ellipsoid plot of **15** in the crystal, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

signals became sharp. Like in **16**, one of the (2-pyridyl)−CH_2 protons showed a difference in chemical shift (of 0.7 ppm) from the other one and from the shift of the free ligand, indicative of a Pd···H interaction. At 80 °C the ring inversion was fast on the NMR time scale.

Nickel-Catalyzed Ethene Oligomerization. Nickel halide complexes bearing pyridine−phosphine ligands have been used as precursors in oligomerization of ethene.[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 com-

Table 4. Selected Angles (deg) and Bond Lengths (Å) in Complex 15

P1−Pd1−N1	95.02(6)	Pd1−N1−C1	126.85(18)
P1−Pd1−Cl1	172.20(3)	N1−C1−C6	119.5(2)
P1−Pd1−C20	85.86(9)	C1−C6−C7	114.1(2)
N1−Pd1−Cl1	92.35(6)	C6−C7−P1	110.97(19)
N1−Pd1−C20	177.21(11)	C7−P1−Pd1	108.94(9)
Cl1−Pd1−C20	86.88(9)		
Pd1−P1	2.1964(8)	N1−C1	1.358(3)
Pd1−N1	2.223(2)	C1−C6	1.505(4)
Pd1−Cl1	2.3837(7)	P1−C7	1.815(3)
Pd1−C20	2.041(3)	C6−C7	1.536(4)

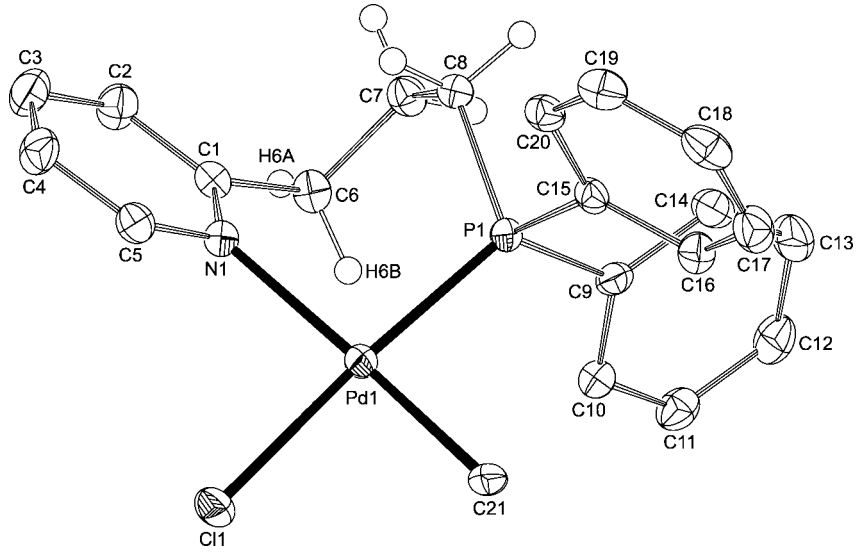
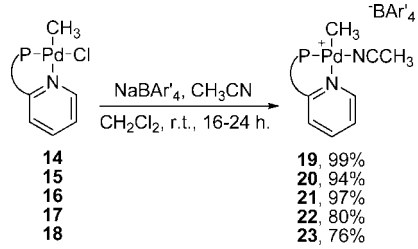


Figure 5. Displacement ellipsoid plots of **16** in the crystal, drawn at the 50% probability level. Aromatic hydrogen atoms and disordered solvent molecules are omitted for clarity.

Table 5. Selected Angles (deg) and Bond Lengths (Å) in Complex 16

P1−Pd1−N1	94.86(5)	Pd1−N1−C1	125.37(16)
P1−Pd1−Cl1	175.96(2)	N1−C1−C6	118.3(2)
P1−Pd1−C21	87.31(7)	C1−C6−C7	111.1(2)
N1−Pd1−Cl1	89.17(5)	C6−C7−C8	114.68(19)
N1−Pd1−C21	176.71(9)	C7−C8−P1	113.65(17)
Cl1−Pd1−C21	88.65(7)	C8−P1−Pd1	113.50(8)
Pd1−P1	2.2204(6)	N1−C1	1.357(3)
Pd1−N1	2.1746(19)	C1−C6	1.502(3)
Pd1−Cl1	2.3923(6)	C6−C7	1.545(3)
Pd1−C21	2.057(2)	C7−C8	1.536(3)
P1−C8	1.839(2)	Pd1···H6B	2.81

Scheme 6. Synthesis of Cationic Palladium Complexes 19−23



14
15
16
17
18

19, 99%
20, 94%
21, 97%
22, 80%
23, 76%

plexes 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.

All complexes form active species after activation, with butenes being the major catalysis product. Activities in general are high and among 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 5 to 10 min. 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%. 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. This chain transfer could lead to a nickel(ethene) hydride complex or proceed via chain transfer to monomer. For nickel complexes, theoretical studies showed that termination is more likely to proceed via the latter pathway.[54] Migratory insertion in a hydride complex is faster than in an alkylmetal complex (formed after every ethene insertion). Chain transfer to monomer requires the consumption of a molecule of ethene. So, both pathways would lead 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 dependent not only on the natural bite angle of the ligand but also on factors such as steric and electronic properties and ligand flexibility. The influence of the bite angle of diphosphine ligands on the outcome of nickel-catalyzed ethene oligomerization has been studied, but the dependence on β_n is not

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Table 6. Ethene Oligomerization Using 9−13 as Catalyst Precursor[a]

			product distribution (%)[c]					
complex	productivity (g C_2H_4/(mol Ni · h))	TOF[b]	C4	C6	C8	C10	C12	1-butene (%)[d]
9	83×10^4	30×10^3	96	4	<1			29
10	196×10^4	70×10^3	86	11	3	<1		18
11	240×10^4	85×10^3	96	3	<1			11
12	218×10^4	78×10^3	92	6	1	<1		10
13	68×10^4	24×10^3	76	17	6	3	1	40

[a] Conditions: 10 μmol of nickel complex, MAO activator (Al/Ni = 230), 10 bar of ethene, 1.0 mmol of heptane (internal standard), toluene solvent, total volume: 25 mL, *T*: 30 °C, time: 30 min. [b] Turnover frequency in (mol C_2H_4)·(mol Ni·h)$^{-1}$. [c] Mol percentage of combined C*n* products. [d] As percentage of total C4 fraction.

uniform.[55] Catalyst precursor **13**, having a backbone that has a similar bite angle to that of complex **11** but that is very rigid, has the lowest rate of isomerization, accompanied with a relatively low productivity. Complex **12** behaves similarly 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 toward ethene after activation with 400 or 800 equiv of MAO, presumably due to decomposition as a result of free trimethylaluminum in the MAO used. When the complex was activated with $EtAlCl_2$, 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.[22] 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 2 to 4 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.[14] Although they tested more activation methods, which sometimes gave better results, the conditions that compare best to our conditions are the activation with 200 equiv 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**.

Table 7. Ethene Oligomerization Using 19−23 as Catalyst Precursor[a]

		product distribution (%)[c]							
complex	TOF[b]	C4	C5	C6	C7	C8	C9	C10	<C10
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				

[a] Conditions: 100 μmol of palladium complex, 10 bar of ethene, 0.10 mmol of heptane (internal standard), toluene solvent, total volume: 25 mL, *T*: 30 °C, time: 120 min. [b] Turnover frequency in (mol C_2H_4)·(mol Pd·h)$^{-1}$. [c] Mol percentage of combined C*n* products.

Palladium-Catalyzed Ethene Oligomerization. Palladium complexes bearing pyridine−phosphine ligands have only sparingly been used as ethene oligomerization catalyst.[13,15] The group of Rieger presented an active catalyst,[15] whereas Liu reported the formation of negligible amounts of oligomers with complexes of this kind.[13] We tested our complexes for their ability to oligomerize ethene, and results are presented in Table 7.

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 TOFs (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 is 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

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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[13] and the active catalyst of Rieger[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 more strongly to palladium than ethene, and the nitrile adduct is an inactive species.[56] The system of Rieger 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 of C6 and higher compared to butenes.[20] 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 difference in the structures of **9** and **10** compared to the nickel dichloride complexes of the same ligands recently reported[14] 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 geometry, 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 24×10^3 and 85×10^3 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 min 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 shows 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

2-[2-(Diphenylphosphino)ethyl]pyridine (**2**),[36] 2-(2-fluorophenyl)pyridine (**7**),[42] 2-[(1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl]pyridine (**8**),[44] (DME)$NiCl_2$,[57] (COD)$Pd(CH_3)Cl$,[58] and $NaBAr'_4$[59] were synthesized according to the published procedures. General experimental considerations are given in the Supporting Information.

X-ray Crystal Structure Determinations. X-ray reflections were measured with Mo Kα radiation ($\lambda = 0.71073$ Å) on a Nonius Kappa CCD diffractometer with rotating anode at a temperature of 150 K up to a resolution of $(\sin \theta/\lambda)_{max} = 0.65$ Å^{-1}. The structures were solved with direct methods (program SHELXS-86[60] for **10**, **12**, and **15**; SIR-97[61] for **16**) Refinement was performed with SHELXL-97[60] against F^2 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 Å^3/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 PLATON,[62] resulting in 31 electrons/unit cell. Geometry calculations and checking for higher symmetry were performed with the PLATON[62] program. Further details about the crystal structure determinations are given in Table 8.

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 h, 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 1 h, water (5 mL) was added, and the THF was evaporated. CH_2Cl_2 was added and the organic layer was washed with water, saturated aqueous $NaHCO_3$, and water again. Purification by column chromatography using Et_2O as the eluent yielded the product as a white solid (3.47 g, 12.5 mmol, 68%, mp 47 °C). ^{1}H NMR δ (500 MHz, $CDCl_3$) 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, CH_2). ^{13}C{^{1}H} NMR δ (125 MHz, $CDCl_3$) 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, CH_2). ^{31}P{^{1}H} NMR δ (121 MHz, $CDCl_3$) ppm: −9.6. Anal. Calcd for $C_{18}H_{16}NP$: C, 77.96; H, 5.82; N, 5.05. Found: C, 78.11; H, 5.94, N, 4.85. MS (EI) *m*/*z* (rel intensity): 277 (85) $[M]^+$, 200 (19) $[M - Ph]^+$, 185 (23) $[PPh_2]^+$, 183 (100) $[PPh_2 - 2H]^+$, 168 (94).

2-[3-(Diphenylphosphino)propyl]pyridine (3). The compound was prepared according to the published procedure.[32] Full NMR characterization was never reported. ^{1}H NMR δ (500 MHz, $CDCl_3$) 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-CH_2), 2.14−2.09 (m, 2H, P-CH_2), 1.95−1.88 (m, 2H, P-CH_2-CH_2). ^{13}C{^{1}H} NMR δ (75 MHz, $CDCl_3$) 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-CH_2), 27.8 (d, $J = 12.2$ Hz, P-CH_2-CH_2), 26.4 (d, $J = 17.1$ Hz, P-CH_2) ^{31}P{^{1}H} NMR δ (121 MHz, $CDCl_3$) 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

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Table 8. Selected Crystallographic Data for Complexes 10, 12, 15, and 16

	10	12	15	16
formula	$C_{19}H_{18}Cl_2NNiP$	$C_{23}H_{18}Cl_2NNiP$	$C_{20}H_{21}ClNPPd$	$C_{21}H_{23}ClNPPd$ + disordered solvent
fw	420.92	468.96	448.20	462.22[a]
cryst color	deep purple	dark red	colorless	yellowish
cryst size [mm^3]	0.30 × 0.10 × 0.10	0.30 × 0.20 × 0.15	0.20 × 0.04 × 0.02	0.30 × 0.09 × 0.04
cryst syst	triclinic	orthorhombic	monoclinic	triclinic
space group	$P\bar{1}$ (no. 2)	*Pbca* (no. 61)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a [Å]	7.4772(10)	17.1048(10)	11.7992(18)	9.6302(2)
b [Å]	8.4117(10)	13.3897(10)	13.940(2)	10.2603(2)
c [Å]	15.416(2)	18.552(2)	11.7544(12)	11.4891(2)
α [deg]	97.787(12)	90	90	110.8761(10)
β [deg]	101.974(14)	90	96.56(3)	95.4957(10)
γ [deg]	101.194(10)	90	90	95.8718(8)
V [Å^3]	914.7(2)	4248.9(6)	1920.7(5)	1044.40(4)
Z	2	8	4	2
D_x [g/cm^3]	1.528	1.466	1.550	1.470[a]
reflns measd/unique	24 320/4167	99 443/4869	42 054/4325	16 860/5775
μ [mm^{-1}]	1.440	1.249	1.189	1.096[a]
abs corr	multiscan	multiscan	multiscan	multiscan
abs corr range	0.77−0.87	0.75−0.83	0.86−0.97	0.62−0.96
params/restraints	217/0	253/0	218/0	227/0
R1/wR2 [$I > 2\sigma(I)$]	0.0236/0.0570	0.0247/0.0584	0.0323/0.0584	0.0282/0.0628
R1/wR2 [all reflns]	0.0277/0.0588	0.0307/0.0609	0.0544/0.0647	0.0369/0.0657
S	1.052	1.035	1.027	1.074
res density [e/Å^3]	−0.40/0.35	−0.29/0.32	−0.63/0.44	−0.51/0.49

[a] Derived parameters do not contain the contribution of the disordered solvent.

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*. Et_2O (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 eluent) yielded the product as a light yellow solid (628 mg, 1.85 mmol, 63%, mp 86 °C). ^{1}H NMR δ (500 MHz, $CDCl_3$) 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). ^{13}C{^{1}H} NMR δ (125 MHz, $CDCl_3$) ppm: 159.0 (d, J = 2.8 Hz, py-C2), 148.8 (s, py-C6), 146.1 (d, J = 24.2 Hz, C_q), 138.3 (d, J = 11.1 Hz, C_q), 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), 128.5 (s, CH), 128.4 (s, CH), 124.3 (d, J = 4.8 Hz, CH), 122.0 (s, CH). ^{31}P{^{1}H} NMR δ (121 MHz, $CDCl_3$) ppm: −10.1. Anal. Calcd for $C_{23}H_{18}NP$: C, 81.40; H, 5.35; N, 4.13. Found: C, 81.35; H, 5.32, N, 4.07. MS (EI) *m/z* (rel intensity): 339 (9) $[M]^+$, 262 (100) $[M - Ph]^+$, 185 (21) $[M - 2Ph]^+$.

2-[(1*S*,2*S*,3*R*,4*S*)-3-(Diphenylphosphino)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]pyridine (5). To a solution of 2-[(1*R*,4*R*)-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 h, water (5 mL) was added, and the mixture was concentrated. Et_2O was added, and the organic layer was washed with water three times and evaporated. Purification using column chromatography (eluent 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]pyridinenickel Dichloride (9). A mixture of 2-[(diphenylphosphino)methyl]pyridine (**1**) (220 mg, 0.79 mmol, 1.0 equiv), (DME)$NiCl_2$ (174 mg, 0.79 mmol, 1.0 equiv), and CH_2Cl_2 (15 mL) was stirred for 20 h. It was filtered through a pad of Celite, washed with CH_2Cl_2, and concentrated *in vacuo*. Et_2O (15 mL) was added, and the mixture was put in a sonification bath for 30 min. The solids were filtered off, washed with Et_2O, 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 $C_{18}H_{16}Cl_2NNiP$: 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 $C_{18}H_{16}ClNNiP$ $[M - Cl]^+$ 370.0062; found 370.0063. μ_{eff} = 2.61 μ_B.

2-[2-(Diphenylphosphino)ethyl]pyridinenickel Dichloride (10). A mixture of 2-[2-(diphenylphosphino)ethyl]pyridine (**2**) (500 mg, 1.72 mmol, 1.0 equiv), (DME)$NiCl_2$ (377 mg, 1.72 mmol, 1.0 equiv), and CH_2Cl_2 (15 mL) was stirred for 16 h. It was filtered through a pad of Celite, washed with CH_2Cl_2, and concentrated *in vacuo*. Washing with hexanes four times yielded the product as a purple solid (697 mg, 1.66 mmol, 96%, mp 203 °C dec). Crystals suitable for X-ray diffraction were obtained by layering a CH_2Cl_2 solution of the product with hexanes. Anal. Calcd for $C_{19}H_{18}Cl_2NNiP$: 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 $C_{19}H_{18}ClNNiP$ $[M - Cl]^+$ 384.0219; found 384.0210. μ_{eff} = 3.12 μ_B.

2-[3-(Diphenylphosphino)propyl]pyridinenickel Dichloride (11). A mixture of 2-[3-(diphenylphosphino)propyl]pyridine (**3**) (200 mg, 0.65 mmol, 1.0 equiv), (DME)$NiCl_2$ (144 mg, 0.65 mmol, 1.0 equiv), and CH_2Cl_2 (20 mL) was stirred for 24 h. It was filtered through a pad of Celite, washed with CH_2Cl_2, and concentrated to a volume of 5 mL. This was slowly dropped to 75 mL of vigorously stirred Et_2O. The solids were filtered off, washed with Et_2O, 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 $C_{20}H_{20}Cl_2NNiP$: 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 $C_{20}H_{20}ClNNiP$ $[M - Cl]^+$ 398.0375; found 398.0361. μ_{eff} = 3.47 μ_B.

2-(2-(Diphenylphosphino)phenyl)pyridinenickel Dichloride (12). This was obtained following the procedure for **11** from 2-(2-(diphenylphosphino)phenyl)pyridine (**4**) (100 mg, 0.29 mmol, 1.0 equiv) and (DME)$NiCl_2$ (65 mg, 0.29 mmol, 1.0 equiv) to yield the product as a light brown solid (104 mg, 0.22 mmol, 76%, mp 268 °C dec). Anal. Calcd for $C_{23}H_{18}Cl_2NNiP$: 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 $C_{23}H_{18}ClNNiP$ $[M - Cl]^+$ 432.0219; found 432.0200. μ_{eff} = 3.23 μ_B.

2-[(1*S*,2*R*,3*R*,4*S*)-3-(Diphenylphosphino)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]pyridinenickel Dichloride (13). A mixture of 2-[(1*S*,2*R*,3*R*,4*S*)-3-(diphenylphosphino)-1,7,7-

trimethylbicyclo[2.2.1]hept-2-yl]pyridine (**5**) (115 mg, 0.29 mmol, 1.0 equiv), (DME)$NiCl_2$ (63 mg, 0.28 mmol, 1.0 equiv), and CH_2Cl_2 (6 mL) was stirred for 24 h. It was filtered through a pad of Celite, washed with CH_2Cl_2, and concentrated to approximately 5 mL, after which the product was precipitated with 30 mL of Et_2O. It was filtrated off and washed with Et_2O. Drying *in vacuo* yielded the product as a purple solid (104 mg, 0.20 mmol, 68%, mp 298 °C dec). Anal. Calcd for $C_{27}H_{30}Cl_2NNiP$: 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 $C_{27}H_{30}ClNNiP$ $[M - Cl]^+$ 492.1158; found 492.1163. $\mu_{eff} = 3.11$ μ_B.

2-[(Diphenylphosphino)methyl]pyridinemethylpalladium Chloride (14). 2-[(Diphenylphosphino)methyl]pyridine (**1**) (71 mg, 0.26 mmol, 1.0 equiv) and (COD)Pd(CH_3)Cl (68 mg, 0.26 mmol, 1.0 equiv) were dissolved in CH_2Cl_2 (5 mL), and the mixture was stirred for 16 h. Then, it was concentrated *in vacuo* to approximately 0.5 mL, after which 5 mL of Et_2O was added under vigorous stirring. The white precipitate was filtrated off and washed with Et_2O. Drying *in vacuo* yielded the product as a white solid (92 mg, 0.21 mmol, 83%). ^{1}H NMR δ (500 MHz, $CDCl_3$) 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, CH_2), 0.78 (d, J = 2.5 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR δ (75 MHz, $CDCl_3$) 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, *C*H_2), −5.2 (s, *C*H_3). ^{31}P{^{1}H} NMR δ (121 MHz, $CDCl_3$) ppm: 41.6. Anal. Calcd for $C_{19}H_{19}ClNPPd$: 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 $C_{19}H_{19}NPPd$ $[M - Cl]^+$ 398.0298; found 398.0294.

2-[2-(Diphenylphosphino)ethyl]pyridinemethylpalladium Chloride (15). This was obtained following the procedure for **14** from 2-[2-(diphenylphosphino)ethyl]pyridine (**2**) (300 mg, 1.03 mmol, 1.1 equiv) and (COD)Pd(CH_3)Cl (273 mg, 1.03 mmol, 1.0 equiv) to yield the product as a white solid (390 mg, 0.87 mmol, 84%, mp 231 °C dec). ^{1}H NMR δ (500 MHz, $CDCl_3$) 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-CH_2), 2.33−2.27 (m, 2H, P-CH_2), 0.67 (d, J = 3.1 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR δ (125 MHz, $CDCl_3$) 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−*C*H_2), 26.1 (d, J = 29.4 Hz, P-*C*H_2), −0.7 (s, *C*H_3). ^{31}P{^{1}H} NMR δ (121 MHz, $CDCl_3$) ppm: 36.3. Anal. Calcd for $C_{20}H_{21}ClNPPd$: C, 53.59; H, 4.72; N, 3.12. Found: C, 53.62; H, 4.67; N, 2.98. HRMS (FAB) *m/z*: calcd for $C_{20}H_{21}NPPd$ $[M - Cl]^+$ 412.0455; found 412.0457.

2-[3-(Diphenylphosphino)propyl]pyridinemethylpalladium Chloride (16). This was obtained following the procedure for **14** from 2-[3-(diphenylphosphino)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) to yield the product as a white solid (131 mg, 0.28 mmol, 85%, mp 208 °C dec). Crystals suitable for X-ray diffraction were obtained by layering a CH_2Cl_2 solution of the product with Et_2O. ^{1}H NMR δ (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 δ (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-C*H*H), 2.93−2.90 (m, 1H, py-CH*H*), 2.16−2.09 (m, 1H, P-C*H*H), 2.00−1.85 (m, 1H, P-CH*H*), 1.80−1.73 (m, 1H, P-CH_2-C*H*H), 1.59−1.50 (m, 1H, P-CH_2-CH*H*), 0.67 (d, J = 3.0 Hz, 3H, CH_3). ^{1}H NMR δ (500 MHz, $Cl_2DCCDCl_2$, 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 δ (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-*C*H_2), 26.3 (d, J = 27.8 Hz, P-*C*H_2), 24.5 (s, P-CH_2−*C*H_2), −0.5 (d, J = 2.7 Hz, *C*H_3) *the signal for the Ph-C1 carbon atom was not observed.* ^{13}C{^{1}H} NMR δ (125 MHz, $Cl_2DCCDCl_2$, 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-*C*H_2), 26.2 (d, J = 27.4 Hz, P-*C*H_2), 24.1 (s, P-CH_2-*C*H_2), −1.2 (d, J = 3.4 Hz, *C*H_3). ^{31}P{^{1}H} NMR δ (121 MHz, $CDCl_3$, 25 °C) ppm: 23.1. Anal. Calcd for $C_{21}H_{23}ClNPPd$: 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 $C_{21}H_{23}NPPd$ $[M - Cl]^+$ 426.0612; found 426.0609.

2-[2-(Diphenylphosphino)phenyl]pyridinemethylpalladium Chloride (17). This was obtained following the procedure for **14** from 2-[2-(diphenylphosphino)phenyl]pyridine (**4**) (128 mg, 0.377 mmol, 1.0 equiv) and (COD)Pd(CH_3)Cl (100 mg, 0.377 mmol, 1.0 equiv) to yield the product as a white solid (170 mg, 0.343 mmol, 91%, mp 213 °C dec). ^{1}H NMR δ (500 MHz, $CDCl_3$) 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, CH_3). ^{13}C{^{1}H} NMR δ (125 MHz, $CDCl_3$) 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, C_q), 127.3 (d, J = 51.9 Hz, C_q), 125.5 (s, CH), 124.1 (s, CH), 1.2 (s, *C*H_3). ^{31}P{^{1}H} NMR δ (121 MHz, $CDCl_3$) ppm: 39.2. Anal. Calcd for $C_{24}H_{21}ClNPPd$: 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 $C_{24}H_{21}NPPd$ $[M - Cl]^+$ 460.0456; found 460.0458.

2-[(1*S*,2*S*,3*R*,4*S*)-3-(Diphenylphosphino)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]pyridinemethylpalladium Chloride (18). This was obtained following the procedure for **14** from 2-[(1*S*,2*R*,3*R*,4*S*)-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(CH_3)Cl (88 mg, 0.33 mmol, 1.0 equiv) to yield the product as a white solid (143 mg, 0.26 mmol, 77%, mp 181 °C dec). ^{1}H NMR δ (500 MHz, $CDCl_3$) ppm: 9.53 (dd, J = 5.6, 1.2 Hz, 1H, py-H6), 7.83−7.77 (m, 2H, Ph^a-H2), 7.76−7.68 (m, 3H, py-H4 + Ph^b-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 δ (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^a-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^b-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_q), 47.7 (d, J = 7.6

Hz, C_q), 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−*C*H_3). $^{31}P\{^1H\}$ NMR δ (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-[(Diphenylphosphino)methyl]pyridinemethylpalladium-(acetonitrile) Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (19). To a mixture of 2-[(diphenylphosphino)methyl]pyridinemethylpalladium chloride (**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_3CN (5 mL) and CH_2Cl_2 (25 mL), and the mixture was stirred for 16 h. It was cannula filtrated, evaporated to dryness, and coevaporated with 5 mL of pentane to yield the product as a white solid (529 mg, 0.406 mmol, 94%). ^1H NMR δ (500 MHz, CD_2Cl_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, NCCH_3), 0.72 (s, 3H, Pd-CH_3). $^{13}C\{^1H\}$ NMR δ (125 MHz, CD_2Cl_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′$_4$ 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, $J = 272.4$, *C*F_3), 124.9 (d, $J = 8.3$ Hz, CH), 124.6 (s, CH), 120.6 (s, N*C*CH_3), 118.1 (m, Ar′-C4), 43.5 (d, $J = 88.5$ Hz, *C*H_2), 3.4 (s, NC*C*H_3), −3.6 (s, Pd-*C*H_3). $^{31}P\{^1H\}$ NMR δ (121 MHz, CD_2Cl_2) ppm: 43.1. $^{19}F\{^1H\}$ NMR δ (282 MHz, CD_2Cl_2) ppm: −63.0. Anal. Calcd for $C_{53}H_{34}BF_{24}N_2PPd$: C, 48.85; H, 2.63; N, 2.15. Found: C, 49.08; H, 2.57; N, 2.20. HRMS (FAB) *m/z*: calcd for $C_{19}H_{19}NPPd$ $[M - BAr'_4 - CH_3CN]^+$ 398.0298; found 398.0299. MS (FD) *m/z*: 439 $[M - BAr'_4]^+$.

2-[2-(Diphenylphosphino)ethyl]pyridinemethylpalladium-(acetonitrile) Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (20). This was obtained following the procedure for **19** from 2-[2-(diphenylphosphino)ethyl]pyridinemethylpalladium chloride (**15**) (381 mg, 0.850 mmol, 1.0 equiv) and sodium tetrakis[(3,5-trifluoromethyl)phenyl]borate (753 mg, 0.850 mmol, 1.0 equiv) to yield the product as a white solid (1.11 g, 0.845 mmol, 99%). ^1H NMR δ (500 MHz, CD_2Cl_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, NCCH_3), 0.55 (d, $J = 2.0$ Hz, Pd-CH_3). $^{13}C\{^1H\}$ NMR δ (125 MHz, CD_2Cl_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, $J = 272.4$, *C*F_3), 120.0 (s, N*C*CH_3), 118.1 (m, Ar′-C4), 34.4 (d, $J = 3.4$ Hz, py-*C*H_2), 25.9, (d, $J = 32.9$ Hz, P-*C*H_2), 3.2 (s, NC*C*H_3), −0.1 (s, Pd-*C*H_3). $^{31}P\{^1H\}$ NMR δ (121 MHz, CD_2Cl_2) ppm: 39.3. $^{19}F\{^1H\}$ NMR δ (282 MHz, CD_2Cl_2) ppm: −63.0. Anal. Calcd for $C_{54}H_{36}BF_{24}N_2PPd$: 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 $C_{20}H_{21}NPPd$ $[M - BAr'_4 - CH_3CN]^+$ 412.0455; found 412.0454. MS (FD) *m/z*: 453 $[M - BAr'_4]^+$.

2-[3-(Diphenylphosphino)propyl]pyridinemethylpalladium-(acetonitrile) Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (21). This was obtained following the procedure for **19** from 2-[3-(diphenylphosphino)propyl]pyridinemethylpalladium chloride (**16**) (173 mg, 0.374 mmol, 1.0 equiv) and sodium tetrakis[(3,5-trifluoromethyl)phenyl]borate (332 mg, 0.374 mmol, 1.0 equiv) to yield the product as a white solid (481 mg, 0.363 mmol, 97%). ^1H NMR δ (500 MHz, CD_2Cl_2, 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-CH_2), 2.23 (s, 3H, NCCH_3), 2.1−1.6 (bs, 4H, P-CH_2-CH_2), 0.59 (d, $J = 2.2$ Hz, 3H, Pd-CH_3). ^1H NMR δ (500 MHz, CD_2Cl_2, −40 °C) ppm: 8.56 (d, $J = 4.9$ Hz, 1H, py-H6), 7.83−7.73 (m, 11H, py-H4 + Ph^a-H2 + Ar′-H2), 7.65−7.61 (m, 2H, Ph^b-H2), 7.60−7.54 (m, 6H, Ph^a-H3 + Ar′-H4), 7.51−7.46 (m, 2H, Ph-H4), 7.44−7.36 (m, 3H, py-H5 + Ph^b-H3), 7.32 (d, $J = 7.8$ Hz, 1H, py-H3), 3.70−3.61 (m, 1H, py-C*H*H), 3.01−2.96 (m, 1H, py-CH*H*), 2.23 (s, 3H, NCCH_3), 2.15−2.08 (m, 1H, P-C*H*H), 2.00−1.87 (m, 1H, P-CH$_2$-C*H*H), 1.76−1.68 (m, 1H, P-CH*H*) 1.51−1.43 (m, 1H, P-CH$_2$-CH*H*), 0.49 (d, $J = 1.9$ Hz, 3H, Pd-CH_3). ^1H NMR δ (500 MHz, $Cl_2DCCDCl_2$, 80 °C) ppm: 8.55 (d, $J = 5.1$ Hz, 1H, py-H6), 7.83 (dt, $J = 7.8$, 1.5 Hz, 1H, py-H4), 7.78−7.74 (m, 8H, Ar′-H2), 7.65−7.59 (m, 6H, Ph-H2 + -H4), 7.59−7.52 (m, 8H, Ph-H3 + Ar′-H4), 7.39−7.34 (m, 1H, py-H5), 7.34 (d, $J = 7.8$ Hz, 1H, py-H3), 3.48−3.42 (m, 2H, py-CH_2), 2.20 (s, 3H, NCCH_3), 1.97−1.92 (m, 2H, P-CH_2), 1.89−1.80 (m, 2H, P-CH$_2$-CH_2), 0.68 (d, $J = 2.0$ Hz, 3H, Pd-CH_3). $^{13}C\{^1H\}$ NMR δ (125 MHz, CD_2Cl_2, 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, $J = 272.4$, *C*F_3), 124.3 (s, CH), 119.6 (s, N*C*CH_3), 118.1 (m, Ar′-C4), 36.8 (d, $J = 8.0$ Hz, py-*C*H_2), 26.2 (d, $J = 31.2$ Hz, P-*C*H_2), 24.4 (s, P-CH$_2$-*C*H_2), 3.2 (s, NC*C*H_3), −0.4 (s, Pd-*C*H_3) *signals for some carbons could not be observed*. $^{13}C\{^1H\}$ NMR δ (125 MHz, CD_2Cl_2, −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, Ph^a-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*, Ph^b-C1), 124.4 (q, $J = 272.4$, *C*F_3), 123.7 (s, CH), 119.1 (d, $J = 12.7$ Hz, N*C*CH_3), 117.5 (m, Ar′-C4), 36.1 (d $J = 8.0$ Hz, py-*C*H_2), 25.0 (d, $J = 30.8$ Hz, P-*C*H_2), 23.7 (s, P-CH$_2$-*C*H_2), 3.3 (s, NC*C*H_3), −1.1 (d, $J = 3.2$ Hz, Pd-*C*H_3). $^{31}P\{^1H\}$ NMR δ (121 MHz, CD_2Cl_2, 25 °C) ppm: 25.3. $^{19}F\{^1H\}$ NMR δ (282 MHz, CD_2Cl_2, 25 °C) ppm: −63.0. Anal. Calcd for $C_{55}H_{38}BF_{24}N_2PPd$: C, 49.63; H, 2.88; N, 2.10. Found: C, 49.60; H, 2.84; N, 2.06. HRMS (FAB) *m/z*: calcd for $C_{21}H_{23}NPPd$ $[M - BAr'_4 - CH_3CN]^+$ 426.0612; found 426.0616. MS (FD) *m/z*: 467 $[M - BAr'_4]^+$.

2-[2-(Diphenylphosphino)phenyl]pyridinemethylpalladium-(acetonitrile) Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (22). This was obtained following the procedure for **19** from 2-[2-(diphenylphosphino)phenyl]pyridinemethylpalladium chloride (**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) to yield the product as a white solid (362 mg, 0.265 mmol, 80%). ^1H NMR δ (500 MHz, CD_2Cl_2) 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, NCCH_3), 0.63 (d, $J = 1.5$ Hz, 3H, Pd-CH_3). $^{13}C\{^1H\}$ NMR δ (125 MHz, CD_2Cl_2) 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, C_q), 125.4 (d, $J = 57.4$ Hz, C_q), 125.3 (s, CH), 125.2 (q, $J = 272.4$, *C*F_3), 119.9 (s, N*C*CH_3), 118.1 (m, Ar′-C4), 3.3 (s, Pd-*C*H_3), 2.0 (s, NC*C*H_3) *signals for two aromatic CH carbons could not be observed due*

to overlap with other signals. $^{31}P\{^1H\}$ NMR δ (121 MHz, CD_2Cl_2) ppm: 40.2. $^{19}F\{^1H\}$ NMR δ (282 MHz, CD_2Cl_2) ppm: −63.0. Anal. Calcd for $C_{58}H_{36}BF_{24}N_2PPd$: 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 $C_{24}H_{21}NPPd$ $[M - BAr'_4 - CH_3CN]^+$ 460.0456; found 460.0454. MS (FD) *m*/*z*: 501 $[M - BAr'_4]^+$.

2-[(1*S*,2*S*,3*R*,4*S*)-3-(Diphenylphosphino)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]pyridinemethylpalladium(acetonitrile) Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (23). This was obtained following the procedure for **19** from 2-[(1*S*,2*S*,3*R*,4*S*)-3-(diphenylphosphino)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]pyridinemethylpalladium chloride (**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) to yield the product as an off-white solid (325 mg, 0.288 mmol, 76%). ^1H NMR δ (500 MHz, CD_2Cl_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^a-H2 + Ar′-H2), 7.66−7.61 (m, Ph^b-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 + NCCH_3), 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). $^{13}C\{^1H\}$ NMR δ (125 MHz, CD_2Cl_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_q), 48.3 (d, J = 7.2 Hz, C_q), 47.1 (d, J = 5.5 Hz, CH), 46.6 (d, J = 25.3 Hz, C3), 33.1 (d, J = 8.9 Hz, CH_2), 28.4 (s, CH_2), 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). $^{31}P\{^1H\}$ NMR δ (121 MHz, CD_2Cl_2) ppm: 42.7. $^{19}F\{^1H\}$ NMR δ (282 MHz, CD_2Cl_2) ppm: −63.0. Anal. Calcd for $C_{62}H_{48}BF_{24}N_2PPd$: 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 $C_{28}H_{33}NPPd$ $[M - BAr'_4 - CH_3CN]^+$ 520.1397; found 520.1391. MS (FD) *m*/*z*: 520 $[M - BAr'_4 - CH_3CN]^+$.

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 three 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 of 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 three times and brought to 10 bar ethene pressure. After 10 min, 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. Ice cold 2 M hydrochloric acid (50 mL) was added to the reaction mixture, and it was stirred vigorously in an ice 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 three times and brought under 10 bar ethene pressure. After the run, the autoclave was vented and opened. Then 50 mL of ice cold 2 M hydrochloric acid was added to the reaction mixture, and it was stirred vigorously in an ice bath. A sample of the organic phase was cooled to −70 °C and evacuated three times to remove ethene before liquid-phase GC analysis was performed.

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Supporting Information Available: A CIF file giving crystal data for **10**, **12**, **15**, and **16** and a file giving the EPR spectrum of **10**, variable-temperature ^1H NMR spectra of **21**, and general experimental considerations. This material is available free of charge via the Internet at http://pubs.acs.org.

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