

# *cis*, *trans* – or Both: Steric Bulk Determines Coordination Mode of Dimeric Palladium Complexes with Bridging Pyridine-Phosphane Ligands

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The coordination mode in a metal complex is critically dependent on the ligands surrounding the metal, on the precursors used, and on the conditions during synthesis. Our goal was to obtain palladium compounds with pyridine-phosphane ligands for catalysis. Therefore, we synthesized ligands **1a–d**, which differ in the bulky aryl substituent at the pyridyl moiety. The palladium complexes **6a–d** of these ligands are insoluble and have been characterized by various techniques, including solid-state NMR and (for **6a**, **b**, and **d**) single-crystal X-ray diffraction, showing that bimetallic complexes are formed in which two ligands span two palladium centers. The configuration around these centers is determined by the steric bulk of the ligand. In complexes **6c,d**,

with the ligands bearing the largest steric groups, both centers have a *trans* configuration of the methyl and chloride anions. With intermediately sized pyridyl substituents, complex **6b** is formed, having one *cis* surrounded and one *trans*-surrounded palladium center in the molecule. This kind of complexation has not been observed before. With the least bulky ligand, complex **6a** is formed. Depending on the synthetic conditions employed, the methyl and the chloride in this complex can be in a *cis* configuration at both palladium atoms, or show the unique *cis-trans* coordination.

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## Introduction

The catalytic performance of palladium complexes is strongly dependent on the ligands coordinated to the metal. Properties such as activity and selectivity can be steered by electronic and steric factors of the ligand. The way in which a ligand coordinates is important as well. Subtle changes in coordination mode, like chelate bite angles, can have large effects on catalysis.<sup>[1]</sup> Likewise, a change of coordination geometry can induce a significant effect in catalysis; palladium complexes that contain chelating ligands in a *cis* configuration can show totally different behavior from that of *trans*-coordinated species. For example, the competition between alkoxy carbonylation or CO/ethene copolymerization activity of palladium catalysts seems to be dependent on the coordination modes of the ligand.<sup>[2]</sup>

Different donor atoms of a chelating ligand induce asymmetry and invoke different *trans*-influence and -effect on their responsive *trans*-ligands. By choosing these features of the ligating groups, selective binding and reactivity of coordinated substrates can be achieved. This is one of the reasons why P,N ligands (chelating ligands with one nitrogen and one phosphorus donor atom) are extensively studied in catalysis.<sup>[3,4]</sup> In our previous work concerning palladium complexes of these bidentates, we have studied the effects on carbonylation<sup>[5]</sup> and allylic alkylation.<sup>[6]</sup> In our current research, we were particularly interested in palladium complexes of pyridine-phosphane ligands.<sup>[4]</sup> Recent applications in catalysis of this class of complexes include ethene oligomerization and polymerization,<sup>[7]</sup> alkene/CO copolymerization,<sup>[8]</sup> allylic substitution,<sup>[9]</sup> carbonylation,<sup>[10]</sup> and Suzuki coupling.<sup>[11a]</sup>

Usually, the 1:1 complexes of pyridine-phosphane ligands with palladium are monometallic with a *cis* configuration around the metal, but *trans*-coordinated monometallic species<sup>[11]</sup> and bimetallic complexes in which two ligands span two palladium centers<sup>[11a,11c,12]</sup> have been reported. The latter type of coordination can be of particular interest for bimetallic catalysis. In this type of catalysis, ideally the two metal centers have a cooperative effect, thus enhancing activity and selectivity.<sup>[13]</sup> This phenomenon is the reason behind the extreme efficiency of many enzymatic systems<sup>[14]</sup> and its value has also been shown in chemical catalysis.<sup>[15]</sup>

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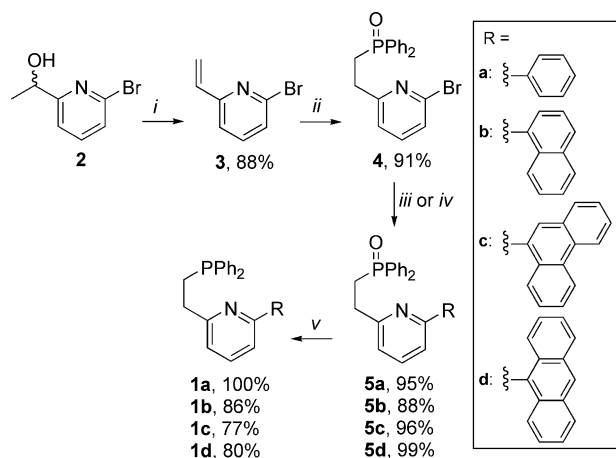
In this article, we present the synthesis and characterization of new pyridine-phosphane bidentate ligands (**1**) and their dimeric methylpalladium chloride complexes (**6**). The ligands differ in the bulky aryl substituents at the pyridine. Recently, Grubbs showed that the introduction of such groups on salicylaldiminato ligands improved their performance in nickel catalyzed ethene polymerization and also suppresses bis-ligation of the metal.<sup>[16]</sup>

The palladium complexes **6** of the ligands **1** appear as bimetallic compounds, in which two ligands span two metal centers. The complexes differ in the coordination mode around palladium (*cis* or *trans*), and this depends on the ligands used. By variation of the steric bulk at the ligand, all possible coordination geometries of the bimetallic complex can be obtained. Remarkably, both *cis* and *trans* coordination in one bimetallic complex is observed. A binuclear complex showing different coordination modes for the two metal centers that have the same ligand, has not been observed previously.

## Results and Discussion

### Ligand Synthesis

The 2-aryl-6-[2-(diphenylphosphanyl)ethyl]pyridine ligands of type **1** which we used in this study have different aryl substituents at C-2 of the pyridine ring, being phenyl (for **1a**), 1-naphthyl (for **1b**), 9-phenanthryl (for **1c**), or 9-anthracyl (for **1d**). They were synthesized as depicted in Scheme 1.



Scheme 1. Synthesis of ligands **1**. *i*: H<sub>2</sub>SO<sub>4</sub>, 90 °C, 90 h; *ii*: 1) HPPH<sub>2</sub>, KO<sup>t</sup>Bu, THF, 60 °C, 16 h; 2) NaClO<sub>4</sub>, room temp., 1 h; *iii* (for **a**, **b**, and **c**): RB(OH)<sub>2</sub>, Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, toluene, water, reflux, 16 h; *iv* (for **d**): RZnCl, Pd(PPh<sub>3</sub>)<sub>4</sub>, THF, 60 °C, 24 h; *v*: PhSiH<sub>3</sub>, reflux, 16 h.

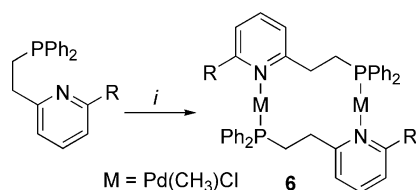
Dehydration of 2-bromo-6-(1-hydroxyethyl)pyridine (**2**)<sup>[17]</sup> yielded 2-bromo-6-vinylpyridine (**3**) in good yield after heating it in sulfuric acid for almost 4 d. When **3** was stored at room temperature for a few days, it decomposed to give a sticky substance, most likely due to polymerization of the compound. It is therefore best stored at low temperatures in the dark or used immediately. Alkene **3** was hydrophos-

phinated with diphenylphosphane using a catalytic amount of KO<sup>t</sup>Bu. Subsequent oxidation with household bleach gave 2-bromo-6-[2-(diphenylphosphino)ethyl]pyridine (**4**) in 91%. The oxidation of this compound was required because test reactions with the non-oxidized 2-bromo-6-[2-(diphenylphosphanyl)ethyl]pyridine did not show any conversion in the palladium-catalyzed cross-coupling. We assume a stable palladium complex is formed, with the phosphorus of the substrate coordinating to the metal. This coordination is prevented by oxidation of the phosphane and consequently the cross-coupling did proceed. This reaction between **4** and phenyl-, 1-naphthyl-, or 9-phenanthrylboronic acid yielded **5a**, **5b** and **5c** in good yields. Unfortunately, when this reaction was carried out with 9-anthracylboronic acid, product **5d** could not be obtained in pure form. Therefore, a Negishi–Takahashi coupling was tried between 9-anthracylzinc chloride and **4**. Using this method, pure **5d** was obtained in almost quantitative yield. Phosphinoyls **5** were reduced using phenylsilane to give ligands **1** in good to excellent yields. Under aerobic conditions in solution, they are oxidized back slowly to compounds **5**. In the solid state, however, they are stable in air. All new compounds were fully characterized.

### Complex Synthesis and Characterization

Palladium complexes were obtained by reaction of the ligands with (COD)Pd(CH<sub>3</sub>)Cl [COD = 1,5-cyclooctadiene], see Scheme 2. To our surprise, all compounds turned out to be insoluble. Solvents like chloroform, THF, acetone, DMSO and toluene were tried, but in none of them the complexes dissolved. We are unable to explain this phenomenon, but it has been observed before for palladium complexes with pyridine-phosphane ligands.<sup>[12a,12c]</sup> As a consequence of the insolubility, solution phase analysis could not be performed and the complexes were characterized by elemental analysis, high resolution mass spectrometry, solid-state NMR and, for **6a**, **6b**, and **6d**, single-crystal X-ray diffraction. As the products are insoluble, crystals of **6** suitable for X-ray diffraction had to be obtained directly from the synthesis. This was accomplished by layering a solution of (COD)Pd(CH<sub>3</sub>)Cl in dichloromethane in a small glass tube, with a solution of the appropriate ligand in a mixture of dichloromethane and ether. Because of diffusion, the reactants slowly mixed and crystals of the product formed at the interface of the two layers. When the mixing of the reactants was too fast (for example, when too concentrated solutions were used), only amorphous products formed.

The crystal structures of complexes **6a**, **6b**, and **6d** revealed dimeric species with two ligands spanning two palladium centers in a head-to-tail fashion forming a 12 membered ring, as shown in Figure 1. The structures are discussed in detail below. The high resolution mass spectra [fast atom bombardment (FAB) ionization] showed the peak for the [(ligand)<sub>2</sub>Pd<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>Cl]<sup>+</sup> ion for all complexes (loss of one chlorine atom is a consequence of the ioniza-



Scheme 2. Synthesis of complexes **6**. *i*: (COD)Pd(CH<sub>3</sub>)Cl, CH<sub>2</sub>Cl<sub>2</sub>, room temp., 16 h.

tion technique employed: the ionization of the complex by proton addition is immediately followed by loss of HCl). Thus, the dimeric nature of the complexes was also demonstrated for **6c**. Elemental analyses were in agreement with the proposed structures. The most striking difference between structures **6a** and **6b** and the structure of **6d** concerns the surrounding of the individual palladium centers. In compound **6d**, having the bulky anthracene substituent on the pyridyl units, both palladium centers have the methyl and chloride anions in mutual *trans* positions. In **6a** and **6b**, one of the two palladium centers exhibits the *cis* configuration (again, with respect to methyl and chloride), while the other center has these anions *trans* to one another.

This is a peculiar and unexpected finding, as the binding mode is usually determined by the ligands coordinating to the metal, the precursors used for the synthesis, and the reaction conditions employed. These are all identical in our case. To the best of our knowledge, these are the first reported examples of a homonuclear, bimetallic complex that has both *cis* and *trans* surrounded metal centers in one complex in which both centers coordinate to identical ligands. Known palladium complexes with the ligand 2-[2-(diphenylphosphanylmethyl)pyridine] (**1** with R = H) all exist as monomeric, *cis*-coordinated species.<sup>[10a,18]</sup> Bridging structures containing the related ligands *N*-[(diphenylphosphanylmethyl)-2-pyridinamine]<sup>[12b,12c]</sup> and *N*-[(diphenylphosphanylmethyl)-2-pyrimidinamine]<sup>[12d]</sup> are known, but in those cases both palladium centers show the *trans* configuration.

The solids were further characterized with <sup>31</sup>P direct polarization magic-angle spinning (DPMAS) NMR spectroscopy. Spectra are shown in Figure 2. The spectrum of **6d**, bearing the 9-anthracyl-substituted ligand, shows one signal at  $\delta = 23.8$  ppm, consistent with the presence of one unique phosphorus nucleus in the crystal structure. For **6b**, which has the 1-naphthyl substituent at the pyridyl-6 position, signals at  $\delta = 38.1$  and 21.1 ppm are observed. Again, this is in agreement with the X-ray crystal structure, which shows two inequivalent phosphanes. We attribute the former signal to the phosphorus *cis* to the pyridine, and the latter to the *trans*-coordinating phosphorus on basis of the chemical shift observed for *trans*-coordinated complex **6d**. The appearance of the *cis*-coordinating phosphorus signal at high ppm value compared to the *trans* signal has been observed for palladium complexes with bridging P,N ligands<sup>[19]</sup> and with chelating diphosphanes.<sup>[20]</sup> Complex **6c**, with the 9-phenanthryl group at the ligand, gives rise to one signal, at  $\delta = 26.9$  ppm. This is in the same region as the

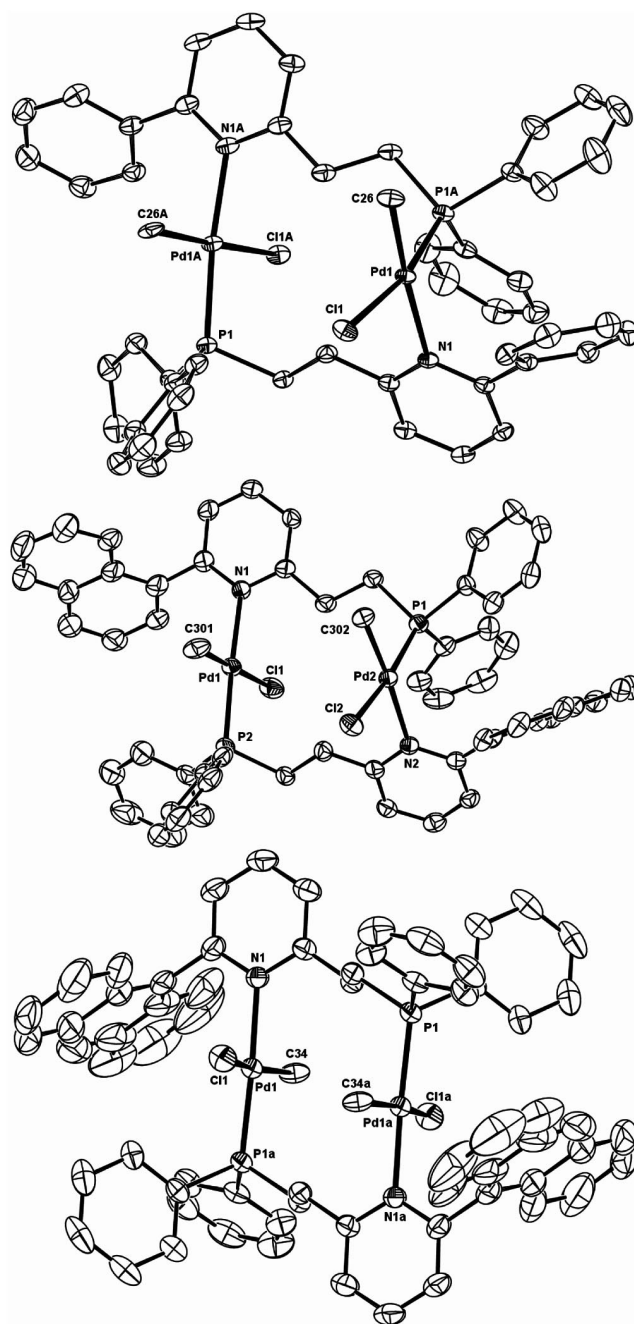


Figure 1. Displacement ellipsoid plots of **6a** (top), **6b** (middle), and **6d** (bottom) in the crystal, drawn at the 50% probability level. Hydrogen atoms and disordered solvent molecules are omitted for clarity. Symmetry operation *a* (compound **6d**):  $1 - x, 1 - y, 1 - z$ .

signal for **6d** and the *trans* signal for **6b**. On the basis of the NMR spectrum and the characterization mentioned above, we propose a structure for **6c** in which two ligands span two *trans*-coordinated Pd(CH<sub>3</sub>)Cl centers in a head-to-tail fashion, similar to the structure of **6d**. The spectrum of **6a** (having the phenyl-substituted ligand) shows one peak at  $\delta = 36.3$  ppm. This is in contrast to the X-ray crystal structure, in which two inequivalent phosphorus nuclei are present. Apparently, the conformation of the amorphous solid

formed from the reaction when stirring is employed is different from that of the single crystals formed after slow diffusion of the reactants. This again emphasizes that subtle changes can give rise to different coordination behavior in these complexes. The mass spectrum proved the dimeric nature of the complex prepared while stirring. We assign a structure to complex **6a** in which both palladium centers have the methyl and chloride anions in a *cis* configuration.

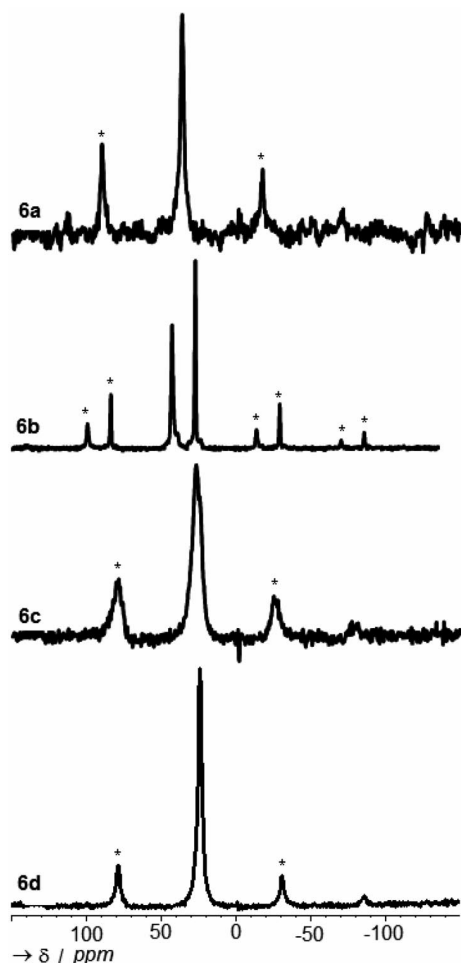


Figure 2. The  $^{31}\text{P}$  MAS solid-state NMR spectra of compound **6a–d**. The asterisk \* denotes spinning sidebands.

Thus, different geometric configurations around each of the palladium centers in the dimeric complex are possible. The influence of the substituent in position 2 of the pyridine ring of the ligand on the outcome is noteworthy. Starting from complex **4** (Scheme 1), different groups can be introduced. Clearly, the steric bulk of the substituent determines the coordination chemistry in the complex: depending on the ligand (and synthetic conditions) a *cis-cis*, *cis-trans*, or *trans-trans* bimetallic complex can be obtained. Therefore, dimeric species with identical or different (but homonuclear) metal centers can be obtained from bidentate ligands and the coordination mode can be varied by choice of the ligand substituent.

## X-ray Crystal Structures

The crystal structures of compounds **6a**, **6b**, and **6d** contain co-crystallized solvent molecules, which are severely disordered. In **6d** the solvent accessible voids are arranged in channels in the crystallographic *a,b*-plane, which occupy 31% of the unit cell volume (see Figure 3). Complexes **6a** and **6b** have no molecular symmetry, while **6d** is located on an inversion center. Details of the crystal structure determinations are summarized in the experimental section. Both metal centers in the crystal structure of **6a** have a slightly distorted square planar surrounding, but with opposite orientations of the ligands. Selected bond lengths and distances are shown in Table 1. The coordination environments of the two Pd centers are significantly different. This might be a consequence of different *trans*-effects of the ligands. Minor substitutional disorder between methyl and chloride fragments, which is rather common in such mixed ligand systems and influences the geometries, cannot be excluded either.<sup>[21]</sup> The intermetallic distance confirms the absence of Pd...Pd interactions. The structure of **6b** is similar to that of **6a**. Selected bond lengths and distances are summarized in Table 2. Both metal centers have a distorted square planar surrounding and the palladium atoms have a

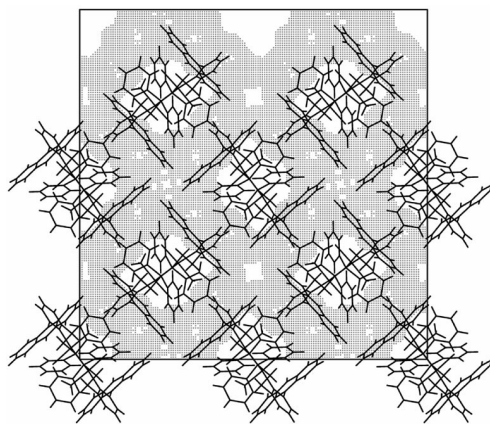


Figure 3. Packing of **6d** in the crystal. View along the crystallographic *c* axis. The Pd complex is shown as a black wire model. The solvent accessible voids are shown in gray. For the treatment of the disordered solvent see Exp. Section.

Table 1. Selected bond lengths [Å], angles [°], and dihedral angles [°] in complex **6a**.

|                                                   |            |                |            |
|---------------------------------------------------|------------|----------------|------------|
| Pd1–Cl1                                           | 2.4116(6)  | Pd1A–Cl1A      | 2.4248(6)  |
| Pd1–C26                                           | 2.058(2)   | Pd1A–C26A      | 2.097(2)   |
| Pd1–P1A                                           | 2.2137(6)  | Pd1A–P1        | 2.2320(6)  |
| Pd1–N1                                            | 2.1953(18) | Pd1A–N1A       | 2.1652(18) |
| Pd1...Pd1A                                        | 5.3353(3)  |                |            |
| Cl1–Pd1–C26                                       | 87.42(7)   | Cl1A–Pd1A–C26A | 176.10(7)  |
| Cl1–Pd1–P1A                                       | 167.52(2)  | Cl1A–Pd1A–P1   | 88.89(2)   |
| Cl1–Pd1–N1                                        | 92.88(5)   | Cl1A–Pd1A–N1A  | 90.42(5)   |
| P1A–Pd1–N1                                        | 95.19(5)   | P1–Pd1A–N1A    | 173.23(5)  |
| P1A–Pd1–C26                                       | 85.30(7)   | P1–Pd1A–C26A   | 93.38(6)   |
| N1–Pd1–C26                                        | 175.30(8)  | N1A–Pd1A–C26A  | 87.70(8)   |
| Pd1-coordination plane $\angle$ N1-pyridyl ring   | 82.76(8)°  |                |            |
| Pd1A-coordination plane $\angle$ N1A-pyridyl ring | 78.58(9)   |                |            |
| Pd1- $\angle$ Pd1A-coordination planes            | 8.67(6)°   |                |            |

nonbonding distance. In Table 3, selected bond lengths and distances are collected for **6d**. The structure of **6d** is centrosymmetric; consequently there is only one independent palladium center. The angles around palladium show a slight distortion from exact square-planar geometry. As a consequence of symmetry, the coordination planes around Pd1 and Pd1<sup>a</sup> are parallel.

Table 2. Selected bond lengths [Å], angles [°], and dihedral angles [°] in complex **6b**.

|                                          |           |              |            |
|------------------------------------------|-----------|--------------|------------|
| Pd1–Cl1                                  | 2.4451(8) | Pd2–Cl2      | 2.3945(8)  |
| Pd1–C301                                 | 2.055(3)  | Pd2–C302     | 2.050(3)   |
| Pd1–P2                                   | 2.2303(8) | Pd2–P1       | 2.2409(8)  |
| Pd1–N1                                   | 2.152(2)  | Pd2–N2       | 2.209(2)   |
| Pd1...Pd2                                | 5.1004(3) |              |            |
| Cl1–Pd1–C301                             | 178.85(9) | Cl2–Pd2–C302 | 86.65(9)   |
| Cl1–Pd1–P2                               | 87.41(3)  | Cl2–Pd2–P1   | 170.42(3)  |
| Cl1–Pd1–N1                               | 92.13(7)  | Cl2–Pd2–N2   | 91.31(6)   |
| P2–Pd1–N1                                | 177.05(7) | P1–Pd2–N2    | 98.26(6)   |
| P2–Pd1–C301                              | 93.34(9)  | P1–Pd2–C302  | 83.80(9)   |
| N1–Pd1–C301                              | 87.16(11) | N2–Pd2–C302  | 175.83(11) |
| Pd1-coordination plane ∠ N1-pyridyl ring |           |              | 76.38(12)  |
| Pd2-coordination plane ∠ N2-pyridyl ring |           |              | 75.53(11)  |
| Pd1- ∠ Pd2-coordination planes           |           |              | 2.63(7)    |

Table 3. Selected bond lengths [in Å], angles [in °], and dihedral angles [in °] in complex **6d**.<sup>[a]</sup>

|                                          |           |             |            |
|------------------------------------------|-----------|-------------|------------|
| Pd1–Cl1                                  | 2.4229(6) | Pd1–N1      | 2.1431(18) |
| Pd1–C34                                  | 2.084(2)  | Pd1...Pd1a  | 4.7131(2)  |
| Pd1–P1a                                  | 2.2273(6) |             |            |
| Cl1–Pd1–C34                              | 167.49(7) | P1a–Pd1–N1  | 172.01(5)  |
| Cl1–Pd1–P1a                              | 97.18(2)  | P1a–Pd1–C34 | 86.64(6)   |
| Cl1–Pd1–N1                               | 89.17(5)  | N1–Pd1–C34  | 88.16(8)   |
| Pd1-coordination plane ∠ N1-pyridyl ring |           |             | 88.33(9)   |

[a] Symmetry operation a: 1 – x, 1 – y, 1 – z.

## Conclusions

We have prepared new pyridine-phosphane bidentate ligands **1a–d**, having substituents with different, tunable steric bulk at C-2 of the pyridine ring. The insoluble methylpalladium chloride complexes **6** of these ligands are dimeric structures, in which two ligands span two palladium centers in a head-to-tail fashion forming a 12-membered ring. In **6c** and **6d**, bearing the largest substituents at the pyridyl unit, both palladium centers exhibit *trans* orientation of the chloride and methyl ligands. Complex **6b**, containing an intermediately sized pyridyl-substituent, consists of one *cis*- and one *trans*-surrounded metal center. Complex **6a**, containing the smallest pyridyl-substituent, can orient the anions at one palladium center *cis* and at the other *trans* (like in **6b**), or have both centers in *cis* configuration, depending on the conditions during synthesis. The unique and tunable coordination behavior of the ligands enables controlled interaction of the metal centers with bifunctional substrates which has great potential in the fields of catalysis and transition metal chemistry.

## Experimental Section

**General Information:** All reactions involving sensitive compounds were carried out under an atmosphere of purified dinitrogen using standard Schlenk techniques. Solvents were dried and distilled under dinitrogen; CH<sub>2</sub>Cl<sub>2</sub> from CaH<sub>2</sub>, toluene from sodium, Et<sub>2</sub>O and THF from sodium/benzophenone, and hexanes from sodium/benzophenone/triglyme. 2-Bromo-6-(1-hydroxyethyl)pyridine (**2**),<sup>[17]</sup> 9-phenanthrylboronic acid,<sup>[22]</sup> and (COD)Pd(CH<sub>3</sub>)Cl<sup>[23]</sup> were prepared according to literature procedures. Zincchloride was dried by refluxing in freshly distilled thionyl chloride for 16 h, removal of the solvent under reduced pressure and drying in vacuo for 24 h. Phenylsilane was distilled under dinitrogen. 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 Mikroanalytisches Laboratorium, Mülheim an der Ruhr (Germany). Electron ionization (EI) mass spectrometry (MS) was carried out on an Agilent Technologies 6890N/5973N GC-MS using an ionizing energy of 70 eV. Samples were dissolved in Et<sub>2</sub>O or CH<sub>2</sub>Cl<sub>2</sub>. Fast Atom Bombardment (FAB) high resolution mass spectrometry (HRMS) was 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. 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 3 keV. During the high resolution FAB-MS measurements a resolving power of 10000 (10% valley definition) was used. Solution phase NMR spectra were recorded on a Varian Mercury 300 operating at 300.1 (<sup>1</sup>H), 75.5 (<sup>13</sup>C), and 121.5 (<sup>31</sup>P) MHz or a Varian Inova 500 operating at 499.8 (<sup>1</sup>H) and 125.7 (<sup>13</sup>C) MHz at ambient temperature. Signals are referenced to TMS (<sup>1</sup>H and <sup>13</sup>C) or 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P) as external standards. The following abbreviations are used: py = pyridyl, naph = naphthyl, phen = phenanthryl, anth = anthracyl.

**Solid State NMR:** The <sup>31</sup>P direct polarisation magic-angle spinning solid-state nuclear magnetic resonance (<sup>31</sup>P-DPMAS SSNMR) spectra were recorded on a triple channel 500 MHz Varian Infinityplus spectrometer operating at a frequency of 202.460 MHz for <sup>31</sup>P. A 4 mm Chemagnetics T3 triple channel MAS probe was used at ambient temperature. The spectrum 6b Figure 2 was recorded on a Bruker 400 MHz Avance III operating at a frequency of 161.976 MHz for <sup>31</sup>P with a 4-mm triple-channel MAS probe. The rotors in were zirconium oxide fitted with vespel end caps. Spinning speeds were 12 kHz (MAS) with a 90° pulse length of 4 μs (Varian) and 3.5 (Bruker) and a 120 s recycle time in both cases. The number of transients varied between 24 and 400 and spectra were referenced to Brushite at δ = –1.6 ppm. The pulse program used is a standard direct-polarization sequence with a spectra width of 100 kHz.

**X-ray Crystal Structure Determinations:** Crystals of **6a**, **6b**, and **6d** suitable for X-ray diffraction were obtained by layering a solution of (COD)Pd(CH<sub>3</sub>)Cl (≈ 10 mg) in CH<sub>2</sub>Cl<sub>2</sub> (≈ 1 mL) in a small glass tube with a solution of the appropriate ligand (1.0 equiv.) in a 2:1 mixture of Et<sub>2</sub>O and CH<sub>2</sub>Cl<sub>2</sub> (≈ 2 mL). Reflections were measured on a Nonius Kappa CCD diffractometer with rotating anode (graphite monochromator, λ = 0.71073 Å) at a temperature of 150 K up to a resolution of (sin θ/λ)<sub>max</sub> = 0.65 Å<sup>–1</sup>. The structures were solved with Direct Methods (SHELXS-97<sup>[24]</sup>) and refined with SHELXL-97<sup>[24]</sup> against F<sup>2</sup> 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. Geometry calculations and checking for higher

Table 4. Details of the X-ray crystal structure determinations.

| Complex                                                                     | <b>6a</b>                                                                                                         | <b>6b</b>                                                                                                         | <b>6d</b>                                                                                                         |
|-----------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------|
| Formula                                                                     | C <sub>52</sub> H <sub>50</sub> Cl <sub>2</sub> N <sub>2</sub> P <sub>2</sub> Pd <sub>2</sub> ·disordered solvent | C <sub>60</sub> H <sub>54</sub> Cl <sub>2</sub> N <sub>2</sub> P <sub>2</sub> Pd <sub>2</sub> ·disordered solvent | C <sub>68</sub> H <sub>58</sub> Cl <sub>2</sub> N <sub>2</sub> P <sub>2</sub> Pd <sub>2</sub> ·disordered solvent |
| Fw                                                                          | 1048.58 <sup>[a]</sup>                                                                                            | 1148.69 <sup>[a]</sup>                                                                                            | 1248.80 <sup>[a]</sup>                                                                                            |
| Crystal colour                                                              | yellow                                                                                                            | yellowish                                                                                                         | yellow                                                                                                            |
| Crystal size [mm <sup>3</sup> ]                                             | 0.40 × 0.18 × 0.09                                                                                                | 0.42 × 0.24 × 0.06                                                                                                | 0.36 × 0.15 × 0.15                                                                                                |
| Crystal system                                                              | triclinic                                                                                                         | triclinic                                                                                                         | tetragonal                                                                                                        |
| Space group                                                                 | <i>P</i> $\bar{1}$ (no. 2)                                                                                        | <i>P</i> $\bar{1}$ (no. 2)                                                                                        | <i>I</i> <sub>4</sub> /a (no. 88)                                                                                 |
| <i>a</i> [Å]                                                                | 11.2408(3)                                                                                                        | 11.2735(2)                                                                                                        | 31.5532(1)                                                                                                        |
| <i>b</i> [Å]                                                                | 13.0342(4)                                                                                                        | 15.1764(2)                                                                                                        | 31.5532(1)                                                                                                        |
| <i>c</i> [Å]                                                                | 16.4293(3)                                                                                                        | 17.9279(3)                                                                                                        | 14.8255(1)                                                                                                        |
| $\alpha$ [°]                                                                | 83.947(1)                                                                                                         | 66.1520(7)                                                                                                        | 90                                                                                                                |
| $\beta$ [°]                                                                 | 77.022(2)                                                                                                         | 80.9984(8)                                                                                                        | 90                                                                                                                |
| $\gamma$ [°]                                                                | 80.589(2)                                                                                                         | 81.8334(8)                                                                                                        | 90                                                                                                                |
| <i>V</i> [Å <sup>3</sup> ]                                                  | 2308.16(10)                                                                                                       | 2760.31(8)                                                                                                        | 14760.33(12)                                                                                                      |
| <i>Z</i>                                                                    | 2                                                                                                                 | 2                                                                                                                 | 8                                                                                                                 |
| <i>D</i> <sub>x</sub> [g/cm <sup>3</sup> ]                                  | 1.509 <sup>[a]</sup>                                                                                              | 1.382 <sup>[a]</sup>                                                                                              | 1.124 <sup>[a]</sup>                                                                                              |
| $\mu$ [mm <sup>-1</sup> ]                                                   | 1.002 <sup>[a]</sup>                                                                                              | 0.845 <sup>[a]</sup>                                                                                              | 0.637 <sup>[a]</sup>                                                                                              |
| Absorption correction method                                                | multi-scan                                                                                                        | multi-scan                                                                                                        | multi-scan                                                                                                        |
| Absorption correction range                                                 | 0.55–0.92                                                                                                         | 0.76–0.95                                                                                                         | 0.81–0.91                                                                                                         |
| Reflections (measured/unique)                                               | 47280/10588                                                                                                       | 36936/12491                                                                                                       | 78094/8442                                                                                                        |
| Parameters/restraints                                                       | 543/0                                                                                                             | 615/0                                                                                                             | 344/0                                                                                                             |
| <i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )] | 0.0261/0.0598                                                                                                     | 0.0386/0.0851                                                                                                     | 0.0349/0.0934                                                                                                     |
| <i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> (all reflections)            | 0.0356/0.0624                                                                                                     | 0.0576/0.0930                                                                                                     | 0.0451/0.0974                                                                                                     |
| <i>S</i>                                                                    | 1.107                                                                                                             | 1.055                                                                                                             | 1.086                                                                                                             |
| $\rho_{\text{min/max}}$ [e/Å <sup>3</sup> ]                                 | –0.42/0.63                                                                                                        | –0.93/1.53                                                                                                        | –0.51/0.68                                                                                                        |

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

symmetry was performed with the PLATON program.<sup>[25]</sup> Further details are given in Table 4.

**6a:** The crystal structure contains voids (93 Å<sup>3</sup>/unit cell) filled with disordered solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of the program PLATON,<sup>[25]</sup> resulting in 31 electrons/unit cell. by back-Fourier transformation using the SQUEEZE routine of the program PLATON,<sup>[25]</sup> resulting in 93 electrons/unit cell.

**6d:** The crystal structure contains large voids (4647 Å<sup>3</sup>/unit cell) filled with disordered solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of the program PLATON,<sup>[25]</sup> resulting in 852 electrons/unit cell.

CCDC-689397 (for **6a**), -689398 (for **6b**), and -689399 (for **6d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**2-Bromo-6-vinylpyridine (3):** 2-Bromo-6-(1-hydroxyethyl)pyridine (**2**) (10.7 g, 52.8 mmol, 1 equiv.) was dissolved in sulfuric acid (50 mL, 938 mmol, 18 equiv.) and stirred at 90 °C using a CaCl<sub>2</sub> tube. After 90 h, the mixture was poured on ice, made basic with sodium carbonate and extracted with Et<sub>2</sub>O. The organic layer was washed with water (2×) and brine, dried with MgSO<sub>4</sub> and concentrated in vacuo to yield the product as a yellowish oil (8.52 g, 46.3 mmol, 88%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.47 (t, *J* = 7.7 Hz, 1 H, py-H4), 7.30 (dd, *J* = 7.9, 0.7 Hz, 1 H, py-H3), 7.24 (dd, *J* = 7.6, 0.7 Hz, 1 H, py-H5), 6.70 (dd, *J* = 17.4, 10.7 Hz, 1 H, vinyl-CH), 6.21 (dd, *J* = 17.4, 1.1 Hz, 1 H, vinyl-CHH), 5.49 (dd, *J* = 10.7, 1.1 Hz, 1 H, vinyl-CHH) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>): δ = 157.2 (py-C6), 142.2 (py-C2), 139.0, 135.6, 126.9, 120.2, 120.1 ppm. MS (EI): *m/z* (%) = 185 (88) [M (<sup>81</sup>Br)]<sup>+</sup>, 183 (91) [M (<sup>79</sup>Br)]<sup>+</sup>, 159 (15) [M (<sup>81</sup>Br) – C<sub>2</sub>H<sub>2</sub>]<sup>+</sup>, 157 (15) [M (<sup>79</sup>Br) – C<sub>2</sub>H<sub>2</sub>]<sup>+</sup>, 104 (100) [M – Br]<sup>+</sup>, 77 (13) [M – Br – (CH<sub>2</sub>CH)]<sup>+</sup>.

C<sub>7</sub>H<sub>6</sub>BrN (184.03): calcd. C 45.68, H 3.29, N 7.61; found C 45.63, H 3.22, N 7.49.

**Note:** When **3** was kept at room temperature for a few days, it decomposed to give a sticky substance, most likely due to polymerization of the compound. It is therefore best stored at low temperatures in the dark or used immediately.

**2-Bromo-2-[2-(diphenylphosphinoyl)ethyl]pyridine (4):** 2-Bromo-6-vinylpyridine (**3**) (2.27 g, 12.4 mmol, 1.0 equiv.) and diphenylphosphane (2.15 mL, 12.4 mmol, 1.0 equiv.) were dissolved in THF (60 mL). KOrBu (139 mg, 1.24 mmol, 0.1 equiv.) was added and the deep blue mixture was stirred at 60 °C for 20 h, after which it turned brown and <sup>31</sup>P NMR showed full conversion. Water (5 mL) was added and the mixture was concentrated in vacuo. The remainder was redissolved in CH<sub>2</sub>Cl<sub>2</sub> and 50 mL of household bleach (4 g active chlorine/100 mL) was added. The mixture was stirred vigorously for 1 h. Water was added, the aqueous phase was extracted twice with CH<sub>2</sub>Cl<sub>2</sub> and the combined organic phases were dried and concentrated to yield an off-white solid. This was purified by column chromatography (5% MeOH in CH<sub>2</sub>H<sub>2</sub> as the eluent) to yield the product as a white solid (4.32 g, 11.1 mmol, 91%); m.p. 160 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.80–7.70 (m, 4 H, *o*-H, Ph), 7.53–7.41 (m, 6 H, *m*- and *p*-H, Ph), 7.35 (t, *J* = 7.7 Hz, 1 H, py-H4), 7.24 (dd, *J* = 7.7, 0.6 Hz, 1 H, py-H3), 7.07 (dd, *J* = 7.7, 0.6 Hz, 1 H, py-H5), 3.15–3.05 (m, 2 H, PCH<sub>2</sub>CH<sub>2</sub>), 2.81–2.71 (m, 2 H, PCH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ = 161.9 (d, *J* = 13.3 Hz, py-C6), 141.8 (s, py-C2), 138.9 (s, CH), 132.8 (d, *J* = 98.9 Hz, *i*-C, Ph), 132.0 (s, CH), 131.0 (d, *J* = 9.4 Hz, CH), 128.8 (d, *J* = 11.6 Hz, CH), 126.0 (s, CH), 122.1 (s, CH), 29.6 (s, PCH<sub>2</sub>CH<sub>2</sub>), 29.1 (d, *J* = 71.4 Hz, PCH<sub>2</sub>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CDCl<sub>3</sub>): δ = 33.4 ppm. HRMS (FAB) *m/z* calcd. for C<sub>19</sub>H<sub>18</sub>BrNOP [M + H]<sup>+</sup>: 386.0309; found 386.0303. C<sub>19</sub>H<sub>17</sub>BrNOP (386.22): calcd. C 59.09, H 4.44, N 3.63; found C 59.15, H 4.48, N 3.55.

**2-[2-(Diphenylphosphinoyl)ethyl]-6-phenylpyridine (5a):** A mixture of 2-bromo-6-[2-(diphenylphosphinoyl)ethyl]pyridine (**4**) (1.50 g,

3.88 mmol, 1.0 equiv.), phenylboronic acid (710 mg, 5.83 mmol, 1.5 equiv.), Pd(PPh<sub>3</sub>)<sub>4</sub> (9.0 mg, 7.7 μmol, 0.002 equiv.), K<sub>2</sub>CO<sub>3</sub> (22.8 g, 165 mmol, 43 equiv.), water (20 mL) and toluene (40 mL) was refluxed for 16 h. EtOAc was added, and the organic phase was washed with water (3 times) and brine, dried, and concentrated in vacuo. The product was purified using column chromatography (eluent: 5% MeOH in CH<sub>2</sub>Cl<sub>2</sub>) to yield the product as an off-white solid (1.41 g, 3.67 mmol, 95%); m.p. 145 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 8.01–7.98 [m, 2 H, *o*-H, Ph(py)], 7.82–7.77 [m, 4 H, *o*-H, Ph(P)], 7.60 (t, *J* = 7.7 Hz, 1 H, py-H4), 7.52 (d, *J* = 7.7 Hz, 1 H, py-H5), 7.51–7.40 [m, 9 H, *o*- + *p*-H, Ph(P) + *o*- + *p*-H, Ph(py)], 7.07 (d, *J* = 7.7 Hz, 1 H, py-H3), 3.25–3.18 (m, 2 H, PCH<sub>2</sub>CH<sub>2</sub>), 2.95–2.89 ppm (m, 2 H, PCH<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ = 160.0 (d, *J* = 13.9 Hz, py-C2), 156.8 (s, py-C6), 139.5 [s, *i*-C, Ph(py)], 137.3 (s, CH), 133.2 [d, *J* = 98.3 Hz, *i*-C, Ph(P)], 131.8 (d, *J* = 2.7 Hz, CH), 131.0 (d, *J* = 9.3 Hz, CH), 129.1 (s, CH), 128.8 (s, CH), 128.7 (s, CH), 127.1 (s, CH), 121.5 (s, CH), 118.3 (s, CH), 30.0 (d, *J* = 2.5 Hz, PCH<sub>2</sub>CH<sub>2</sub>), 29.2 ppm (d, *J* = 71.7 Hz, PCH<sub>2</sub>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CDCl<sub>3</sub>): δ = 33.1 ppm. HRMS (FAB): *m/z* calcd. for C<sub>25</sub>H<sub>23</sub>NOP [M + H]<sup>+</sup>: 384.1517; found 384.1512. C<sub>25</sub>H<sub>23</sub>NOP (383.42): calcd. C 78.31, H 5.78, N 3.65; found C 78.24, H 5.79, N 3.57.

**2-[2-(Diphenylphosphinoyl)ethyl]-6-(1-naphthyl)pyridine (5b):** A mixture of 2-bromo-6-[2-(diphenylphosphinoyl)ethyl]pyridine (**4**) (2.51 g, 6.49 mmol, 1.0 equiv.), 1-naphthylboronic acid (1.68 mg, 9.74 mmol, 1.5 equiv.), Pd(PPh<sub>3</sub>)<sub>4</sub> (15 mg, 13 μmol, 0.002 equiv.), K<sub>2</sub>CO<sub>3</sub> (38.1 g, 276 mmol, 43 equiv.), water (30 mL) and toluene (60 mL) was refluxed for 16 h. EtOAc was added, and the organic phase was washed with water (3 times) and brine, dried and concentrated in vacuo. The product was purified by column chromatography (eluent: 5% MeOH in CH<sub>2</sub>Cl<sub>2</sub>) to yield the product as a white solid (2.46 mg, 5.69 mmol, 88%); m.p. 153 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 8.07 (d, *J* = 8.4 Hz, 1 H, naph-H4), 7.92–7.89 (m, 2 H, naph-H6 + -H7), 7.80–7.73 (m, 4 H, *o*-H, Ph), 7.66 (t, *J* = 7.7 Hz, 1 H, py-H4), 7.59–7.53 (m, 2 H, naph-H8 + -H5), 7.52–7.45 (m, 4 H, *p*-H, Ph + naph-H2 + -H3), 7.44–7.39 (m, 4 H, *m*-H, Ph), 7.37 (d, *J* = 7.7 Hz, 1 H, py-H5), 7.19 (d, *J* = 7.7 Hz, 1 H, py-H3), 3.30–3.18 (m, 2 H, PCH<sub>2</sub>CH<sub>2</sub>), 2.93–2.82 (m, 2 H, PCH<sub>2</sub>) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 160.0 (d, *J* = 13.9 Hz, py-C2), 158.7 (s, py-C6), 137.0 (s, C<sub>q</sub>), 138.5 (s, C<sub>q</sub>), 134.1 (s, C<sub>q</sub>), 133.0 (d, *J* = 98.5 Hz, *i*-C, Ph), 131.8 (d, *J* = 2.7 Hz, CH), 131.3 (s, C<sub>q</sub>), 131.0 (d, *J* = 9.3 Hz, CH), 129.0 (s, CH), 128.8 (d, *J* = 11.6 Hz, CH), 128.5 (s, CH), 127.7 (s, CH), 126.4 (s, CH), 126.0 (s, CH), 125.9 (s, CH), 125.5 (s, CH), 123.0 (s, CH), 121.5 (s, CH), 30.0 (d, *J* = 1.9 Hz, PCH<sub>2</sub>CH<sub>2</sub>), 29.3 (d, *J* = 71.5 Hz, PCH<sub>2</sub>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CDCl<sub>3</sub>): δ = 32.9 ppm. HRMS (FAB): *m/z* calcd. for C<sub>29</sub>H<sub>25</sub>NOP [M + H]<sup>+</sup>: 434.1674; found 434.1673. C<sub>29</sub>H<sub>25</sub>NOP (433.48): calcd. C 80.35, H 5.58, N 3.23; found C 80.23, H 5.62, N 3.28.

**2-[2-(Diphenylphosphinoyl)ethyl]-6-(9-phenanthryl)pyridine (5c):** A mixture of 2-bromo-6-[2-(diphenylphosphinoyl)ethyl]pyridine (**4**) (1.36 g, 3.52 mmol, 1.0 equiv.), 9-phenanthrylboronic acid (1.17 g, 5.27 mmol, 1.5 equiv.), Pd(PPh<sub>3</sub>)<sub>4</sub> (8 mg, 10 μmol, 0.002 equiv.), K<sub>2</sub>CO<sub>3</sub> (20.6 g, 149 mmol, 43 equiv.), water (20 mL) and toluene (40 mL) was refluxed for 16 h. Then EtOAc was added, and the organic phase was washed with water (4 times) and brine, dried and concentrated in vacuo. The product was purified by column chromatography (5% MeOH/CH<sub>2</sub>Cl<sub>2</sub>) to yield the product as a white solid (1.64 g, 3.39 mmol, 96%); m.p. 178 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 8.76 (d, *J* = 8.3 Hz, 1 H, phen-H4), 8.71 (d, *J* = 8.3 Hz, 1 H, phen-H5), 8.07 (d, *J* = 8.2 Hz, 1 H, phen-H8), 7.92 (d, *J* = 7.5 Hz, 1 H, phen-H1), 7.81 (s, 1 H, phen-H10), 7.79–7.74 (m, 4 H, *o*-H, Ph), 7.69–7.65 (m, 3 H, py-H4 + phen-H3 +

-H6), 7.63–7.59 (m, 1 H, phen-H2), 7.56–7.52 (m, 1 H, phen-H7), 7.48–7.44 (m, 2 H, *p*-H, Ph), 7.43–7.38 (m, 5 H, py-H5 + *m*-H, Ph), 7.21 (d, *J* = 7.7 Hz, 1 H, py-H3), 3.32–3.21 (m, 2 H, PCH<sub>2</sub>CH<sub>2</sub>), 2.95–2.83 ppm (m, 2 H, PCH<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ = 160.0 (d, *J* = 13.9 Hz, py-C2), 158.9 (s, py-C6), 137.3 (s, C<sub>q</sub>), 137.0 (s, CH), 133.0 (d, *J* = 98.4 Hz, *i*-C, Ph), 131.8 (d, *J* = 2.7 Hz, CH), 131.4 (s, C<sub>q</sub>), 130.9 (d, *J* = 9.3 Hz, CH), 130.9 (s, C<sub>q</sub>), 130.5 (s, C<sub>q</sub>), 130.4 (s, C<sub>q</sub>), 129.0 (s, CH), 128.7 (d, *J* = 11.6 Hz, CH), 128.5 (s, CH), 127.1 (s, CH), 126.9 (s, CH), 126.8 (s, CH), 126.7 (s, CH), 126.6 (s, CH), 123.0 (s, CH), 122.9 (s, CH), 122.6 (s, CH), 121.5 (s, CH), 30.0 (d, *J* = 2.6 Hz, PCH<sub>2</sub>CH<sub>2</sub>), 29.2 ppm (d, *J* = 71.5 Hz, PCH<sub>2</sub>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CDCl<sub>3</sub>): δ = 33.4 ppm. HRMS (FAB): *m/z* calcd. for C<sub>33</sub>H<sub>27</sub>NOP [M + H]<sup>+</sup>: 484.1830; found 484.1841. C<sub>33</sub>H<sub>26</sub>NOP (483.54): calcd. C 81.97, H 5.42, N 2.90; found C 81.90, H 5.37, N 2.79.

**2-(9-Anthracyl)-6-[2-(diphenylphosphinoyl)ethyl]pyridine (5d):** To a solution of 9-bromoanthracene (3.21 g, 12.5 mmol, 5.0 equiv.) in THF (20 mL) was slowly dropped a 2.5 M solution of *n*-butyllithium (5.0 mL, 12.5 mmol, 5.0 equiv.) in hexanes at –78 °C. The mixture was stirred at that temperature for 30 min, after which a solution of ZnCl<sub>2</sub> (1.70 g, 12.5 mmol, 5.0 equiv.) in THF (15 mL) was added. The mixture was stirred for 1 h at room temperature, after which a solution of Pd(PPh<sub>3</sub>)<sub>4</sub> (144 mg, 0.125 mmol, 5%) in THF (5 mL) was added. The mixture was cooled to 0 °C, a solution of 2-bromo-6-[2-(diphenylphosphinoyl)ethyl]pyridine (**4**) (966 mg, 2.50 mmol, 1.0 equiv.) in THF (40 mL) was added and the mixture was stirred at 60 °C for 24 h. After that, water was added, the mixture was concentrated in vacuo and EtOAc was added. The organic layer was washed with water, a solution of potassium oxalate (4.00 g, 22.0 mmol) in water, water again, and finally brine, then dried and concentrated in vacuo. Column chromatography (eluent: CH<sub>2</sub>Cl<sub>2</sub> to 5% MeOH in CH<sub>2</sub>Cl<sub>2</sub>) yielded the product as a yellow solid (1.19 g, 2.46 mmol, 99%); m.p. 188 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 8.51 (s, 1 H, anth-H10), 8.03 (d, *J* = 8.4 Hz, 2 H, anth-H1), 7.77–7.71 (m, 4 H, *o*-H, Ph), 7.55 (d, *J* = 8.8 Hz, 2 H, anth-H4), 7.48–7.43 (m, 5 H, py-H4 + *p*-H, Ph + anth-H2), 7.42–7.38 (m, 4 H, *m*-H, Ph), 7.37–7.29 (m, 4 H, py-H3 + -H5 + anth-H3), 3.34–3.26 (m, 2 H, PCH<sub>2</sub>CH<sub>2</sub>), 2.87–2.80 ppm (m, 2 H, PCH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ = 160.7 (d, *J* = 13.7 Hz, py-C6), 157.8 (s, py-C2), 136.8 (s, CH), 135.4 (s, C<sub>q</sub>), 133.0 (d, *J* = 98.5 Hz, *i*-C, Ph), 131.8 (d, *J* = 2.5 Hz, CH), 131.6 (s, C<sub>q</sub>), 131.0 (d, *J* = 9.3 Hz, CH), 130.2 (s, C<sub>q</sub>), 128.8 (d, *J* = 11.6 Hz, CH), 128.6 (s, CH), 127.7 (s, CH), 126.3 (s, CH), 125.9 (s, CH), 125.3 (s, CH), 124.8 (s, CH), 121.7 (s, CH), 30.1 (s, PCH<sub>2</sub>CH<sub>2</sub>), 29.4 ppm (d, *J* = 71.4 Hz, PCH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CDCl<sub>3</sub>): δ = 33.4 ppm. HRMS (FAB): *m/z* calcd. for C<sub>33</sub>H<sub>27</sub>NOP [M + H]<sup>+</sup>: 484.1830; found 484.1843; C<sub>33</sub>H<sub>26</sub>NOP (483.54): calcd. C 81.97, H 5.42, N 2.90; found C 81.85, H 5.47, N 2.82.

**2-[2-(Diphenylphosphinoyl)ethyl]-6-phenylpyridine (1a):** 2-[2-(Diphenylphosphinoyl)ethyl]-6-phenylpyridine (**5a**) (1.00 g, 2.61 mmol, 1.0 equiv.) was dissolved in phenylsilane (5.0 mL, 40 mmol, 15 equiv.) and the mixture was refluxed overnight, after which <sup>31</sup>P 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 with Et<sub>2</sub>O as the eluent and a second column with CH<sub>2</sub>Cl<sub>2</sub> as the eluent to yield the product as a white solid (960 mg, 2.61 mmol, 100%); m.p. 94 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 8.04 [dd, *J* = 8.6, 1.4 Hz, 2 H, *o*-H, Ph(py)], 7.64 (t, *J* = 7.7 Hz, 1 H, py-H4), 7.56 (d, *J* = 7.7 Hz, 1 H, py-H5), 7.54–7.47 [m, 6 H, *o*-H, Ph(P) + *m*-H, Ph(py)], 7.45–7.41 [m, 1 H, *p*-H, Ph(py)], 7.39–7.33 [m, 6 H, *m*- + *p*-H, Ph(P)], 7.07 (d, *J* = 7.7 Hz, 1 H, py-H3), 2.99–3.06 (m, 2 H, CH<sub>2</sub>CH<sub>2</sub>), 2.66–2.61 ppm (m, 2 H, PCH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ =

161.9 (d,  $J = 13.1$  Hz, py-C2), 157.0 (s, py-C6), 140.1 [s, *i*-C, Ph(py)], 139.5 [d,  $J = 14.7$  Hz, *i*-C, Ph(P)], 136.9 (s, CH), 133.2 (d,  $J = 18.7$  Hz, CH), 129.0 (s, CH), 128.8 (d,  $J = 17.4$  Hz, CH), 128.7 (d,  $J = 12.4$  Hz, CH), 128.4 (s, CH), 127.4 (s, CH), 121.1 (s, CH), 117.7 (s, CH), 35.2 (d,  $J = 17.9$  Hz, PCH<sub>2</sub>CH<sub>2</sub>), 28.5 ppm (d,  $J = 13.3$  Hz, PCH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CDCl<sub>3</sub>):  $\delta = -14.3$  ppm. MS (EI):  $m/z$  (%) = 367 (6) [M]<sup>+</sup>, 290 (100) [M – Ph]<sup>+</sup>, 182 (18) [M – PPh<sub>2</sub>]<sup>+</sup>. C<sub>25</sub>H<sub>22</sub>NP (367.42): calcd. C 81.72, H 6.04, N 3.81; found C 81.63, H 5.96, N 3.72.

**2-[2-(Diphenylphosphanyl)ethyl]-6-(1-naphthyl)pyridine (1b):** 2-[2-(Diphenylphosphinoyl)ethyl]-6-(1-naphthyl)pyridine (**5b**) (1.06 g, 2.45 mmol, 1.0 equiv.) was dissolved in phenylsilane (12 mL, 97 mmol, 40 equiv.) and the mixture was refluxed overnight, after which <sup>31</sup>P NMR showed full conversion. The mixture was concentrated in vacuo and purified by column chromatography using CH<sub>2</sub>Cl<sub>2</sub> as the eluent. Co-evaporation with hexanes yielded the product as a white solid (875 mg, 2.10 mmol, 86%); m.p. 64 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 8.13$  (d,  $J = 8.4$  Hz, 1 H, naph-H4), 7.90 (d,  $J = 8.2$  Hz, naph-H6 + -H7), 7.70 (t,  $J = 7.7$  Hz, 1 H, py-H4), 7.59 (d,  $J = 6.4$  Hz, 1 H, naph-H2), 7.56–7.52 (m, 1 H, naph-H5), 7.50–7.45 (m, 5 H, *o*-H, Ph + naph-H8), 7.44–7.40 (m, 1 H, naph-H3), 7.38 (d,  $J = 7.7$  Hz, 1 H, py-H5), 7.35–7.30 (m, 6 H, *m*- + *p*-H, Ph), 7.15 (d,  $J = 7.7$  Hz, 1 H, py-H3), 3.08–3.00 (m, 2 H, PCH<sub>2</sub>CH<sub>2</sub>), 2.65–2.59 ppm (m, 2 H, PCH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta = 161.7$  (d,  $J = 12.5$  Hz, py-C2), 159.0 (s, py-C6), 138.9 (s, C<sub>q</sub>), 138.7 (d,  $J = 13.1$  Hz, *i*-C, Ph), 136.9 (s, CH), 134.2 (s, C<sub>q</sub>), 133.0 (d,  $J = 18.5$  Hz, CH), 131.5 (s, C<sub>q</sub>), 129.0 (s, CH), 128.8 (s, CH), 128.6 (d,  $J = 6.6$  Hz, CH), 128.5 (s, CH), 127.7 (s, CH), 126.5 (s, CH), 126.1 (s, CH), 126.0 (s, CH), 125.5 (s, CH), 122.7 (s, CH), 121.1 (s, CH), 34.9 (d,  $J = 17.5$  Hz, PCH<sub>2</sub>CH<sub>2</sub>), 28.3 (d,  $J = 12.6$  Hz, PCH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CDCl<sub>3</sub>):  $\delta = -14.7$  ppm. MS (EI):  $m/z$  (%) = 417 (6) [M]<sup>+</sup>, 340 (100) [M – Ph]<sup>+</sup>, 232 (13) [M – PPh<sub>2</sub>]<sup>+</sup>. C<sub>29</sub>H<sub>24</sub>NP (417.48): calcd. C 83.43, H 5.79, N 3.36; found C 83.56, H 5.83, N 3.28.

**2-[2-(Diphenylphosphanyl)ethyl]-6-(9-phenanthryl)pyridine (1c):** 2-[2-(Diphenylphosphinoyl)ethyl]-6-(9-phenanthryl)pyridine (**5c**) (500 mg, 1.03 mmol, 1.0 equiv.) was dissolved in phenylsilane (5.0 mL, 40 mmol, 39 equiv.) and the mixture was refluxed overnight, after which <sup>31</sup>P 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 with Et<sub>2</sub>O as the eluent and a second column with CH<sub>2</sub>Cl<sub>2</sub> as the eluent to yield the product as a white solid (371 mg, 0.79 mmol, 77%); m.p. 74 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 8.77$  (d,  $J = 8.3$  Hz, 1 H, phen-H4), 8.72 (d,  $J = 8.3$  Hz, 1 H, phen-H5), 8.10 (d,  $J = 8.1$  Hz, 1 H, naph-H8), 7.92 (d,  $J = 7.8$  Hz, 1 H, naph-H1), 7.84 (s, 1 H, naph-H10), 7.73 (t,  $J = 7.6$  Hz, 1 H, py-H4), 7.69–7.64 (m, 2 H, naph-H3 + -H6), 7.63–7.59 (m, 1 H, naph-H2), 7.53–7.50 (m, 1 H, naph-H7), 7.50–7.45 (m, 4 H, *o*-H, Ph), 7.44 (d,  $J = 7.6$  Hz, 1 H, py-H5), 7.35–7.30 (m, 6 H, *m*- + *p*-H, Ph), 7.19 (d,  $J = 7.6$  Hz, 1 H, py-H3), 3.09–3.02 (m, 2 H, PCH<sub>2</sub>CH<sub>2</sub>), 2.66–2.60 ppm (m, 2 H, PCH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta = 161.7$  (d,  $J = 6.3$  Hz, py-C2), 159.1 (s, py-C6), 138.7 (d,  $J = 13.0$  Hz, *i*-C, Ph), 137.6 (s, C<sub>q</sub>), 137.0 (s, CH), 133.1 (s, CH), 133.0 (s, CH), 131.6 (s, C<sub>q</sub>), 131.1 (s, C<sub>q</sub>), 130.7 (s, C<sub>q</sub>), 130.6 (s, C<sub>q</sub>), 129.2 (s, CH), 128.8 (s, CH), 128.6 (d,  $J = 6.5$  Hz, CH), 128.5 (s, CH), 127.5 (s, CH), 127.0 (s, CH), 126.9 (s, CH), 126.7 (d,  $J = 4.1$  Hz, CH), 123.1 (s, CH), 122.8 (s, CH), 122.7 (s, CH), 121.3 (s, CH), 34.9 (d,  $J = 17.5$  Hz, PCH<sub>2</sub>CH<sub>2</sub>), 28.3 ppm (d,  $J = 12.6$  Hz, PCH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CDCl<sub>3</sub>):  $\delta = -14.8$  ppm. MS (EI):  $m/z$  (%) = 467 (9) [M]<sup>+</sup>, 390 (100) [M – Ph]<sup>+</sup>, 280 (14) [M – PPh<sub>2</sub>]<sup>+</sup>. C<sub>33</sub>H<sub>26</sub>NP (467.54): calcd. C 84.77, H 5.61, N 3.00; found C 84.70, H 5.68, N 2.94.

**6-(9-Anthracyl)-2-[2-(diphenylphosphanyl)ethyl]pyridine (1d):** 6-(9-Anthracyl)-2-[2-(diphenylphosphinoyl)ethyl]pyridine (**5d**) (853 mg, 1.76 mmol, 1.0 equiv.) was dissolved in phenylsilane (10 mL, 81 mmol, 46 equiv.) and the mixture was refluxed overnight, after which <sup>31</sup>P NMR showed full conversion. The mixture was concentrated in vacuo and purified by column chromatography using CH<sub>2</sub>Cl<sub>2</sub> as the eluent. Co-evaporation with hexanes yielded the product as a yellow solid (656 mg, 1.40 mmol, 80%); m.p. 145 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 8.52$  (s, 1 H, anth-H10), 8.04 (d,  $J = 8.5$  Hz, 2 H, anth-H1), 7.79 (t,  $J = 7.7$  Hz, 1 H, py-H4), 7.62 (d,  $J = 8.8$  Hz, 2 H, anth-H4), 7.48–7.42 (m, 6 H, *o*-H, Ph + anth-H2), 7.34 (d,  $J = 7.7$  Hz, 1 H, py-H3), 7.34–7.30 (m, 8 H, *m*- + *p*-H, Ph + anth-H3), 7.27 (d,  $J = 7.7$  Hz, 1 H, py-H5), 3.10–3.04 (m, 2 H, PCH<sub>2</sub>CH<sub>2</sub>), 2.62–2.58 ppm (m, 2 H, PCH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta = 162.3$  (d,  $J = 12.1$  Hz, py-C6), 157.9 (s, py-C2), 138.6 (d,  $J = 13.1$  Hz, *i*-C, Ph), 136.7 (s, CH), 135.5 (s, anth-C9), 133.0 (d,  $J = 18.5$  Hz, CH), 131.7 (s, C<sub>q</sub>), 130.3 (s, C<sub>q</sub>), 128.7 (d,  $J = 12.0$  Hz, CH), 128.6 (s, CH), 127.7 (s, CH), 126.4 (s, CH), 125.9 (s, CH), 125.3 (s, CH), 124.6 (s, CH), 121.5 (s, CH), 34.9 (d,  $J = 17.8$  Hz, PCH<sub>2</sub>CH<sub>2</sub>), 28.6 ppm (d,  $J = 12.6$  Hz, PCH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CDCl<sub>3</sub>):  $\delta = -14.8$  ppm. MS (EI):  $m/z$  (%) = 467 (10) [M]<sup>+</sup>, 390 (100) [M – Ph]<sup>+</sup>, 280 (25) [M – PPh<sub>2</sub>]<sup>+</sup>. C<sub>33</sub>H<sub>26</sub>NP (467.54): calcd. C 84.77, H 5.61, N 3.00; found C 84.68, H 5.65, N 2.93.

**Dichloro-μ-{2-[2-(diphenylphosphanyl-1κP)ethyl]-6-phenylpyridine-2κN}-μ-{2-[2-(diphenylphosphanyl-2κP)ethyl]-6-phenylpyridine-1κN}(dimethyl)dipalladium (6a):** 2-[2-(Diphenylphosphanyl)ethyl]-6-phenylpyridine (**1a**) (141 mg, 0.38 mmol, 1.0 equiv.) and (COD)Pd(CH<sub>3</sub>)Cl (102 mg, 0.38 mmol, 1.0 equiv.) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and the mixture was stirred for 16 h. Then, it was filtered and washed with CH<sub>2</sub>Cl<sub>2</sub> and Et<sub>2</sub>O. Drying in vacuo yielded the product as an off-white solid (131 mg, 0.25 mmol, 65%). <sup>31</sup>P-DPMAS NMR:  $\delta = 36.3$  ppm. HRMS (FAB):  $m/z$  calcd. for C<sub>52</sub>H<sub>50</sub>Cl<sub>2</sub>N<sub>2</sub>P<sub>2</sub>Pd<sub>2</sub> [M – Cl]<sup>+</sup>: 1013.1228; found 1013.1238. C<sub>52</sub>H<sub>50</sub>Cl<sub>2</sub>N<sub>2</sub>P<sub>2</sub>Pd<sub>2</sub> (1048.66): calcd. C 59.56, H 4.81, N 2.67; found C 59.65, H 4.77, N 2.56.

**Dipalladium Complex 6b:** 2-[2-(Diphenylphosphanyl)ethyl]-6-(1-naphthyl)pyridine (**1b**) (148 mg, 0.355 mmol, 1.0 equiv.) and (COD)Pd(CH<sub>3</sub>)Cl (94 mg, 0.355 mmol, 1.0 equiv.) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and the mixture was stirred for 16 h. Then, it was filtered off and washed with CH<sub>2</sub>Cl<sub>2</sub> and Et<sub>2</sub>O. Drying in vacuo yielded the product as a white solid (146 mg, 0.254 mmol, 72%); m.p. 184 °C (dec.). <sup>31</sup>P-DPMAS NMR:  $\delta = 38.1$ , 21.1 ppm. HRMS (FAB):  $m/z$  calcd. for C<sub>60</sub>H<sub>54</sub>Cl<sub>2</sub>N<sub>2</sub>P<sub>2</sub>Pd<sub>2</sub> [M – Cl]<sup>+</sup>: 1113.1544; found 1113.1531. C<sub>60</sub>H<sub>54</sub>Cl<sub>2</sub>N<sub>2</sub>P<sub>2</sub>Pd<sub>2</sub> (1148.78): calcd. C 62.73, H 4.74, N 2.44; found C 62.58, H 4.66, N 2.32.

**Dipalladium Complex 6c:** 2-[2-(Diphenylphosphanyl)ethyl]-6-(9-phenanthryl)pyridine (**1c**) (200 mg, 0.43 mmol, 1.0 equiv.) and (COD)Pd(CH<sub>3</sub>)Cl (113 mg, 0.43 mmol, 1.0 equiv.) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and the mixture was stirred for 16 h. Then, it was concentrated in vacuo to approximately 1 mL, after which 10 mL Et<sub>2</sub>O was added under vigorous stirring. The white precipitate was filtered off and washed with Et<sub>2</sub>O. Drying in vacuo yielded the product as a white solid (219 mg, 0.35 mmol, 82%); m.p. 182 °C (dec.). <sup>31</sup>P-DPMAS NMR:  $\delta = 26.9$  ppm. HRMS (FAB):  $m/z$  calcd. for C<sub>68</sub>H<sub>58</sub>Cl<sub>2</sub>N<sub>2</sub>P<sub>2</sub>Pd<sub>2</sub> [M – Cl]<sup>+</sup>: 1213.1860; found 1213.1869. C<sub>68</sub>H<sub>58</sub>Cl<sub>2</sub>N<sub>2</sub>P<sub>2</sub>Pd<sub>2</sub> (1248.90): calcd. C 65.40, H 4.68, N 2.24; found C 65.28, H 4.62, N 2.15.

**Dipalladium Complex 6d:** 6-(9-Anthracyl)-2-[2-(diphenylphosphanyl)ethyl]pyridine (**1d**) (386 mg, 0.83 mmol, 1.0 equiv.) and (COD)Pd(CH<sub>3</sub>)Cl (219 mg, 0.83 mmol, 1.0 equiv.) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and the mixture was stirred for 16 h. Then, it

was concentrated in vacuo to approximately 2 mL, after which 20 mL Et<sub>2</sub>O was added under vigorous stirring. The white precipitate was filtered off and washed with Et<sub>2</sub>O. Drying in vacuo yielded the product as a white solid (443 mg, 0.69 mmol, 84%); m.p. 178 °C (dec.). <sup>31</sup>P-DPMAS NMR:  $\delta$  = 23.8 ppm. HRMS (FAB): *m/z* calcd. for C<sub>68</sub>H<sub>58</sub>ClN<sub>2</sub>P<sub>2</sub>Pd<sub>2</sub> [M – Cl]<sup>+</sup>: 1213.1860; found 1213.1854. C<sub>68</sub>H<sub>58</sub>Cl<sub>2</sub>N<sub>2</sub>P<sub>2</sub>Pd<sub>2</sub> (1248.90): calcd. C 65.40, H 4.68, N 2.24; found C 65.12, H 4.74, N, 2.15.

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