Synthesis of Cyclopalladated Derivatives of (E)-N-Benzylidene-2-(2,6-dichlorophenyl)ethanamine and Their Reactivity towards Monodentate andSymmetric Bidentate Lewis Bases

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Abstract

Treatment of the monoimine (E)-N-benzylidene-2-(2,6-dichlorophenyl)ethanamine (**1**) with a stoichiometric amount of $Pd(OAc)_2$ in acetic acid at 60 °C under nitrogen produced the corresponding acetato-bridged endo five-membered ortho-cyclopalladated dimer $[Pd\{C_6H_4CH=N(CH_2)2(2,6\text{-}Cl_2C_6H_3)\}(\mu\text{-}OAc)]_2$ (**2**), which was isolated in pure form in 80% yield. Reaction of **2** with an excess of LiCl in acetone gave rise to the corresponding chlorido-bridged cyclopalladated dimer $[Pd\{C_6H_4CH=N(CH_2)_2(2,6\text{-}Cl_2C_6H_3)\}(\mu\text{-}Cl)]_2$ (**3**) in 88% yield. Compounds **2** and **3** reacted with an excess of $[D_5]$pyridine or a stoichiometric amount of PPh_3 to give the mononuclear compounds trans-***N,L***-$[Pd\{C_6H_4CH=N(CH_2)_2\text{-}(2,6\text{-}Cl_2C_6H_3)\}(X)(L)]$ (**4**: X = OAc, L = $[D_5]$py; **5**: X = Cl, L = $[D_5]$py; **6:** X = OAc, L = PPh_3; **7**: X = Cl, L = PPh_3). Compounds **4** and **5** were prepared in a $CDCl_3$/$[D_5]$py solution and studied by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, but they were not isolated. Compound **3** was treated with different types of symmetric bidentate Lewis bases in a 1:1 molar ratio to give high yields of the dinuclear compounds *trans*-***N,L***-$[(Pd\text{-}\{C_6H_4CH=N(CH_2)_2(2,6\text{-}Cl_2C_6H_3)\}Cl)_2\{\mu\text{-}L_2\}]$ [**8**: L_2 = Ph_2 - $PCH_2CH_2PPh_2$; **9**: L_2 = *trans*-$Ph_2PCH=CHPPh_2$; **10**: L_2 = 4,4'-bipyridine; **11**: L_2 = $NH_2CH_2CH_2OCH_2CH_2OCH_2CH_2NH_2$; **12**: L_2 = $NH_2CH_2(CHOH)CH_2NH_2$)] in which the symmetric bidentate Lewis base bridged two identical cyclopalladated units. Compounds **1–3** and **6–12** were fully characterized by elemental analysis, mass spectrometry, IR and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. In addition, the crystal structures of **2**, **8**·$2CH_2Cl_2$, **10**·$4CHCl_3$ and **11**·$2CH_2Cl_2$ were determined by single-crystal X-ray diffraction analysis. Also reported is the theoretical study of the differences in the absolute Gibbs free energies in acetone or $CHCl_3$ solution between the cis- and *trans*-***N,L*** stereoisomers of compounds [Pd(C-N)(X)(L)] in which Pd(C-N) is a model of an endo fivemembered *ortho*-cyclopalladated imine, X is OAc, Cl, Br or I and L is py, NH_3 or PH_3.

1. INTRODUCTION

Since Onoue and Moritani reported the synthesis of the first *endo* five-membered *ortho*-cyclopalladated imines,[1] compounds of this kind (Figure 1) have attracted attention due to their use as starting materials in organic synthesis,[2] as pre-catalysts in Heck and Suzuki C–C coupling reactions[3] and as liquid crystals if they possess appropriate substituents on the imine ligands and co-ligands at the palladium(II) centres.[4] In 1987, Clark et al.[5] introduced the descriptors *endo* and *exo* to differentiate between structural isomers of *ortho*-cyclopalladated benzyl-benzylideneamines (Figure 2). Since then, the use of these descriptors has been extended to refer to cyclometallated imines, oxaz-olines and iminophosphoranes with a C=N or P=N bond inside the metallacycle (*endo*-cyclometallated compounds) or outside the metallacycle (*exo*-cyclometallated compounds).[6]

In recent years, the reactivity of *endo*-cyclopalladated imines towards bidentate Lewis bases has been extensively studied by Vila and co-workers.[2b,7–13] These studies are relevant to the field of supramolecular chemistry. Figure 3 shows schematically the structures proposed for the compounds obtained in the reactions between mono- or di-*endo*-cyclopalladated imines and bidentate Lewis bases in a Pd/bidentate Lewis base molar ratio of 2:1 in which the bidentate Lewis base acts as a bridging ligand. In Figure 3, the L_2 bridging ligand is generally a biphosphane, X is Cl, Y is PF_6^- and Pd(C-N) is an *endo* five-membered *ortho*-cyclopalladated imine. A large number of compounds **I** have been prepared,[7] as have a few compounds **II**.[8] In addition, in one case,[9] a compound characterized as **II** in solution adopts structure **I** in the solid state. The molecular structures of representative compounds **III**,[10] **V**,[2b] **VI**[11] and **VII**[12] have been determined by X-ray diffraction. The molecules found in the solid state were also assumed to be present in solution.[2b,10–12] This should be the case because the bidentate L_2 bridging ligands are biphosphane ligands and the formation of palladium(II)–phosphane complexes is quite exergonic at the experimental temperature,[14] which points to the stability of the Pd^{II}–P(phosphane) bond. For compounds **IV**, although other oligomeric structures would be compatible with the NMR spectroscopic data in solution, the mass spectrometry data are

consistent with the structure depicted in Figure 3.[13] Interestingly, some of the compounds shown in Figure 3 can be classified as metallomacrocycles or molecular cages.

In this paper we present the synthesis of cyclopalladated derivatives of the monoimine (*E*)-*N*-benzylidene-2-(2,6-dichlorophenyl)ethanamine and a study of their reactivity towards monodentate and symmetric bidentate Lewis bases. These studies have allowed the preparation of dinuclear compounds with different types of symmetric bidentate Lewis bases acting as bridging ligands between two identical cyclopalladated units. Note that the synthesis of cyclopalladated compounds derived from (*E*)-*N*-benzylidene-2-phenylethanamines has not been described in detail.[15] In addition, we report a theoretical study of the differences in the absolute Gibbs free energies in acetone or CHCl3 solution between the *cis*- and *trans*-***N,L*** stereoisomers of compounds [Pd(C-N)(X)(L)] in which Pd(C-N) is a model of an *endo* five-membered *ortho*-cyclopalladated imine, X is OAc, Cl, Br or I and L is py, NH_3 or PH_3.

2. RESULTS AND DISCUSSION

Scheme 1 shows the structural formulae of the new compounds prepared in this study and the numbering of their protons and carbon atoms for the discussion that follows. Compounds **1**–**3** and **6**–**12** were fully characterized by elemental analysis (C, H and N), mass spectrometry, IR and ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy. Compounds **6**–**9** were also studied by $^{31}P\{^{1}H\}$ and $^{1}H\{^{31}P\}$ NMR spectroscopy. Compounds **4** and **5** were prepared in $CDCl_3$/[D_5]py solution and studied by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy, but they were not isolated. The assignments of the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were inferred from the results of two-dimensional COSY, NOESY, HSQC and HMBC experiments. In addition, the crystal structures of **2**, **8**·$2CH_2Cl_2$, **10**·$4CHCl_3$ and **11**·$2CH_2Cl_2$ were determined by single-crystal X-ray diffraction analysis.

Synthesis and Characterization of Compounds 1–3

Imine **1** was prepared by a condensation reaction between benzaldehyde and 2-(2,6-dichlorophenyl)ethanamine. Imine **1** is a solid that is highly soluble in $CDCl_3$; in this solvent, ^{1}H and $^{13}C\{^{1}H\}$ NMR analysis produced a single set of signals. These NMR spectroscopic data suggested that imine **1** consists of only the E geometrical isomer.[16] In agreement with this assumption, the NOESY spectrum of **1** shows a cross-peak between the CH=N and the N–CH_2 protons. The methinic proton and carbon atom of **1** appear at 8.26 and 161.7 ppm, respectively, and C=N stretching produced an intense band at 1645 cm^{-1}. In addition, the MALDI-TOF(+) MS analysis of **1** gave rise to an intense signal at *m/z* = 278.2, which corresponds to $[M+ H]^{+}$.

Treatment of imine **1** with a stoichiometric amount of $Pd(OAc)_2$ in acetic acid at 60°C under nitrogen produced the corresponding acetato-bridged *endo* five-membered *ortho*-cyclopalladated dimer **2**, which was easily converted by a metathesis reaction with LiCl into the chlorido-bridged cyclopalladated dimer **3** (Scheme 1). Compounds **2** and **3** were isolated in pure form in 80 and 88% yields, respectively. Compound **2** is a deep-yellow

127 solid that is very soluble in $CDCl_3$ and compound **3** is a yellow solid that is partially soluble
128 in $CDCl_3$. The solutions of compounds **2** and **3** in $CDCl_3$ were stable on contact with air.

129 Intense C=N stretching bands for compounds **2** and **3** appear at 1609 cm^{-1}, shifted
130 to lower wavenumbers in relation to **1**, which is consistent with the coordination of the iminic
131 nitrogens to the palladium(**II**) centres.[1] The asymmetric and symmetric stretchings of the
132 carboxylic functions of **2** produced broad intense bands at 1568 and 1433 cm^{-1}, respectively,
133 which indicates that the acetato ligands of **2** present a bridging coordination mode.[17] On
134 the other hand, the Pd–Cl stretchings of the chlorido-bridged cyclopalladated dimer **3** gave
135 rise to two bands at 296 and 264 cm^{-1}, which have been assigned to Pd–Cl stretching trans
136 to the iminic nitrogen and trans to the palladated carbon atom, respectively.[18] In addition,
137 MALDI-TOF(+) MS analysis of compounds **2** and **3** produced intense peaks for the cations
138 $[M - X]^+$, in which X is acetate for **2** and chloride for **3**, in agreement with dimeric structures
139 with acetato- and chlorido-bridged ligands, respectively.[2c]

140 The principal features of the ^1H NMR spectrum of compound **2** in $CDCl_3$ solution
141 are i) the upfield shift by 0.70 ppm of the methinic proton in relation to the free imine, ii)
142 the diastereotopic nature of the N–CH_2–CH_2– methylene protons and iii) the single singlet
143 produced by the methyl protons of the acetato ligands at δ = 2.20 ppm. These data are
144 consistent with a dimeric folded structure with a *trans* configuration for compound **2**, which
145 is the usual structure adopted for acetato-bridged cyclopalladated dimers in $CDCl_3$ solution
146 and in the solid state.[19] In this dimeric structure, the acetato ligands bridge two
147 palladium(II) centres and the imines are coordinated to them in a chelate mode through their
148 iminic nitrogen and C1 aromatic carbon atoms (Figure 4, A). Furthermore, the ^1H NMR
149 spectrum of compound **2** in $CDCl_3$ solution is also consistent with its *ortho*-cyclopalladated
150 nature as two *ortho* protons, one from each imine ligand, are absent from the spectrum. In
151 accord with the structure proposed for compound **2**, its $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$
152 produced a single set of signals, which presented as principal features i) a downfield shift of
153 10.6 and 27.2 ppm of the methanic and metallated carbon atoms, respectively, in relation to

the free imine ligand and ii) a single set of signals afforded by the carbon atoms of the acetato ligands at 181.3 and 24.6 ppm. Note that compound **2** in $CDCl_3$ solution presents an apparent C_2 symmetry, as deduced from the ^1H and $^{13}C\{^1H\}$ NMR spectra at 298 K. In addition, the ^1H NMR spectrum of compound **3** in $CDCl_3$ at 298 K produced two set of signals, which we tentatively assigned to its planar *trans* and *cis* geometrical isomers (Figure 4, B).[20]

X-ray Crystal Structure of Compound 2

Yellow crystals of compound **2** suitable for a single-crystal X-ray diffraction analysis were obtained by evaporating the solvent of a saturated solution of **2** in diethyl ether. Compound **2** crystallized in the triclinic space group $P\bar{1}$ with $Z = 2$. Figure 5 shows an ORTEP view of the X-ray molecular structure of **2** and also gives selected bond lengths and angles. The X-ray molecular structure confirmed the proposed structure for compound **2**. Thus, compound **2** presents a dimeric trans folded structure with the acetato ligands bridging the two palladium(II) centres with the imines chelated to them through the N1 and C1 and the N2 and C21 atoms, respectively. The molecule of 2 in the crystal form is asymmetric. The two halves differ in the conformation of the $CH_2CH_2(2,6\text{-}Cl_2C_6H_3)$ groups [compare the torsion angles N1–C8–C9–C10 –172.5(4)° and C9–C10–C11–Cl1 0.0(7)° with N2–C28–C29–C30 67.8(5)° and C29–C30–C31–Cl3 2.0(6)°] and in the small differences in the distances and angles [for instance, compare Pd1–N1 2.114(4) Å with Pd2–N2 2.028(4) Å and O3–Pd1–C1 176.80(15)° with O2–Pd2–C21 173.80(15)°].

The two palladacycles Pd1–N1–C1–C6–C7 and Pd2–N2–C21–C26–C27 are almost planar [maximum deviations: C1 –0.073(5) Å and N2 0.052(4) Å] and the angle between them is 25.0(2)°. In addition, i) the distances Pd1–O3 2.147(3) Å and Pd2–O2 2.194(3) Å are greater than the distances Pd1–O1 2.126(3) Å and Pd2–O4 2.058(3) Å due to the greater *trans* influence of the metallated carbon atom in relation to the iminic nitrogen atom[18] and ii) the chelate bite angles C1–Pd1–N1 80.38(16)° and C21–Pd2–N2 80.10(19)° are those of the coordination spheres of the palladium(II) centres with the largest deviations from the ideal angles. The distance between the palladium atoms [2.9881(10) Å] is at the upper limit accepted for a palladium–palladium single bond length, which is between 2.5 and 3.0 Å.[21]

Reactivity of Compounds 2 and 3 Towards Monodentate Lewis Bases

Compounds **2** and **3** reacted with an excess of [D5]py or a stoichiometric amount of PPh_3 to give the mononuclear compounds **4**–**7**. Compounds **4** and **5** were prepared in $CDCl_3$/[D5]py solution and studied by ^1H and $^{13}C\{^1H\}$ NMR, but they were not isolated. Compounds **4** and **5** are highly soluble in $CDCl_3$/[D5]py. Compounds **6** and **7** were prepared in acetone and isolated in pure form as pale-yellow solids in 83 and 74% yields, respectively, and are quite soluble in $CDCl_3$. Solutions of compounds **6** and **7** in $CDCl_3$ as well as solutions of compounds **4** and **5** in $CDCl_3$/[D5]py were stable on contact with air. The MALDI-TOF(+) MS analyses of compounds **6** and **7** produced intense peaks for the cations $[M - X]^+$ for which X is acetate for **6** and chloride for **7.** The C=N stretching and the q X-sensitive mode of the coordinated PPh_3 appear at 1620 and 1097 cm^{-1} for compound **6** and at 1624 and 1096 cm^{-1} for compound **7**.[22] In addition, the carboxylate function of the acetato ligand of compound **6** produced intense bands at 1601 and 1369 cm^{-1}, in agreement with its monodentate coordination mode.[16] In addition, the Pd–Cl stretching of compound **7** appears at 300 cm^{-1}.

The ^1H NMR spectroscopic data for the mononuclear compounds **4**–**7** are consistent with their proposed stereochemistry, with the L ligand located *trans* to the iminic nitrogen and the X ligand *trans* to the palladated carbon atom (see Scheme 1). We refer to this arrangement as *trans*-***N***,***L*** stereochemistry. In accord with this stereochemistry, the aromatic protons of the palladated ring of compounds **4**–**7** appear upfield shifted in relation to the free imine because they are located in the shielding zone of the aromatic ring of the [D5]py ligand in compounds **4** and **5** and of the phenyl substituents of the PPh_3 ligand for compounds **6** and **7**.[23] As a result, the H2 protons of compounds **4**–**7** are shifted upfield in relation to the free imine by around 1.20 ppm for compounds **4** and **5** and by around 1.00 pm for compounds **6** and **7**. Further indications of the stereochemistry of compounds **6** and **7** are given by $^{31}P\{^1H\}$ NMR, with resonances observed at 40.0 and 42.0 ppm, respectively. These chemical shifts are in the range expected for mononuclear cyclopalladated compounds of

general formula *trans*-***N,P***-[Pd(C-N)(X)(PPh_3)] (X = OAc, Cl, Br, I) containing a five-membered palladacycle and a phenyl- or naphthyl-metallated carbon atom (43–40 ppm).[6e,8a,24]

In the $^{13}C\{^1H\}$ NMR spectra of compounds **4**–**7**, the CH=N and the C1-metallated carbon atoms appear downfield shifted by around 14 and 30 ppm, respectively, in relation to the free imine, which is in agreement with the chelate coordination mode of the imine ligand through the iminic nitrogen and the C1 carbon atoms. In addition, for compound **6**, the acetato ligand produced singlet signals at δ = 177.0 and 23.5 ppm. Interestingly, for compounds **4** and **5** the [D_5]py coordinated molecules are not observed in the $^{13}C\{^1H\}$ NMR spectra in $CDCl_3$/[D_5]py solution at 298 K. This is an indication that compounds **4** and **5** in $CDCl_3$/[D_5]py solution are involved in a dynamic process in which coordinated and free [D_5]py molecules are exchanged. Analogous dynamic processes have been described for related systems.[25]

Reactivity of Compound 3 Towards Symmetric Bidentate Lewis Bases

Compound **3** reacted in a 1:1 molar ratio with the symmetric bidentate Lewis bases $Ph_2PCH_2CH_2PPh_2$, *trans*-$Ph_2PCH{=}CHPPh_2$, 4,4'-bipyridine, $NH_2CH_2CH_2OCH_2$-$CH_2OCH_2CH_2NH_2$ and $NH_2CH_2(CHOH)CH_2NH_2$ to give high yields of the dinuclear compounds *trans-N,L*-[(Pd{$C_6H_4CH{=}N(CH_2)_2(2,6\text{-}Cl_2C_6H_3)$}Cl)$_2${μ-$L_2$}] [**8**: L_2 = $Ph_2PCH_2CH_2PPh_2$; **9**: L_2 = *trans*-$Ph_2PCH{=}CHPPh_2$; **10**: L_2 = 4,4'-bipyridine; **11**: L_2 = NH_2 $CH_2CH_2OCH_2CH_2$-$OCH_2CH_2NH_2$; **12**: L_2 = $NH_2CH_2(CHOH)CH_2NH_2$] in which the symmetric bidentate L_2 Lewis base bridges two identical cyclopalladated units. The high chemo- and stereoselectivity of these reactions are remarkable, especially the reactions with the ligands $Ph_2PCH_2CH_2PPh_2$ (**a**), $NH_2CH_2CH_2OCH_2CH_2OCH_2CH_2NH_2$ (**b**) and NH_2CH_2-$(CHOH)CH_2NH_2$ (**c**), which could alternatively act as chelate (**a**–**c**) or chelate-bridging ligands (**b**–**c**), for instance.

These results confirm previous work by our group on the reactivity of cyclopalladated derivatives with 1,2-bis(diphenylphosphanyl) ethane (dppe)[6g] in which the dppe ligand bridges cyclopalladated units if the reaction is performed with a palladium/dppe molar ratio of 2:1. In contrast, when the same reaction was performed with a palladium/dppe molar ratio of 1:1, anionic compounds [Pd(CN)(dppe)]Br or neutral derivatives with no Pd–N bond of formula [Pd(C-N)(Br)(dppe)] were obtained.

Compounds **8**–**12** are pale-yellow solids quite soluble in $CDCl_3$, with the exception of compound **9**, which is more soluble in CD_2Cl_2 than in $CDCl_3$. The deuteriated solutions of these compounds were air-stable, with the exception of that of compound **12**, which slowly evolved to yield unidentified compounds. In the IR spectra of compounds **8**–**12**, the C=N stretching bands appear at 1626, 1624, 1608, 1613 and 1612 cm^{-1}, respectively. For compounds 8 and 9, the q X-sensitive modes of the coordinated $Ph_2PCH_2CH_2PPh_2$ and trans-Ph_2PCH=$CHPPh_2$ ligands appear at 1101 or 1099 cm^{-1}, respectively.[22] For compound **10**, which contains the 4,4'-bipyridine ligand, the band equivalent to the ν_4 stretching mode of the pyridine ligand appears at 1608 cm^{-1},[26] which coincides with the C=N stretching of the imine ligand. For compound **11**, the NH_2 asymmetric and symmetric stretchings produced bands at 3321 and 3263 cm^{-1}, and for compound **12**, the bands at 3385, 3295 and 3236 cm^{-1} were assigned to NH_2 and OH stretchings. Furthermore, the far-IR spectra of compounds **8**–**12** present bands at around 300 cm^{-1}, which have been assigned to terminal Pd–Cl stretching. In addition, the mass spectrometry experiments for compounds **8**–**11** produced intense signals with appropriate isotopic patterns for cations $[M - Cl]^+$. However, a mass spectrum providing evidence for the dinuclear structure of compound **12** could not be obtained.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of compounds **8** and **10**–**12** in $CDCl_3$ and the ^1H and $^{13}C\{^1H\}$ NMR spectra of compound **9** in CD_2Cl_2 at 298 K show that these compounds present a molecular structure with an apparent centre of inversion (compounds **8**–**11**) or an apparent plane of symmetry (compound **12**), which divides the molecules into two symmetrical parts. This is in agreement with the structures proposed for these compounds

with symmetric L_2 ligands i) bridging the two palladium(II) centres and ii) coordinated to the cyclopalladated units with *trans*-***N,L*** stereochemistry. In addition, the $^{31}P\{^{1}H\}$ NMR spectra of compounds **8** and **9** in $CDCl_3$ each show a singlet at δ = 38.2 and 34.7 ppm, respectively, as expected for the proposed structures. Furthermore, for compounds **8**–**10**, in accord with the presence of aromatic rings in the bridging ligand close to the H2 protons, the H2 protons are shifted upfield by between 0.8 and 1.0 ppm in relation to the free ligand. In contrast, for compounds **11** and **12**, which do not have aromatic rings in the bridging ligand, the H2 protons are shifted upfield by only between 0.4 and 0.5 ppm in relation to the free ligand.

For compound **8**, the aliphatic P–CH_2 protons produced an apparent doublet at δ = 2.97 ppm with an apparent coupling constant with the phosphorus atom of 2.1 Hz. For compound **9**, the alkenyl protons of the *trans*-$Ph_2PCH{=}CHPPh_2$ bridging ligand afforded an apparent triplet by their virtual coupling with the two phosphorus atoms. For compound **10**, the 4,4'-bipyridine bridging ligand afforded doublets at δ = 9.11 and 7.72 ppm with a coupling constant of around 6 Hz. For compound **11**, the coordinated NH_2 groups produced a broad triplet centred at δ = 3.40 ppm. In contrast, for compound **12**, the protons of the coordinated NH_2 groups and the CH_2 groups of the bridging ligand produced four signals centred at 3.42, 3.29, 3.15 and 2.93 ppm, each signal integration revealing two protons. Thus, the protons of the same NH_2 or CH_2 group in the bridging ligand are not equivalent. This is consistent with the proposed apparent C_s symmetry for this compound in $CDCl_3$ solution. In addition, for compound 12, the OH proton appears as a broad signal at δ = 5.38 ppm.

Interestingly, the CH=N and H2 protons of compounds **8** and **9** were virtually coupled with the two phosphorus atoms of the $Ph_2PCH_2CH_2PPh_2$ and trans-$Ph_2PCH{=}CHPPh_2$ bridging ligands, respectively. For instance, for compound **9**, the CH=N and H2 protons afforded signals of multiplicity three and five, respectively, both signals showing second-order effects. These virtual couplings were corroborated by $^{1}H\{^{31}P\}$ NMR as the CH=N and H2 protons of compounds **8** and **9** appear as a singlet and doublet, respectively, in these latter experiments. The most interesting features of the $^{13}C\{^{1}H\}$ NMR spectra of compounds **8**–**12** are the downfield shifts of around 13–14 and 30 ppm for the

CH=N and C1 carbon atoms, respectively, relative to the free imine ligand, which is consistent with the chelate coordination mode of the imine ligands through the iminic nitrogen and C1 carbon atoms to the palladium(II) centres.

X-ray Crystal Structures of the Adducts 8·2CH_2Cl_2, 10·4$CHCl_3$ and 11·2CH_2Cl_2

Yellow single crystals of the adducts **8**·2CH_2Cl_2, **10**·4$CHCl_3$ and **11**·2CH_2Cl_2 were obtained by slow evaporation of the solvent of a dichloromethane solution of **8** and a chloroform solution of **10** and by slow diffusion of hexanes into a CH_2Cl_2 solution of **11**, respectively. These three adducts crystallized in the triclinic space group $P\bar{1}$ with $Z = 1$ with the molecules **8**, **10** and **11** located in an inversion centre. Therefore these molecules consist of two symmetrically equivalent parts in these crystals. Figures 6, 7 and 8 show ORTEP views of **8**, **10** and **11** and also give selected bond lengths and angles for these molecules.

The X-ray molecular structures of compounds **8**, **10** and **11** confirmed the structures proposed upon NMR analysis. Thus, in the X-ray molecular structures of compounds **8**, **10** and 11, the symmetric bidentate Lewis bases bridge the two palladium(II) centres and are coordinated to the cyclopalladated units in a *trans-**N,L*** stereochemistry. The palladacycles of compounds **8**, **10** and **11** are almost planar. The maximum deviations from the best plane of the palladacycles are C7 –0.057(7) Å for **8**, N1 0.017(2) Å for **10** and N1 –0.017(6) Å for 11. The chelate bite angles C1–Pd1–N1 80.2(2)° for **8**, N1–Pd1–C1 81.01(11)° for **10** and N1–Pd2–C1 79.7(3)° for **11** are those of the coordination spheres of the palladium(II) centres with the largest deviations from the ideal angles. The palladium–nitrogen iminic distances are 2.028(3) Å for **10**, 2.092(5) Å for **11** and 2.086(5) Å for **8**. The variations in these distances did not match those expected taking into account the *trans* influence of the ligand *trans* to the iminic nitrogen in these compounds: a pyridine ligand in compound **10**, a primary amine ligand in compound **11** and a phosphane ligand in compound **8**.[27]

For compounds **8**, **10** and **11**, their P–C28–C28a–Pa, C19–C18–C18a–C19a and O1–C18–C18a–O1a central fragments are planar and the torsion angles defined by these atoms are 180°. This is because the molecules are located in an inversion centre of the crystal. For compound **11**, the torsion angles C18a–C18–O1–C17, C18–O1–C17–C16 and O1–C17–C16–N2 are –176.3(5), –173.0(6) and 57.3(7)°, respectively. For compounds **8**, **10** and **11**,

the angles between the cyclopalladated rings and the central planar fragments P–C28–C28a–Pa, C19–C18–C18a–C19a and O1–C18–C18a–O1a are 73.0(9), 64.01(13) and 68.0(4)°, respectively. In addition, for compound **11**, the torsion angle C16–N2–Pd2–Cl1 is 63.3(4)° and the distance N2–Pd2 [2.073(5) Å] is greater than the Pd1–N2 distance in compound **10** [2.053(3) Å]. The variations in these distances agree with the expectation that the length of a Pd–N(sp^3) σ bond should be greater than the length of a Pd–N(sp^2) σ bond.

Compound **11** does not present intermolecular N–H···O hydrogen bonds. Nevertheless, the conformation adopted by the O1–C17–C16–N2 fragment of this molecule in the crystal [torsion angle O1–C17–C16–N2 57.3(7)°] may be a consequence of the intramolecular N2–H2A···O1 hydrogen bond with a H2A···O1 distance of 2.50 Å.

Theoretical Study of the Stereochemistry of Compounds of Formula [Pd(C-N)(X)(L)]

The results obtained in this study (see chapter Reactivity of Compounds **2** and **3** Towards Monodentate Lewis Bases) confirm the high selectivity of the splitting reactions of cyclopalladated dimers of N-donor ligands of general formula $[Pd(C\text{-}N)(\mu\text{-}X)]_2$ (X = OAc or Cl) with Lewis bases such as monophosphanes, -pyridines or -amines, which transformed these dimers with complete selectivity into the mononuclear compounds *trans*-**N**,**L**-[Pd(C-N)(X)(L)] (X = OAc or Cl; L = monophosphane, -pyridine or -amine) in most of the cases (see this work and ref.[23–25]). Furthermore, the selectivity of these reactions is also maintained in more complex situations when mono- or di-cyclopalladated complexes react with rigid or flexible bidentate Lewis bases such as diphosphanes, bipyridines or diamines in a Pd/bidentate

Lewis base molar ratio of 2:1 (see chapter Reactivity of Compound **3** Towards Symmetric Bidentate Lewis Bases and ref.[2c,7–13]).

The high selectivity of these splitting reactions has formed the basis for the successful application of cyclopalladated compounds of optically active N-donor ligands i) as derivatizing agents for the optical resolution of chiral phosphanes[28] and for the determination by NMR of the optical purity of optically active phosphanes and α-amino acids[29] and ii) as chiral Lewis acid templates for the promotion of asymmetric Diels–Alder,

hydroamination, hydrophosphination and hydroarsination reactions.[30] Furthermore, this *trans*-**N**,**L** stereochemistry also allows the self-assembly of mono- or di-cyclopalladated compounds and the bidentate Lewis bases discussed in the Introduction to produce the metallomacrocycles and molecular cages **II**–**VII** shown in Figure 1.

In a few cases, compounds of the type [Pd(C-N)(Cl)(py)] with *cis*-***N***,***N*** stereochemistry have been observed (compounds **a**; see Figure 9 for the schematic structural formulae of compounds **a**–**d**)[31] and metallated compounds of general formula *trans*-[Pd(C-N)(X)(monophosphane)$_2$] (X = Cl or Br), in which the Pd–N bond has been broken, have also been reported. The formation of these latter compounds depends on the stability of the metallacycle and the basicity of the monophosphane ligand.[1,32]

Recently, examples of compounds of formula [Pd(CN)(X)(py)] with X = Br or I and a *cis*-***N***,***N*** stereochemistry have also been described (compounds **b**).[33] In addition, two compounds of formula [Pd(C-N)(Br)(py)] with *trans*-***N***,***N*** stereochemistry (compounds **c**) have also been reported[25] as well as compounds of formula [Pd(C-N)-(X)(monophosphane)] with X = Br or I that adopt *trans*-***N***,***P*** stereochemistry.[6e,23b,25] Interestingly, for compounds **a** and **b**, with the exception of one of the compounds **a** (compound **a'**), the C–N ligand is an imine ligand, whereas for compounds c the C–N ligand is an amine ligand. Thus, on going from compounds **a** and **b** to compounds **c**, the nitrogen atom of the C–N ligand changes from an sp^2 to a softer sp^3 nitrogen atom and the pyridine ligand changes from *cis* to the iminic nitrogen atom (compounds **a** and **b**) to *trans* to the aminic nitrogen atom (compounds **c**). In compound **a**', which has *cis*-***N***,***N*** stereochemistry, the C–N ligand is an amine ligand, but instead of a pyridine, compound **a**' contains 3,4,5-trichloropyridine, which is harder than pyridine itself.[34]

Note that in all compounds **a**, the iminic nitrogen atom of the C–N ligand is bonded to a σ-acceptor group, such as phenyl or 1-naphthyl,[31] but compounds of general formula [Pd(C–N)(Cl)(py)], in which C–N is an iminic ligand with a σ-donor group, such as –CHMePh, –CH_2–CH_2–aryl or –CH_2–(1-naphthyl) bonded to the iminic nitrogen atom of the C–N ligand (compounds **d**), adopt a *trans*-***N***,***N*** stereochemistry (see, for instance, this work and ref.[2c,24a]). Thus, on going from compounds **d** to compounds **a**, the hardness of the

iminic nitrogen of the C–N ligand increases and the pyridine ligand moves from *trans* to the iminic nitrogen in compounds **d** to *cis* to the iminic nitrogen in compounds **a**.

Thus, if we consider that the pyridine ligand is slightly harder than the chlorido ligand,[35] these results are consistent with the finding that the splitting reactions of cyclopalladated dimers of general formula $[Pd(C\text{-}N)(\mu\text{-}X)]_2$ with monodentate Lewis bases lead generally to mononuclear compounds of formula [Pd(C-N)(X)(L)] with complete stereoselectivity. This is as expected, according to the anti-symbiotic effect, which establishes that two soft ligands in mutual *trans* positions have a destabilizing effect on each other when attached to a soft metal atom.[36] Thus, in compounds [Pd(C-N)(X)(L)], the hardest X or L ligand tends to be trans to the palladated carbon atom and the softest X or L ligand tends to be *trans* to the nitrogen atom.

Previous theoretical studies with model compounds of type [PdCl(R)(P–N)] (R = CH_3 or η^1-CH_2–CH=CH_2; P–N = PH_2–O–CH_2–CH=NH] showed that the geometrical isomers with the chlorido ligand *trans* to the phosphorus atom are 7.1 (R = CH_3) and 5.3 kcalmol^{-1} (R = η^1-CH_2–CH=CH_2) more stable than the geometrical isomers with the chlorido ligand *trans* to the nitrogen atom. These results are consistent with experimental observations.[37] Interested in this theoretical work, we calculated the differences in the electronic energies, absolute enthalpies and absolute Gibbs free energies in vacuo and in acetone or $CHCl_3$ solutions between the *cis*- and *trans*-***N,L*** stereoisomers of the *endo* five-membered *ortho*-cyclopalladated imine models of formula [Pd(CH=CH–CH=NH)(X)(L)], hereafter referred to as compounds **A**, in which X is OAc, Cl, Br or I and L is py, NH_3 or PH_3. Table 1 summarizes the results and Figure 10 shows the structures of the *cis*- and *trans*-***N,L*** stereoisomers of compounds **A**. To facilitate a comparison with the experimental results, we have focused the discussion on the differences in the absolute Gibbs free energies in acetone and chloroform solution between the *cis*- and *trans*-***N,L*** stereoisomers of compounds **A** [ΔG(a) and ΔG(c), respectively; columns with values printed in bold in Table 1].

With the anionic X ligand fixed, comparison of the ΔG(a) and ΔG(c) values for neutral L ligands shows that in all cases the order of stabilization of the *trans*-***N,L***

stereoisomer is PH_3 > NH_3 > py. Thus, an increment in the hardness of the ligand L leads to a stabilization of the *cis*-***N***,***L*** stereoisomer (see, for instance, entries 10–12). On the other hand, for the anionic X ligand, if we take as reference the compounds containing the PH_3 ligand (entries 3, 6, 9 and 12), the order of stabilization of the *trans*-***N***,***L*** stereoisomer is OAc > Cl > Br > I, that is, it increases with the hardness of the anionic X ligand. The solvent (acetone or chloroform) seems to have little influence on the difference between the absolute Gibbs free energies of the *cis* and *trans* isomers, except for the combination OAc and py (entry 1) in which the acetone solvent seems to favour the *cis* isomer more than chloroform does.

Interestingly, despite the simplicity of these models, the calculations predict quite well the extreme situations found experimentally. Thus, if L is PH_3, independently of the anionic X ligand (OAc, Cl, Br or I), the favoured stereoisomer is the *trans*-*N*,*P* isomer, which is the result observed experimentally. Thus, compounds of the type [Pd(C-N)(X)(monophosphane)] (X = OAc, Cl, Br or I) adopt a *trans*-***N***,***P*** stereochemistry (see, for instance, ref.[6e,7–13,23–25]). On the other hand, the combination X = Br or I and L = py favours the *cis* isomer (entries 7 and 10), but can give rise experimentally to the *trans*-***N***,***N*** isomer,[25] mixtures of *trans*- ***N***,***N*** and *cis*-***N***,***N*** isomers or only the *cis*-***N***,***N*** isomer.[33] Furthermore, the combination Cl and py (entry 4), according to theoretical calculations, favours the *trans*-***N***,***N*** isomer, which is the result most often observed experimentally (see, for instance, ref.[23a,24a]), although there are some exceptions that give rise to the *cis*-***N***,***N*** isomer.[31]

Finally, it should be noted that our computational studies failed to reproduce the relative stability of the *cis* and *trans* isomers for the combinations OAc/pyridine (entry 1) and OAc/NH_3 (entry 2) as they favour the *cis*-***N***,***N*** isomer, but compounds of formula [Pd(C-N)(OAc)(L)] with L = pyridine or monoamine adopt a *trans*-***N***,***L*** stereochemistry (see, for instance, ref.[2a,24a]).

3. EXPERIMENTAL SECTION

Instruments and Reagents: NMR spectra were recorded with the following spectrometers: a Varian Inova 500, a Varian Mercury 400, a Varian Unity 300, a Varian Inova 300 or a Bruker DRX 250. Chemical shifts (in ppm) were measured relative to $SiMe_4$ for ^{1}H, to residual solvent peaks for ^{13}C and to 85% H_3PO_4 for ^{31}P. Shifts are reported as δ and coupling constants are expressed in Hz. CHN microanalyses were performed with a Carlo–Erba EA 1108 instrument. IR spectra were collected with a Thermo Nicolet 5700 and Nicolet Avatar 300 FT-IR spectrometers using KBr discs. Far-IR spectra were recorded with a Bomem DA3 FT-IR instrument using polyethylene (PE) pellets. MALDI-TOF(+) mass spectra were registered with a VOYAGER-DE-RP spectrometer using dithranol (DTH), 2,5-dihydroxybenzoic acid (DHB) or *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix. ESI(+) mass spectra were acquired with a LC/MSD-TOF mass spectrometer using 1:1 H_2O/CH_3CN as eluent. Abbreviations used for fragments in the mass spectra are as follows: L indicates the metallated ligand (*E*)-*N*-benzylidene-2-(2,6-dichlorophenyl) ethanamine, NN expresses the corresponding [N,N] bidentate Lewis base (1,3-diamino-2-propanol or 4,4'-bipyridine) and PP refers to the corresponding diphosphane [1,2-bis(diphenylphosphanyl) ethane or *trans*-1,2-bis(diphenylphosphanyl)ethylene]. All chemicals were of commercial grade and used as received.

Preparation of 1: A mixture of benzaldehyde (403 mg, 386 µL, 3.80 mmol) and 2,6-dichlorophenethylamine (723 mg, 553 µL, 3.80 mmol) was gently heated at reflux in absolute ethanol (40 mL) for approximately 5 h. After this period, the slightly pink solution was concentrated to a final volume of around 1 mL by rotary evaporation. The oily product was then refrigerated overnight to promote precipitation. The salmon-coloured precipitate was filtered off and dried in air (1051 mg, 99% yield). IR (KBr): $\tilde{\nu}$ = 1645 (CH=N st) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.26 (s, 1 H, CH=N), 7.74–7.72 (m, 2 H, 1-H), 7.42–7.40 (m, 3 H, 2-H, 3-H), 7.28 (d, $^{3}J_{HH}$ = 8.0 Hz, 2 H, 12-H), 7.08 (t, $^{3}J_{HH}$ = 8.0 Hz, 1 H, 13-H), 3.84 (td, $^{3}J_{HH}$ = 7.7, $^{4}J_{HH}$ = 1.1 Hz, 2 H, 8-H), 3.34 (t, $^{3}J_{HH}$ = 7.7 Hz, 2 H, 9-H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, CDCl3, 298 K): δ = 161.7 (s, CH=N), 136.2 (s, C-6), 135.8

(s, C-11), 135.6 (s, C-10), 130.6 (s, C-3), 128.5 (s, C-2), 128.2 (s, overlapped, C-1 + C-12), 127.9 (s, C-13), 59.2 (s, C-8), 32.9 (s, C-9) ppm. MS (MALDI-TOF, +, DHB): calcd. for [M + H]$^+$ 278.0; found 278.2. $C_{15}H_{13}Cl_2N$ (278.18): calcd. C 64.76, H 4.71, N 5.04; found C 64.26, H 4.76, N 5.23.

Preparation of 2: A Schlenk tube was charged with palladium(II) acetate (509 mg, 2.27 mmol) and (*E*)-N-benzylidene-2-(2,6-dichlorophenyl) ethanamine (635 mg, 2.28 mmol). An evacuation/nitrogen backfill cycle was applied three times. Then glacial acetic acid (35 mL) was added to suspend the solids. The resulting mixture was heated at 60 °C for 5 h whilst stirring and subsequently concentrated to dryness. Ethanol (5 mL) was next poured into the Schlenk tube and concentrated under vacuum to efficiently remove the residual acetic acid. The crude was purified by silica gel chromatography eluting with 100:1 to 100:4 chloroform/methanol. The coloured eluted band was concentrated to yield an orange resin. A small amount of diethyl ether (2 mL) was then added to the flask. The mixture was allowed to cool for 10 min to ensure complete precipitation of the product. The deep-yellow solid obtained was collected by suction filtration and air-dried (801 mg, 80% yield). An additional crop may be obtained from the ether mother liquor. IR (KBr): $\tilde{\nu}$ = 1609 (CH=N st), 1568 (COO as st), 1433 (COO sym st) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.24 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, 12-H), 7.12 (s, 1 H, CH=N), 7.09–7.05 (m, partially overlapped, 1 H, 13-H), 7.06 (d, $^3J_{HH}$ = 8.3 Hz, partially overlapped, 1 H, 2-H), 6.96–6.90 (m, 3 H, 3-H, 4-H, 5-H), 3.49–3.42 (m, 2 H, 8-H, 9-H), 3.14–3.05 (m, 1 H, 9-H), 2.71–2.62 (m, 1 H, 8-H), 2.20 (s, 3 H, CH_3) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 181.3 (s, COO), 172.3 (s, CH=N), 155.4 (s, C-1), 145.6 (s, C-6), 135.7 (s, C-11), 134.6 (s, C-10), 132.1 (s, C-2), 129.1 (s, C-5), 128.2 (s, C-13), 128.1 (s, C-12), 126.3 (s, C-3), 123.7 (s, C-4), 57.0 (s, C-8), 31.9 (s, C-9), 24.6 (s, CH_3) ppm. MS (MALDI-TOF, +, DTH): calcd. for [M – OAc]$^+$ 822.9; found 822.4. $C_{34}H_{30}Cl_4N_2O_4Pd_2$ (885.23): calcd. C 46.13, H 3.42, N 3.16; found C 46.63, H 3.53, N 3.13.

Preparation of 3: An excess of lithium chloride (79 mg, 1.86 mmol) was added to an orange solution of **2** (266 mg, 0.30 mmol) in acetone (50 mL). The reaction mixture was

stirred at room temperature for 1 d. The crude was then concentrated to dryness. Upon addition of diethyl ether (5 mL) a pale-yellow precipitate appeared, which was filtered off and placed in a flask. Deionised water (15 mL) was added and the resulting suspension stirred vigorously overnight. After this time, the solid was collected by filtration and washed exhaustively with further portions of water (5 X 5 mL). The salt-free product was next transferred to a flask along with acetone (20 mL). The solvent was removed under reduced pressure and diethyl ether (5 mL) was added to yield the required product as a pale-yellow powder (222 mg, 88% yield). IR (KBr): $\tilde{\nu}$ = 1609 (CH=N st) cm^{-1}. Far-IR (PE): $\tilde{\nu}$ = 296 ([Pd–Cl*trans*N]b_{ridge} st), 264 ([Pd–C*l*$_{trans}$C]$_{bridge}$ st) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.57 (br. s, 0.56 H, CH=N), 7.48 (br. s, 0.44 H, CH=N), 7.43 (dd, $^{3}J_{HH}$ = 7.6, $^{4}J_{HH}$ = 1.2 Hz, 1 H, 2-H or 5-H), 7.30–7.26 (m, obscured by residual solvent peak, 2 H, 12-H), 7.13–6.99 (m, 4 H, 2-H or 5-H, 3-H, 4-H, 13-H), 3.93 (t, $^{3}J_{HH}$ = 6.9 Hz, 2 H, 8-H), 3.54 (t, $^{3}J_{HH}$ = 6.9 Hz, 2 H, 9-H) ppm. The poor solubility of 3 in common deuteriated solvents precluded the acquisition of meaningful carbon NMR spectroscopic data. MS (MALDI-TOF, +, DHB): calcd. for $[M - Cl]^{+}$ 798.8; found 799.0. $C_{30}H_{24}Cl_6N_2Pd_2$ (838.05): calcd. C 42.99, H 2.89, N 3.34; found C 42.22, H 3.11, N 3.24.

Preparation of 4 and 5 in $CDCl_3$/[D_5]py Solution: An orange solution or a suspension formed by mixing the dimeric cyclopalladated compound **2** or **3** (10 mg), respectively, in $CDCl_3$ (0.7 mL) was treated with 2 drops of deuteriated pyridine and shaken for a few seconds. The formation of a yellow or colourless solution (compound **4** or **5**, respectively) indicated the quantitative formation of the corresponding monomeric cyclopalladated derivative. Characterization data for compound **4**: ^{1}H NMR (400 MHz, $CDCl_3$ + [D_5]py, 298 K): δ = 7.70 (s, 1 H, CH=N), 7.29 (d, $^{3}J_{HH}$ = 8.0 Hz, 2 H, 12-H), 7.18 (dd, $^{3}J_{HH}$ = 7.4, $^{4}J_{HH}$ = 1.4 Hz, 1 H, 5-H), 7.11 (t, $^{3}J_{HH}$ = 8.0 Hz, 1 H, 13-H), 6.99 (t, $^{3}J_{HH}$ = 7.4 Hz, 1 H, 4-H), 6.90 (td, $^{3}J_{HH}$ = 7.5, $^{4}J_{HH}$ = 1.4 Hz, 1 H, 3-H), 6.20 (d, $^{3}J_{HH}$ = 7.5 Hz, 1 H, 2-H), 3.82 (t, $^{3}J_{HH}$ = 7.2 Hz, 2 H, 8-H), 3.51 (t, $^{3}J_{HH}$ = 7.3 Hz, 2 H, 9-H), 1.96 (s, 3 H, CH_3) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$ + [D_5]py, 298 K): δ = 178.1 (s, COO), 175.0

(s, CH=N), 156.6 (s, C-1), 146.7 (s, C-6), 135.8 (s, C-11), 134.7 (s, C-10), 132.6 (s, C-2), 130.0 (s, C-3), 128.3 (s, C-13), 128.2 (s, C-12), 127.3 (s, C-5), 124.1 (s, C-4), 57.4 (s, C-8), 32.1 (s, C-9), 24.8 (s, CH_3) ppm. Owing to the rapid exchange between the coordinated and free [D_5]pyridine, carbon NMR signals of the coordinated [D_5]pyridine were not observed. Characterization data for compound **5**: 1H NMR (300 MHz, $CDCl_3$ + [D_5]py, 298 K): δ = 7.43 (s, 1 H, CH=N), 7.26 (d, $^3J_{HH}$ = 7.4 Hz, partially obscured by residual solvent peak, 2 H, 12-H), 7.10 (d, $^3J_{HH}$ = 7.4 Hz, partially overlapped, 1 H, 5-H), 7.09 (t, $^3J_{HH}$ = 7.4 Hz, partially overlapped, 1 H, 13-H), 6.99 (td, $^3J_{HH}$ = 7.3, $^4J_{HH}$ = 1.0 Hz, 1 H, 4-H), 6.92 (t, $^3J_{HH}$ = 7.4 Hz, 1 H, 3-H), 6.16 (d, $^3J_{HH}$ = 7.2 Hz, 1 H, 2-H), 4.17 (t, $^3J_{HH}$ = 6.2 Hz, 2 H, 8-H), 3.63 (t, $^3J_{HH}$ = 6.3 Hz, 2 H, 9-H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, CDCl3 + [D_5]py, 298 K): δ = 175.0 (s, CH=N), 158.3 (s, C-1), 146.6 (s, C-6), 136.1 (s, C-11), 134.8 (s, C-10), 131.7 (s, C-2), 130.2 (s, C-3), 128.3 (s, C-13), 128.2 (s, C-12), 127.1 (s, C-5), 124.2 (s, C-4), 58.4 (s, C-8), 32.1 (s, C-9) ppm. Owing to the rapid exchange between the coordinated and free [D_5]pyridine, carbon NMR signals of the coordinated [D_5]pyridine were not observed.

Preparation of 6: A deep-yellow solution of acetato-bridged dimer 2 (56 mg, 0.06 mmol) in acetone (20 mL) was treated at room temperature with a stoichiometric amount of PPh_3 (33 mg, 0.13 mmol). Approximately 1 h later, the solution began to lighten. The reaction mixture was stirred for an additional hour, after which time volatiles were evaporated under reduced pressure. Trituration with diethyl ether (ca. 4 mL) rendered an extremely pale-yellow solid, which was filtered and air-dried (74 mg, 83% yield). IR (KBr): $\tilde{\nu}$ = 1620 (CH=N st), 1601 (C=O st), 1369 (C–O st), 1096 (q X-sensitive mode of coordinated PPh_3) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.83–7.78 (m, 6 H, *o*-C_6H_5), 7.71 (d, $^4J_{HP}$ = 7.4 Hz, 1 H, CH=N), 7.45–7.41 (m, 3 H, p-C_6H_5), 7.37 (td, $^3J_{HH}$ = 7.3, $^4J_{HP}$ = 1.8 Hz, 6 H, *m*-C_6H_5), 7.26 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, 12-H), 7.09 (t, $^3J_{HH}$ = 8.2 Hz, partially overlapped, 1 H, 13-H), 7.09 (dd, $^3J_{HH}$ = 7.3, $^4J_{HH}$ = 1.3 Hz, partially overlapped, 1 H, 5-H), 6.83 (t, $^3J_{HH}$ = 7.3 Hz, 1 H, 4-H), 6.51 (td, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.2 Hz, 1 H, 3-H), 6.41

(dd, $^{3}J_{HH}$ = 7.4, $^{4}J_{HP}$ = 5.4 Hz, 1 H, 2-H), 3.93–3.89 (m, 2 H, 8-H), 3.48 (t, $^{3}J_{HH}$ = 6.6 Hz, 2 H, 9-H), 1.33 (s, 3 H, CH_3) ppm. $^{1}H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.80 (d, $^{3}J_{HH}$ = 7.9 Hz, 6 H, *o*-C_6H_5), 7.71 (s, 1 H, CH=N), 7.46–7.34 (m, 9 H, *m*-C_6H_5 + *p*-C_6H_5), 7.26 (d, $^{3}J_{HH}$ = 7.9 Hz, 2 H, 12-H), 7.12–7.06 (m, 2 H, 5-H, 13-H), 6.83 (td, $^{3}J_{HH}$ = 7.3, $^{4}J_{HH}$ = 0.9 Hz, 1 H, 4-H), 6.51 (td, $^{3}J_{HH}$ = 7.6, $^{4}J_{HH}$ = 1.5 Hz, 1 H, 3-H), 6.41 (d, $^{3}J_{HH}$ = 7.8 Hz, 1 H, 2-H), 3.91 (t, $^{3}J_{HH}$ = 6.6 Hz, 2 H, 8-H), 3.48 (t, $^{3}J_{HH}$ = 6.6 Hz, 2 H, 9-H), 1.32 (s, 3 H, CH_3-COO) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K): δ = 177.0 (s, COO), 174.7 (d, $3J_{CP}$ = 3.6 Hz, CH=N), 155.7 (d, $^{2}J_{CP}$ = 4.0 Hz, C-1), 148.0 (s, C-6), 138.6 (d, $^{3}J_{CP}$ = 10.5 Hz, C-2), 136.0 (s, C-11), 135.5 (d, $^{2}J_{CP}$ = 12.2 Hz, *o*-C_6H_5), 135.0 (s, C-10), 130.6 (d, $^{1}J_{CP}$ = 49.0 Hz, *i*-C_6H_5), 130.5 (s, *p*-C_6H_5), 129.6 (d, $^{4}J_{CP}$ = 5.0 Hz, C-3), 128.2 (s, overlapped, C-12, C-13), 128.1 (d, $^{3}J_{CP}$ = 10.9 Hz, *m*-C_6H_5), 127.8 (s, C-5), 123.6 (s, C-4), 56.5 (s, C-8), 31.9 (s, C-9), 23.5 (s, CH_3) ppm. $^{31}P\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K): δ = 40.0 (s) ppm. MS (MALDI-TOF, +, DCTB): calcd. for $[M - OAc]^{+}$ 644.0; found 644.3. $C_{35}H_{30}Cl_2NO_2PPd$ (704.91): calcd. C 59.63, H 4.29, N 1.99; found C 59.60, H 4.45, N 2.00.

Preparation of 7: Chlorido-bridged dimer **3** (191 mg, 0.23 mmol) and PPh_3 (119 mg, 0.45 mmol) were combined in acetone (50 mL) and stirred for 48 h at room temperature. The yellow filtrate obtained was then concentrated to dryness, redissolved in a minimum amount of 100:0.5 chloroform/methanol and loaded onto a chromatography column packed with silica. The eluent polarity was gradually increased from 100:0.5 to 100:2 and 100:5. The coloured eluted band was concentrated to dryness with a rotary evaporator to afford a yellowish solid after the addition of diethyl ether (5 mL). The product was filtered off and air-dried (230 mg, 74% yield). IR (KBr): $\tilde{\nu}$ = 1624 (CH=N st), 1096 (q X-sensitive mode of coordinated PPh_3) cm^{-1}. Far-IR (PE): $\tilde{\nu}$ = 300 ($[Pd–Cl]_{terminal}$ st) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.76 (ddd, $^{3}J_{HP}$ = 11.6, $^{3}J_{HH}$ = 8.3, $^{4}J_{HH}$ = 1.2 Hz, 6 H, *o*-C_6H_5), 7.56 (d, $^{4}J_{HP}$ = 7.8 Hz, 1 H, CH=N), 7.46–7.42 (m, 3 H, *p*-C_6H_5), 7.39–7.34 (m, 6 H, *m*-

C_6H_5), 7.26 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, 12-H), 7.08 (t, $^3J_{HH}$ = 8.0 Hz, slightly overlapped, 1 H, 13-H), 7.05 (dd, $^3J_{HH}$ = 7.4, $^4J_{HH}$ = 1.5 Hz, slightly overlapped, 1 H, 5-H), 6.83 (td, $^3J_{HH}$ = 7.4, $^4J_{HH}$ = 0.8 Hz, 1 H, 4-H), 6.51 (td, $^3J_{HH}$ = 7.4, $^4J_{HH}$ = 1.1 Hz, 1 H, 3-H), 6.39 (app. t, $^3J_{HH}$ = $^4J_{HP}$ = 7.0 Hz, 1 H, 2-H), 4.27 (m, 2 H, 8-H), 3.58 (t, $^3J_{HH}$ = 6.3 Hz, 2 H, 9-H) ppm. $^1H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.78–7.74 (m, 6 H, *o*-C_6H_5), 7.56 (s, 1 H, CH=N), 7.43 (tt, $^3J_{HH}$ = 7.2, $^4J_{HH}$ = 1.5 Hz, 3 H, *p*-C_6H_5), 7.39–7.33 (m, 6 H, *m*-C_6H_5), 7.26 (d, $^3J_{HH}$ = 8.1 Hz, 2 H, 12-H), 7.10–7.03 (m, 2 H, 5-H, 13-H), 6.83 (td, $^3J_{HH}$ = 7.2, $^4J_{HH}$ = 0.9 Hz, 1 H, 4-H), 6.51 (td, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.6 Hz, 1 H, 3-H), 6.40 (d, $^3J_{HH}$ = 7.8 Hz, 1 H, 2-H), 4.28 (t, $^3J_{HH}$ = 6.2 Hz, 2 H, 8-H), 3.58 (t, $^3J_{HH}$ = 6.3 Hz, 2 H, 9-H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 298 K): δ = 175.0 (d, $^3J_{CP}$ = 3.1 Hz, CH=N), 158.4 (s, C-1), 147.9 (s, C-6), 138.1 (d, $^3J_{CP}$ = 10.3 Hz, C-2), 136.2 (s, C-11), 135.5 (d, $^2J_{CP}$ = 12.0 Hz, *o*-C_6H_5), 135.3 (s, C-10), 131.2 (d, $^1J_{CP}$ = 50.7 Hz, *i*-C_6H_5), 130.7 (d, $^4J_{CP}$ = 2.4 Hz, *p*-C_6H_5), 129.7 (d, $^4J_{CP}$ = 5.1 Hz, C-3), 128.2 (s, C-12), 128.1 (s, C-13), 128.0 (d, $^3J_{CP}$ = 10.9 Hz, m-C_6H_5), 127.6 (s, C-5), 123.7 (s, C-4), 57.5 (s, C-8), 32.4 (s, C-9) ppm. $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$, 298 K): δ = 42.0 (s) ppm. MS (MALDI-TOF, +, DHB): calcd. for $[M - Cl]^+$ 644.0; found 644.1; calcd. for [M – Cl – Pd]+ 538.1; found 538.1. $C_{33}H_{27}Cl_3NPPd$ (681.32): calcd. C 58.17, H 3.99, N 2.06; found C 58.41, H 4.12, N 2.09.

Preparation of 8: 1,2-Bis(diphenylphosphanyl)ethane (44 mg, 0.11 mmol) was added to a stirred suspension of chlorido-bridged dimer **3** (90 mg, 0.11 mmol) in chloroform (30 mL) under nitrogen. The mixture was allowed to stand at room temperature for 6 h. After this period, the resulting light-yellow solution was filtered through a 2-cm-thick pad of silica and washed through with acetone and then dichloromethane. After removal of the solvent, the desired product precipitated on addition of diethyl ether (5 mL). The pale-yellow solid obtained was isolated by filtration and airdried (102 mg, 77% yield). IR (KBr): $\tilde{\nu}$ = 1626 (CH=N st), 1101 (q X-sensitive mode of coordinated $PPh_2CH_2CH_2PPh_2$) cm^{-1}. Far-IR (PE): $\tilde{\nu}$ = 296 ($[Pd–Cl]_{terminal}$ st) $cm^{-1.}$ ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.01–7.96 (m, 4

608 H, *o*-C_6H_5), 7.54–7.52 (m, 1 H, CH=N), 7.41–7.33 (m, 6 H, *m*-C_6H_5, *p*-C_6H_5), 7.25 (d, $^3J_{HH}$
609 = 8.0 Hz, partially obscured by residual solvent peak, 2 H, 12-H), 7.08 (dd, $^3J_{HH}$ = 8.4, $^3J_{HH}$
610 = 7.7 Hz, 1 H, 13-H), 6.99 (dd, $^3J_{HH}$ = 7.4, $^4J_{HH}$ = 1.4 Hz, 1 H, 5-H), 6.78 (td, $^3J_{HH}$ = 7.4,
611 $^4J_{HH}$ = 0.7 Hz, 1 H, 4-H), 6.49 (td, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.4 Hz, 1 H, 3-H), 6.33–6.30 (m, 1 H,
612 2-H), 4.25 (br. s, 2 H, 8-H), 3.58 (t, $^3J_{HH}$ = 6.3 Hz, 2 H, 9-H), 2.97 (d, $^2J_{HP}$ = 2.1 Hz, 2 H,
613 CH_2–P) ppm. $^1H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.99 (dd, $^3J_{HH}$ = 7.9, $^4J_{HH}$ =
614 1.6 Hz, 4 H, *o*-C_6H_5), 7.53 (s, 1 H, CH=N), 7.42–7.31 (m, 6 H, *m*-C_6H_5, *p*-C_6H_5), 7.25 (d,
615 $^3J_{HH}$ = 8.0 Hz, 2 H, 12-H), 7.08 (dd, $^3J_{HH}$ = 8.6, $^3J_{HH}$ = 7.4 Hz, 1 H, 13-H), 6.99 (dd, $^3J_{HH}$
616 = 7.4, $^4J_{HH}$ = 1.5 Hz, 1 H, 5-H), 6.78 (td, $^3J_{HH}$ = 7.4, $^4J_{HH}$ = 1.0 Hz, 1 H, 4-H), 6.49 (td, $^3J_{HH}$
617 = 7.6, $^4J_{HH}$ = 1.6 Hz, 1 H, 3-H), 6.32 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, 2-H), 4.26 (t, $^3J_{HH}$ = 6.3 Hz, 2
618 H, 8-H), 3.58 (t, $^3J_{HH}$ = 6.3 Hz, 2 H, 9-H), 2.97 (s, 2 H, CH_2-P) ppm. $^{13}C\{^1H\}$ NMR (101
619 MHz, $CDCl_3$, 298 K): δ = 174.7 (br. s, CH=N), 158.5 (d, $^2J_{CP}$ = 2.3 Hz, C-1), 147.7 (s, C-
620 6), 137.7–137.6 (m, C-2), 136.2 (s, C-11), 135.2 (s, C-10), 134.9 (app. t, J_{CP} = 6.2 Hz, *o*-
621 C_6H_5), 130.8 (s, *p*-C_6H_5), 129.9–129.8 (m, C-3), 128.5–128.2 (m, overlapped, C-12, C-13,
622 *m*-C_6H_5), 127.5 (s, C-5), 123.6 (s, C-4), 56.7 (s, C-8), 32.3 (s, C-9), 25.9 (br. s, CH_2-P) ppm.
623 The carbon signal of i-C_6H_5 could not be identified owing to its weak intensity. $^{31}P\{^1H\}$
624 NMR (101 MHz, $CDCl_3$, 298 K): δ = 34.7 (s) ppm. MS (MALDI-TOF, +, DHB): calcd. for
625 $[M - Cl]^+$ 1197.0; found 1196.8; calcd. For $[Pd(L)(PP)]^+$ 780.1; found 780.2.
626 $C_{56}H_{48}Cl_6N_2P_2Pd_2$ (1236.47): calcd. C 54.40, H 3.91, N 2.26; found C 53.82, H 3.64, N
627 2.35.

628

629 **Preparation of 9:** A Schlenk tube was loaded with chlorido-bridged dimer **3** (89 mg,
630 0.11 mmol) and then evacuated and backfilled with nitrogen (three times). Acetone (30 mL)
631 was then added to suspend the solid. *trans*-1,2-Bis(diphenylphosphanyl)ethylene (42 mg,
632 0.10 mmol) was the added to give a yellow solution. After 3 h of stirring, the solvent was
633 removed under reduced pressure. Crude mixture was then subjected to column
634 chromatography (SiO_2) eluting with 100:2 to 100:5 dichloromethane/methanol to yield the
635 product as a pale-yellow solid (117 mg, 89% yield). IR (KBr): $\tilde{\nu}$ = 1624 (CH=N st), 1099 (q
636 X-sensitive mode of coordinated *trans* - $Ph_2PCH=CHPPh_2$) cm^{-1}. Far-IR (PE): $\tilde{\nu}$ = 302

([Pd–Cl]$_{terminal}$ st) cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 7.83–7.78 (m, 4 H, *o*-C_6H_5), 7.55–7.53 (m, 1 H, CH=N), 7.48 (t, $^{3}J_{HH}$ = 7.4 Hz, 2 H, *p*-C_6H_5), 7.40 (t, $^{3}J_{HH}$ = 7.3 Hz, 4 H, *m*-C_6H_5), 7.27 (d, $^{3}J_{HH}$ = 7.9 Hz, 2 H, 12-H), 7.12 (dd, $^{3}J_{HH}$ = 8.5, $^{3}J_{HH}$ = 7.5 Hz, 1 H, 13-H), 7.06 (dd, $^{3}J_{HH}$ = 7.4, $^{4}J_{HH}$ = 1.4 Hz, partially overlapped, 1 H, 5-H), 7.01 (app. t, J_{HP} = 20.3 Hz, partially overlapped, 1 H, =CH–P), 6.85 (td, $^{3}J_{HH}$ = 7.4, $^{4}J_{HH}$ = 0.8 Hz, 1 H, 4-H), 6.53 (td, $^{3}J_{HH}$ = 7.6, $^{4}J_{HH}$ = 1.5 Hz, 1 H, 3-H), 6.40–6.36 (m, 1 H, 2-H), 4.24 (br. s, 2 H, 8-H), 3.56 (t, $^{3}J_{HH}$ = 6.1 Hz, 2 H, 9-H) ppm. ^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.90 (d, $^{3}J_{HH}$ = 8.1 Hz, 4 H, *o*-C_6H_5), 7.50 (s, 1 H, CH=N), 7.43–7.34 (m, 6 H, m-C_6H_5, *p*-C_6H_5), 7.24 (d, $^{3}J_{HH}$ = 7.8 Hz, 2 H, 12-H), 7.11–7.01 (m, 2 H, 5-H, 13-H), 6.89 (s, 1 H, =CH–P), 6.82 (t, $^{3}J_{HH}$ = 7.4 Hz, 1 H, 4-H), 6.52 (t, $^{3}J_{HH}$ = 7.5 Hz, 1 H, 3-H), 6.40 (d, $^{3}J_{HH}$ = 7.7 Hz, 1 H, 2-H), 4.29 (t, $^{3}J_{HH}$ = 6.0 Hz, 2 H, 8-H), 3.59 (t, $^{3}J_{HH}$ = 6.0 Hz, 2 H, 9-H) ppm. ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 298 K): δ = 175.7 (d, $^{3}J_{CP}$ = 1.8 Hz, CH=N), 158.8 (s, C-1), 148.6 (s, C-6), 140.3-139.9 (m, =CH-P), 138.2 (app. t, J_{CP} = 5.2 Hz, C-2), 136.7 (s, C-11), 135.8 (app. t, J_{CP} = 6.3 Hz, o-C_6H_5), 135.6 (s, C-10), 131.8 (s, *p*-C_6H_5), 130.5–130.4 (m, C-3), 129.1 (app. t, J_{CP} = 5.5 Hz,

Preparation of 10: Compound **10** was synthesized under nitrogen by adding 4,4'-bipyridine (0.0200 g, 0.13 mmol) to a suspension of chlorido-bridged dimer **3** (106 mg, 0.13 mmol) in chloroform (30 mL). After 3 h of stirring at room temperature, the resulting yellow solution was concentrated under reduced pressure. Upon addition of diethyl ether (ca. 5 mL) a yellow solid precipitated, which was recovered by filtration, thoroughly washed with toluene (5x 1 mL) and acetone (3x 0.5 mL) and finally dried in vacuo (95 mg, 75% yield). IR (KBr): $\tilde{\nu}$ = 1608 (CH=N st and st equivalent to the ν_4 stretching of pyridine for 4,4'-bipyridine) cm^{-1}. Far-IR (PE): $\tilde{\nu}$ = 309 ([Pd–Cl]$_{terminal}$ st) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 9.11 (d, $^{3}J_{HH}$ = 6.5 Hz, 2 H, 14-H), 7.72 (d, $^{3}J_{HH}$ = 6.4 Hz, 2 H, 15-H), 7.45 (s, 1 H, CH=N), 7.23 (d, $^{3}J_{HH}$ = 8.0 Hz, 2 H, 12-H), 7.13–7.09 (m, 2 H, 5-H, 13-H),

7.02 (t, $^{3}J_{HH}$ = 7.4 Hz, slightly overlapped, 1 H, 4-H), 6.97 (td, $^{3}J_{HH}$ = 7.6, $^{4}J_{HH}$ = 1.4 Hz, slightly overlapped, 1 H, 3-H), 6.26 (d, $^{3}J_{HH}$ = 7.4 Hz, 1 H, 2-H), 4.18 (t, $^{3}J_{HH}$ = 6.3 Hz, 2 H, 8-H), 3.63 (t, $^{3}J_{HH}$ = 6.4 Hz, 2 H, 9-H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K): δ = 175.2 (s, CH=N), 158.3 (s, C-1), 154.2 (s, C-14), 146.6 (s, C-6), 145.9 (s, C-16), 136.1 (s, C-11), 134.7 (s, C-10), 131.6 (s, C-2), 130.4 (s, C-3), 128.4 (s, C-13), 128.3 (s, C-12), 127.3 (s, C-5), 124.5 (s, C-4), 123.0 (s, C-15), 58.6 (s, C-8), 32.1 (s, C-9) ppm. MS (ESI, +, H_2O/CH_3CN, 1:1): calcd. for $[M - Cl + CH_3CN]^+$ 995.9; found 995.9; calcd. for $[M - Cl]^+$ 954.9; found 954.9; calcd. For $[Pd(L)(NN)]^+$ 538.0; found 538.0; calcd. for $[Pd(L)(NN)(CH_3CN)]^+$ 579.0; found 579.0; calcd. for $[Pd(L)(CH_3CN)]^+$ 423.0; found 423.0. $C_{40}H_{32}Cl_6N_4Pd_2$ (994.24): calcd. C 48.32, H 3.24, N 5.64; found C 47.60, H 3.25, N 5.58.

Preparation of 11: A suspension of **3** (0.0804 g, 0.096 mmol) in chloroform (30 mL) was treated with 2,2'-(ethylenedioxy)bis(ethylamine) (0.0142 g, 14.00 μL, 0.096 mmol). The reaction mixture was stirred at room temperature for around 3 h under nitrogen. The resulting yellow solution was concentrated to dryness. The subsequent addition of diethyl ether (5 mL) led to a light-yellow solid, which was filtered off and dried under vacuum (79 mg, 83% yield). IR (KBr): $\tilde{\nu}$ = 3321 (NH_2 as st), 3263 (NH_2 sym st), 1613 (CH=N st) cm–1. Far-IR (PE): $\tilde{\nu}$ = 296 ($[Pd–Cl]_{terminal}$ st) cm^{-1}. ^{1}H NMR (400 MHz, CDCl3, 298 K): δ = 7.29 (s, 1 H, CH=N), 7.23 (d, $^{3}J_{HH}$ = 8.0 Hz, 2 H, 12-H), 7.11–7.05 (m, 3 H, 3-H, 5-H, 13-H), 7.00 (app. t, $^{3}J_{HH}$ = 7.1 Hz, 2 H, 2-H, 4-H), 3.97 (t, $^{3}J_{HH}$ = 6.4 Hz, 2 H, 8-H), 3.77 (t, $^{3}J_{HH}$ = 4.6 Hz, 2 H, 15-H), 3.71 (s, 2 H, 16-H), 3.50 (t, $^{3}J_{HH}$ = 6.5 Hz, 2 H, 9-H), 3.42-3.39 (br. t, 2 H, NH_2), 3.31–3.26 (m, 2 H, 14-H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K): δ = 174.2 (s, CH=N), 155.9 (s, C-1), 147.0 (s, C-6), 136.0 (s, C-11), 134.8 (s, C-10), 130.1 (s, overlapped, C-2, C-3), 128.3 (s, C-13), 128.2 (s, C-12), 127.4 (s, C-5), 124.4 (s, C-4), 70.7 (s, C-15), 70.4 (s, C-16), 58.5 (s, C-8), 45.6 (s, C-14), 32.0 (s, C-9) ppm. MS (ESI, +, H_2O/CH_3CN, 1:1): calcd. for $[M - Cl]^+$ 947.0; found 947.0; calcd. for $[Pd(L)(CH_3CN)_2]^+$ 464.0; found 464.0; calcd. For $[Pd(L)(CH_3CN)]^+$ 423.0; found 423.0;

690 calcd. for $[Pd(L)]^+$ 381.9; found 381.9; $C_{36}H_{40}Cl_6N_4O_2Pd_2$ (986.26): calcd. C 43.84, H
691 4.09, N 5.68; found C 43.62, H 3.89, N 5.51.

692

693 **Preparation of 12:** A Schlenk tube was loaded with dimer **3** (75 mg, 0.09 mmol)
694 and then evacuated and backfilled with nitrogen (three times). Chloroform (24 mL) was then
695 added to suspend the solid. A chloroform solution of 1,3-diamino-2-propanol (0.09 m, 1 mL)
696 was then added and the crude was stirred for 4 h at room temperature. After this period, the
697 solvent was removed in vacuo and diethyl ether (5 mL) was added to furnish the desired
698 product as a yellow solid, which was recovered by filtration (75 mg, 90% yield). The sample
699 must be stored under nitrogen and kept under refrigeration to avoid decomposition. IR
700 (KBr): $\tilde{\nu}$ = 3385, 3295, 3236 (NH_2 and OH stretchings), 1612 (CH=N st) cm^{-1}. Far-IR (PE):
701 $\tilde{\nu}$ = 300 ($[Pd–Cl]_{terminal}$ st) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.38 (s, 2 H,
702 CH=N), 7.25 (d, $^3J_{HH}$ = 8.0 Hz, partially obscured by residual solvent peak, 4 H, 12-H),
703 7.15 (td, $^3J_{HH}$ = 7.4, $^4J_{HH}$ = 1.6 Hz, 2 H, 3-H), 7.11–7.00 (m, 6 H, 4-H, 5-H, 13-H), 6.93
704 (d, $^3J_{HH}$ = 7.5 Hz, 2 H, 2-H), 5.38 (br. s, 1 H, OH), 4.72 (br. s, 1 H, CH-OH), 4.05–3.94 (m,
705 4 H, 8-H), 3.48 (t, $^3J_{HH}$ = 6.8 Hz, 4 H, 9-H), 3.45–3.39 (m, slightly overlapped, 2 H, NH_2),
706 3.31–3.27 (br. t, 2 H,NH_2), 3.19–3.12 (m, 2 H, CH_2-NH_2), 2.97–2.89 (m, 2 H, CH_2-NH_2)
707 ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 298 K, under nitrogen): δ = 174.3 (s, CH=N), 155.7
708 (s, C-1), 146.7 (s, C-6), 136.0 (s, C-11), 134.7 (s, C-10), 130.6 (s, C-3), 130.2 (s, C-2), 128.3
709 (s, C-13), 128.2 (s, C-12), 127.4 (s, C-5), 124.4 (s, C-4), 70.7 (s, CH-OH), 58.3 (s, C-8), 48.6
710 (s, CH_2-NH_2), 32.0 (s, C-9) ppm. MS (MALDI-TOF, +, DHB): calcd. for $[Pd(L)(NN)]^+$
711 472.0; found 472.0. $C_{33}H_{34}Cl_6N_4OPd_2$ (928.18): calcd. C 42.70, H 3.69, N 6.04; found C
712 42.50, H 3.58, N 5.96.

713

714 **Theoretical Calculations:** All DFT calculations were carried out with the Gaussian
715 03[38] package of programs using the B3LYP hybrid functional.[39] The basis set was
716 chosen as follows: for Pd, Br and I LANL2DZ was used[40] with an effective core potential
717 to replace the 36 innermost electrons of Pd and I and the 18 innermost electrons of Br; a

polarization function was added for Br and I.[41] For H, C, N, O, P, and Cl the 6-31G(d) basis set including polarization functions for non-hydrogen atoms[42] was used. Geometry optimizations and frequency calculations were performed in vacuo with no imposed symmetry restrictions. Solvent effects were calculated on the pre-optimized geometries using the C-PCM model.[43]

X-ray Diffraction Studies: Yellow single crystals of **2, 8**·$2CH_2Cl_2$, **10**·$4CHCl_3$ and **11**·$2CH_2Cl_2$ were obtained by slow evaporation of the solvent of a diethyl ether solution of **2**, a dichloromethane solution of 8 and a chloroform solution of **10** and by slow diffusion of hexanes into a CH_2Cl_2 solution of **11**, respectively. In each case, a prismatic crystal was mounted on a MAR345 diffractometer with an image plate detector. Unit cell parameters were determined from 586 reflections for **2**, 171 for **8**·$2CH_2Cl_2$, 101 for **10**·$4CHCl_3$ and 67 for **11**·$2CH_2Cl_2$ ($3 < \theta < 31°$) and refined by least-squares methods. Intensities were collected with graphite-monochromatized Mo-Kα radiation. For **2**, 7898 reflections were measured in the range $2.51 \leq \theta \leq 31.62°$, 6828 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. For **8**·$2CH_2Cl_2$, 15791 reflections were measured in the range $2.79 \leq \theta \leq 32.45°$, 8393 were non-equivalent by symmetry [Rint(I) = 0.049] and 5358 were assumed as observed applying the condition $I > 2\sigma(I)$. For **10**·$4CHCl_3$, 15981 reflections were measured in the range $2.67 \leq \theta \leq 32.41°$, 8639 were non-equivalent by symmetry [$R_{int}(I) = 0.03$] and 4761 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. For **11**·$2CH_2Cl_2$, 13416 reflections were measured in the range $2.89 \leq \theta \leq 32.38°$, 7132 were non-equivalent by symmetry [$R_{int}(I) = 0.071$] and 2521 were assumed as observed applying the condition $I > 2\sigma(I)$. Lorentzian polarization and absorption corrections were made in all cases. The structures were solved by direct methods for **2**, **10**·$4CHCl_3$ and **11**·$2CH_2Cl_2$ and by a Patterson synthesis for **8**·$2CH_2Cl_2$ using the SHELXS computer program[44] and refined by full-matrix least-squares methods with the SHELX97 computer program.[45] The function minimized was $\Sigma w||F_o|^2-|F_c|^2|^2$, $w = [\sigma^2(I) + (0.0688P)^2 +$

3.3096P]–1 for **2**, $w = [\sigma^2(I) + (0.0483P)^2 + 2.7466P]^{-1}$ for **8**·2CH_2Cl_2, w = [$^{\sigma 2}(I)$ + $(0.0276P)^2$]–1 for **10**·4$CHCl_3$ and $w = [\sigma^2(I) + (0.0471P)^2 + 2.9985P]^{-1}$ for **11**·2CH_2Cl_2, and $P = (|F_o|^2 + 2|F_c|^2)/3$. Values of f, *f*' and *f*'' were taken from the International Tables of X-ray Crystallography.[46] All H atoms were computed and refined, using a riding model, with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atom to which they are linked. Table 2 gives selected crystal data and structure refinement for **2**, **8**·2CH_2Cl_2, **10**·4$CHCl_3$ and **11**·2CH_2Cl_2.

CCDC-780754 (for **2**), -780755 (for **8**·2CH_2Cl_2), -780756 (for **10**·4$CHCl_3$) and -780757 (for **11**·2CH_2Cl_2) contain the 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.

ACKNOWLEDGEMENTS

We are grateful to the Ministerio de Ciencia y Tecnología (MCYT) for financial support (grant number CTQ2009-11501/BQU).

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933 **Table 1** Energy differences between *cis*- and *trans*-***N,L*** stereoisomers of compounds **A**.

934 Positive values indicate that the *trans*-***N,L*** isomer is more stable.[a]

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Entry	X	L	ΔE [kcal mol^{-1}]								
			ΔE(v)	ΔE(a)	ΔE(c)	ΔH(v)	ΔH(a)	ΔH(c)	ΔG(v)	ΔG(a)	ΔG(c)
1	OAc	py	5.90	0.25	1.45	5.79	0.14	1.34	3.53	–2.12	–0.92
2	OAc	NH_3	–0.88	–0.86	–0.64	–1.02	–1.01	–0.78	–1.07	–1.05	–0.83
3	OAc	PH_3	5.60	5.31	5.46	5.26	4.98	5.12	4.85	4.57	4.71
4	Cl	py	0.02	1.14	0.96	–0.09	1.04	0.86	–0.71	0.41	0.23
5	Cl	NH_3	0.13	2.25	1.99	–0.10	2.02	1.75	–0.44	1.68	1.42
6	Cl	PH_3	3.92	4.90	4.81	3.64	4.62	4.53	3.21	4.19	4.09
7	Br	py	–0.43	0.63	0.53	–0.56	0.50	0.40	–1.15	–0.08	–0.19
8	Br	NH_3	–0.31	1.70	1.35	–0.57	1.44	1.09	–0.91	1.10	0.75
9	Br	PH_3	3.66	4.52	4.43	3.34	4.19	4.10	2.81	3.67	3.58
10	I	py	–0.97	0.27	0.03	–1.11	0.14	–0.11	–1.67	–0.43	–0.67
11	I	NH_3	–0.87	1.07	0.82	–1.13	0.81	0.57	–1.44	0.50	0.25
12	I	PH_3	3.22	4.01	3.94	2.92	3.71	3.63	2.42	3.20	3.13

[a] ΔE = electronic energy$_{cis\text{-}N,L}$ – electronic energy$_{trans\text{-}N,L}$, ΔH = absolute enthalpy$_{cis\text{-}N,L}$ – absolute enthalpy$_{trans\text{-}N,L}$, ΔG = absolute Gibbs free energy$_{cis\text{-}N,L}$ – absolute Gibbs free energy$_{trans\text{-}N,L}$. v = vacuum, a = acetone solution, c = chloroform solution.

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Table 2. Selected crystal data and structure refinement for 2, 8·2(CH_2Cl_2), **10**·4($CHCl_3$) and **11**·2(CH_2Cl_2).

	2	**8**·2CH_2Cl_2	**10**·4$CHCl_3$	**11**·2CH_2Cl_2
Formula	$C_{34}H_{30}Cl_4N_2O_4Pd_2$	$C_{58}H_{52}Cl_{10}N_2P_2Pd_2$	$C_{44}H_{36}Cl_{18}N_4Pd_2$	$C_{38}H_{44}Cl_{10}N_4O_2Pd_2$
Formula mass	885.20	1406.26	1471.67	1156.07
Crystal size [mm³]	0.15 × 0.09 × 0.08	0.20 × 0.10 × 0.09	0.09 × 0.08 × 0.07	0.09 × 0.08 × 0.08
Temperature [K]	203(2)	293(2)	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	8.950(4)	10.795(6)	10.690(7)	9.865(8)
b [Å]	12.202(4)	11.908(5)	10.971(4)	11.733(7)
c [Å]	17.117(5)	14.377(6)	14.073(7)	12.634(6)
α [°]	71.41(2)	68.62(4)	97.06(4)	117.09(4)
β [°]	82.22(2)	68.40(3)	109.40(3)	99.95(4)
γ [°]	83.22(2)	65.29(3)	104.52(3)	103.75(5)
Volume [Å³]	1749.9(11)	1511.7(12)	1468.1(13)	1196.0(16)
Z	2	1	1	1
Calcd. density [Mg m⁻³]	1.680	1.545	1.665	1.605
Absorption coefficient [mm⁻¹]	1.373	1.128	1.467	1.347
F(000)	880	706	726	578
θ range for data collection [°]	2.51 to 31.62	2.79 to 32.45	2.67 to 32.41	2.89 to 32.38
Limiting indices	$-11 \le h \le 10$ $-15 \le k \le 16$ $0 \le l \le 23$	$-14 \le h \le 16$ $-16 \le k \le 17$ $-21 \le l \le 21$	$-16 \le h \le 16$ $-16 \le k \le 13$ $-17 \le l \le 17$	$-14 \le h \le 14$ $-17 \le k \le 17$ $-18 \le l \le 18$
Reflections collected	7898	15791	15981	13416
Reflections unique	7898	8393	8639	7132
R(int)	0.0557	0.0496	0.0320	0.0707
Completeness to θ = 25.00° [%]	87.3	93.6	93.5	93.7
Absorption correction	empirical			
Max. and min. transmission	0.87 and 0.84	0.89 and 0.87	0.86 and 0.84	0.91 and 0.89
Refinement method	full-matrix least-squares on F^2			
Data / restraints / parameters	7898 / 1 / 416	8393 / 5 / 286	8639 / 4 / 325	7132 / 13 / 271
Goodness-of-fit on F^2	1.132	1.121	0.870	1.316
Final R indices	R_1 = 0.0444	R_1 = 0.0744	R_1 = 0.0399	R_1 = 0.0741
[$I > 2\sigma(I)$]	wR_2 = 0.1414	wR_2 = 0.1607	wR_2 = 0.0746	wR_2 = 0.1572
R indices	R_1 = 0.0508	R_1 = 0.1216	R_1 = 0.0858	R_1 = 0.0811
(all data)	wR_2 = 0.1444	wR_2 = 0.1824	wR_2 = 0.0822	wR_2 = 0.1605
Largest diff. peak and hole [e Å⁻³]	1.108 and –0.884	1.261 and –0.776	0.381 and –0.422	1.316 and –0.770

Figures Captions

Figure 1. Most common structural formulae of *endo* five-membered *ortho*-cyclopalladated imines.

Figure 2. *endo* and *exo* structural isomers of *ortho*-cyclopalladated benzyl-benzylidene-amine.

Figure 3. Structural formulae of compounds with a bridging bidentate ligand obtained by reactions between mono- or dicyclopalladated compounds and bidentate Lewis bases in a Pd/bidentate Lewis base molar ratio of 2:1. In general, L_2 is a biphosphane, X is Cl, Y is PF_6^- and Pd(C-N) is an *endo* five-membered *ortho*-cyclopalladated imine.

Scheme 1. Reagents and conditions: i) Pd(OAc)2 (stoichiometric), HOAc, 60 °C, 5h, under N2; ii) LiCl (excess), acetone, room temp., 24h; iii) **4** and **5**: [D_5]py (excess), $CDCl_3$, room temp.; **6**: PPh3 (stoichiometric), acetone, room temp., 2h; **7**: PPh_3 (stoichiometric), acetone, room temp., 48h; iv) **8**: $Ph_2PCH_2CH_2PPh_2$ (stoichiometric), $CHCl_3$, room temp., 6h, under N2; **9**: trans-$Ph_2PCH{=}CHPPh_2$ (stoichiometric), acetone, room temp., 3h, under N2; **10**: 4,4'-bipyridine (stoichiometric), $CHCl_3$, room temp., 3h, under N_2; **11**: $NH_2CH_2CH_2OCH_2$- $CH_2OCH_2CH_2NH_2$ (stoichiometric), $CHCl_3$, room temp.,3 h, under N_2; **12**: $NH_2CH_2(CHOH)CH_2NH_2$ (stoichiometric), $CHCl_3$, room temp., 4h, under N2.

Figure 4. A) *trans*-folded structure of compound **2**. B) Planar *trans* and *cis* geometrical isomers of compound **3**. C-N stands for $C_6H_4CH{=}N(CH_2)2(2,6\text{-}Cl_2C_6H_3)$.

Figure 5. ORTEP view of the X-ray molecular structure of compound **2** and labelling of the atoms. Selected bond lengths [Å] and bond angles [°]: Pd1–C1 1.979(4), Pd1–N1 2.114(4), Pd1–O1 2.126(3), Pd1–O3 2.147(3), Pd2–C21 1.998(5), Pd2–N2 2.028(4), Pd2–O4 2.058(3), Pd2–O2 2.194(3), C21–Pd2–N2 80.10(19), C21–Pd2–O4 93.77(18), N2–Pd2–O4 173.66(15), C1–Pd1–N1 80.38(16), C1–Pd1–O1 92.62(16), N1–Pd1–O1 172.69(13), C1–Pd1–O3 176.80(15), N1–Pd1–O3 97.68(14), O1–Pd1–O3 89.41(13), C21–Pd2–O2 173.80(15), N2–Pd2–O2 95.93(15), O4–Pd2–O2 90.31(14).

Figure 6. ORTEP view of the X-ray molecular structure of compound **8** and labelling of the atoms. Selected bond lengths [Å] and bond angles [°]: Pd–C1 2.068(3), Pd–N1 2.086(5), Pd–P 2.2647(17), Pd–Cl1 2.387(2), C1–Pd–N1 80.16(18), C1–Pd–P 94.22(12), N1–Pd–P 174.36(16), C1–Pd–Cl1 171.49(11), N1–Pd–Cl1 91.38(16), P–Pd–Cl1 94.24(7).

Figure 7. ORTEP view of the X-ray molecular structure of compound **10** and labelling of the atoms. Selected bond lengths [Å] and bond angles [°]: Pd1–C1 2.010(3), Pd1–N1 2.028(3), Pd1–N2 2.054(3), Pd1–Cl1 2.4092(13), C1–Pd1–N1 81.01(11), C1–Pd1–N2 95.66(11), N1–Pd1–N2 176.02(8), C1–Pd1–Cl1 174.06(8), N1–Pd1–Cl1 95.71(7), N2–Pd1–Cl1 87.80(7).

Figure 8. ORTEP view of the X-ray molecular structure of compound **11** and labelling of the atoms. Selected bond lengths [Å] and bond angles [°]: Pd2–C1 2.001(6), Pd2–N2 2.073(5), Pd2–N1 2.092(5), Pd2–Cl1 2.410(2), C1–Pd2–N2 94.3(3), C1–Pd2–N1 79.7(3), N2–Pd2–N1 172.9(2), C1–Pd2–Cl1 175.9(2), N2–Pd2–Cl1 88.74(16), N1–Pd2–Cl1 97.02(16).

Figure 9. Schematic structural formulae of compounds **a**–**d**. Compounds **a**, **b** and **d1** are *endo* cyclopalladated compounds with an aromatic- or ferrocenylic-metallated carbon atom. Compound **d2** is an *exo* compound with a naphthylic-metallated carbon atom.

Figure 10. Structures of the *cis*- and *trans*-***N,L*** stereoisomers of compounds **A**.

994 **Figure 1**

995

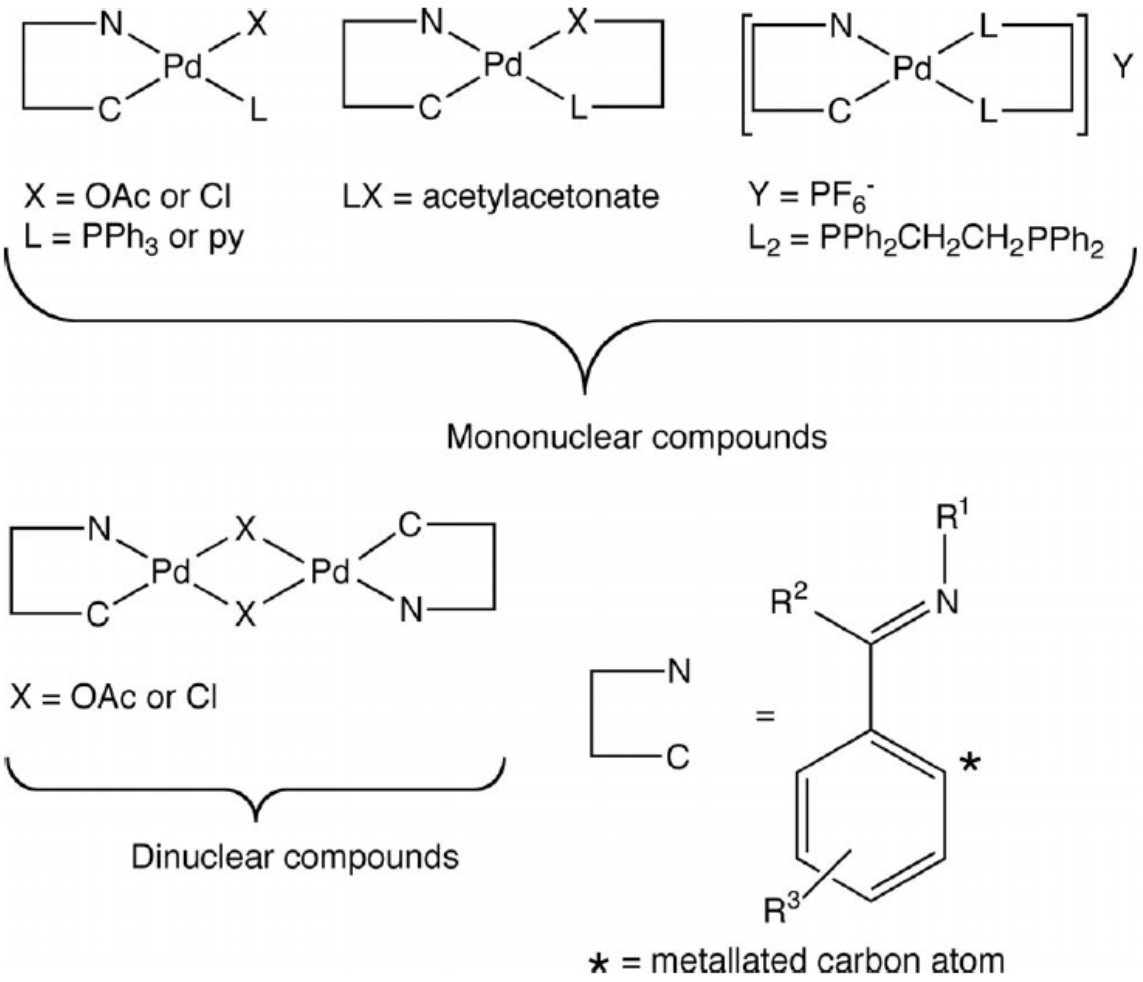

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Figure 2

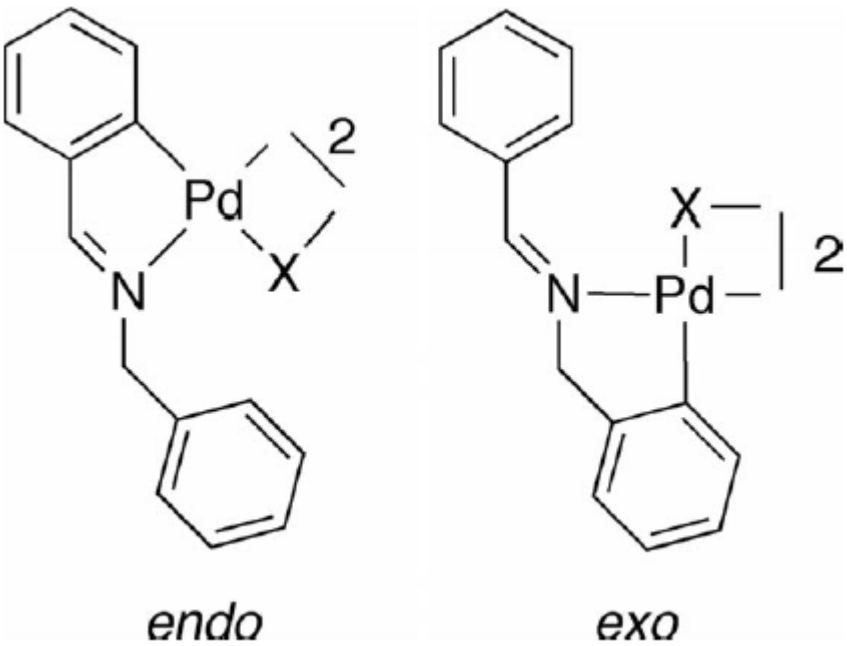
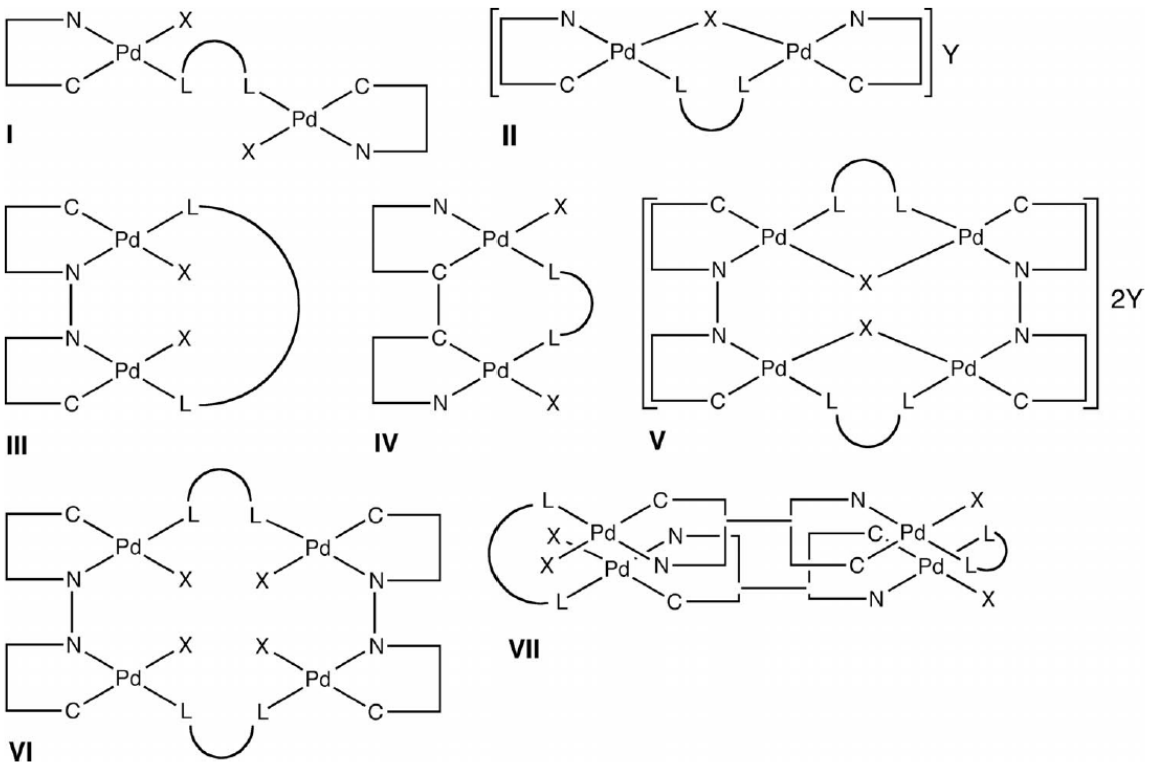


Figure 3



Scheme 1

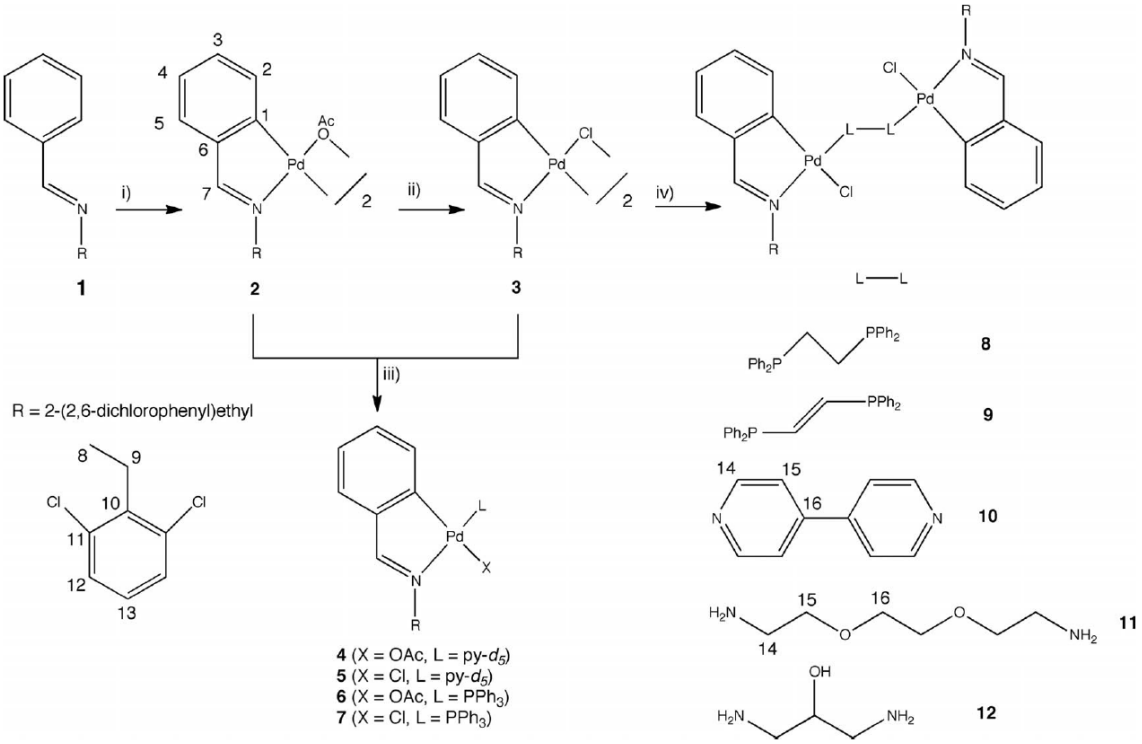

i)
ii)
iii)
iv)
R = 2-(2,6-dichlorophenyl)ethyl
1
2
3
4 (X = OAc, L = py-d_5)
5 (X = Cl, L = py-d_5)
6 (X = OAc, L = PPh_3)
7 (X = Cl, L = PPh_3)
8
9
10
11
12

Figure 4

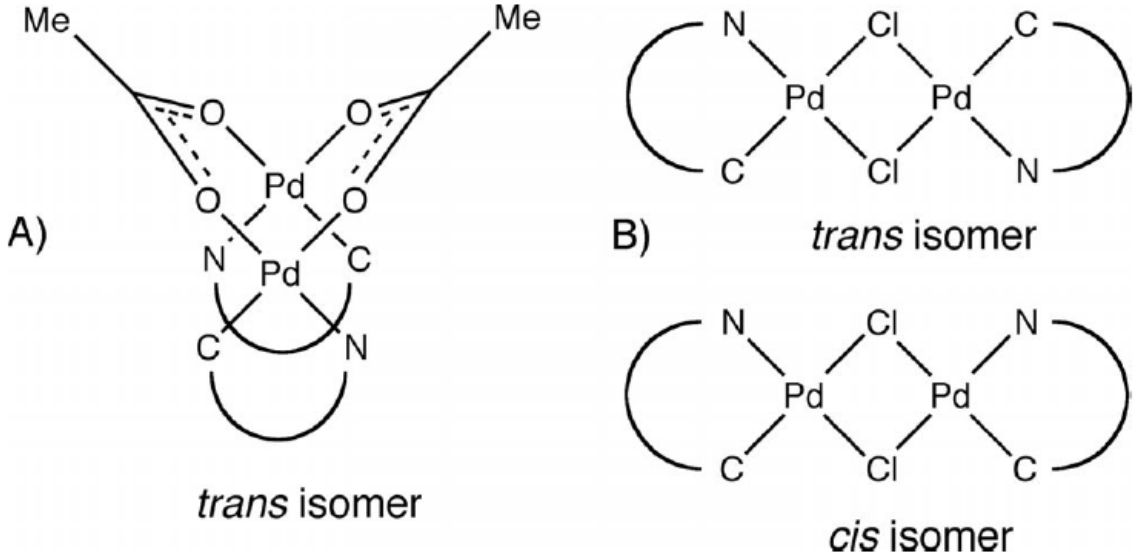

Me
Me
O
O
O
O
Pd
N
Pd
C
C
N
A)
trans isomer
N
Cl
C
Pd
Pd
C
Cl
N
B)
trans isomer
N
Cl
N
Pd
Pd
C
Cl
C
cis isomer

Figure 5

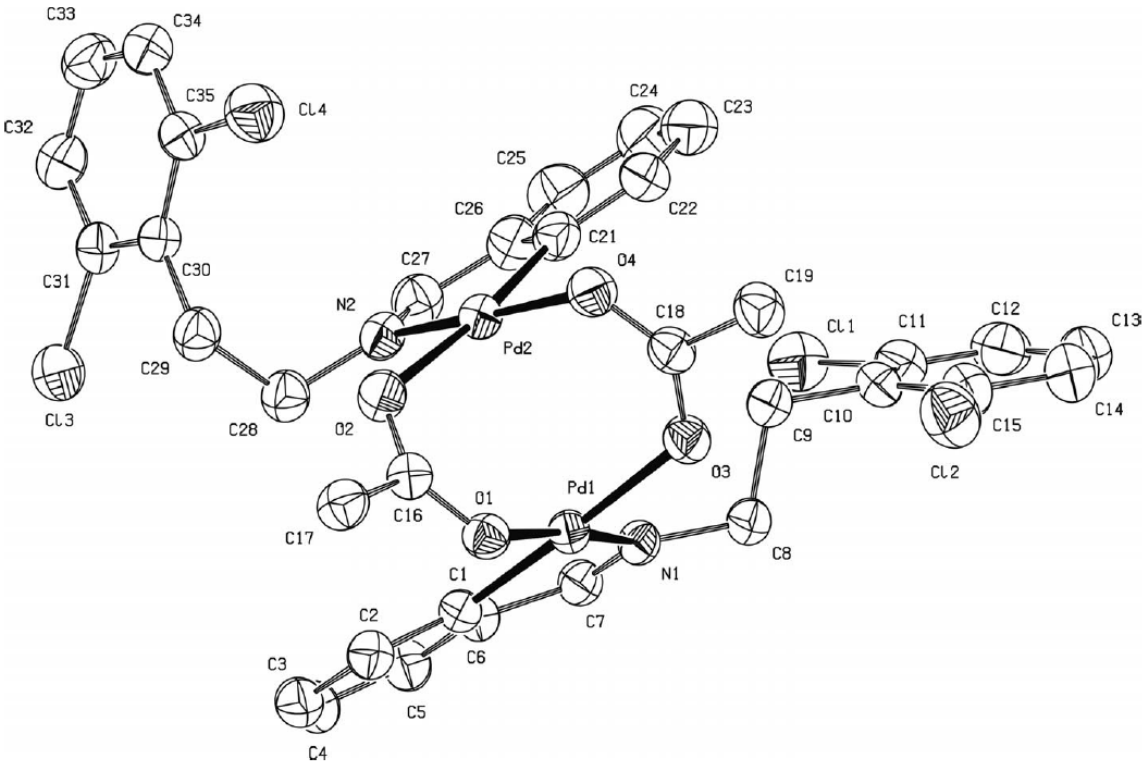

C33
C34
C35
Cl4
C32
C24
C23
C25
C26
C22
C21
C27
O4
C19
C31
C30
N2
C18
Cl1
C11
C12
C13
Pd2
C29
Cl3
C28
O2
C9
C10
C15
C14
O3
Cl2
Pd1
O1
C16
C17
C8
C1
N1
C7
C2
C6
C3
C5
C4

Figure 6

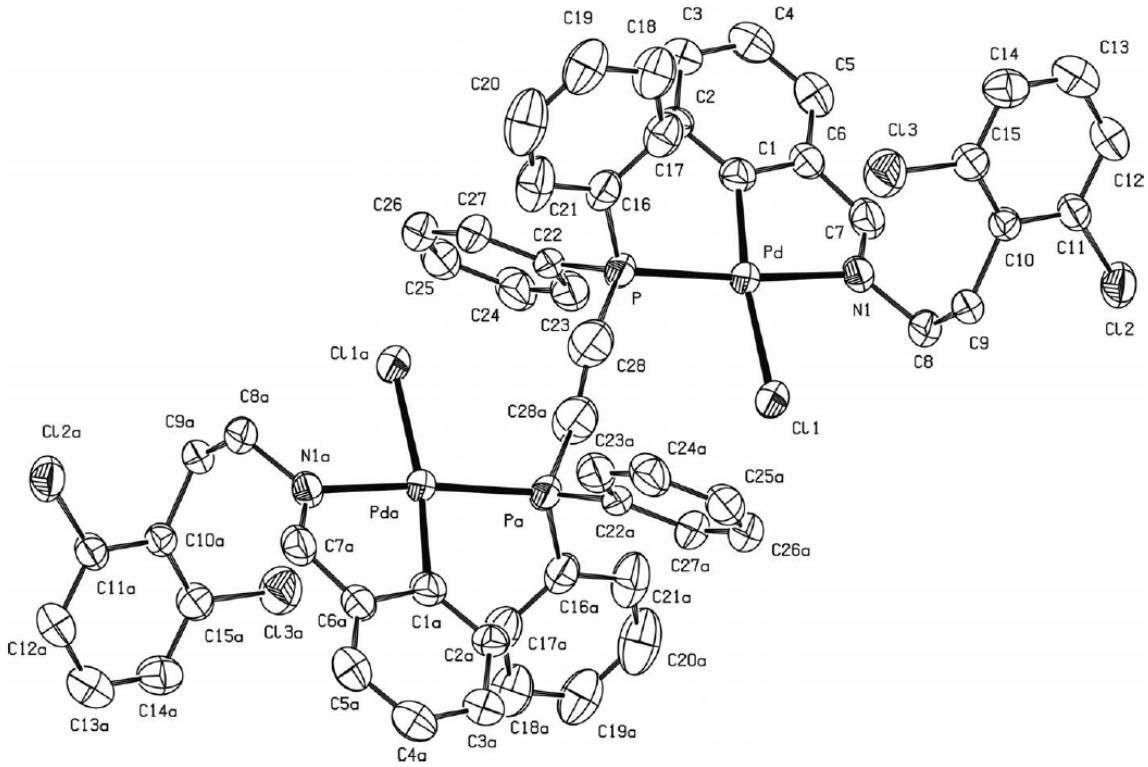

C19
C18
C3
C4
C5
C20
C2
C14
C13
C6
C1
CL3
C15
C17
C12
C26
C27
C21
C16
C7
C22
Pd
C10
C11
C25
P
N1
C24
C23
C9
CL2
C8
CL1a
C28
C8a
C28a
CL1
C9a
CL2a
N1a
C23a
C24a
C25a
Pda
Pa
C22a
C10a
C7a
C26a
C27a
C11a
C16a
C21a
C6a
C1a
C15a
CL3a
C17a
C12a
C2a
C20a
C5a
C14a
C18a
C19a
C13a
C3a
C4a

Figure 7

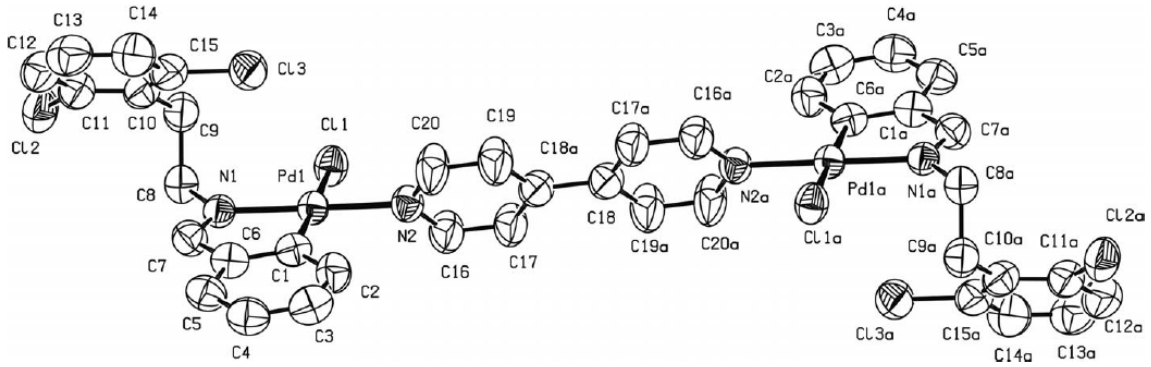

C13
C14
C12
C15
Cl3
C11
C10
C9
Cl2
C8
N1
Pd1
Cl1
C20
C19
C18a
C17a
C16a
N2a
C18
C19a
C20a
Cl1a
Pd1a
N1a
C8a
C6
C7
C1
C2
N2
C16
C17
C5
C3
C4
C3a
C4a
C5a
C2a
C6a
C1a
C7a
C9a
C10a
C11a
Cl2a
Cl3a
C15a
C14a
C13a

Figure 8

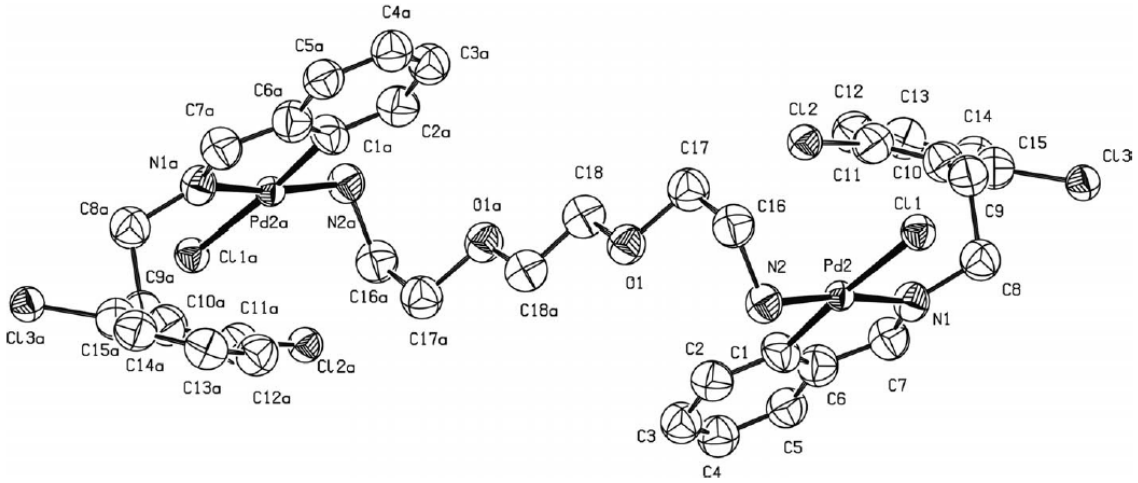

C4a
C5a
C3a
C6a
C7a
C2a
C1a
N1a
C8a
Pd2a
N2a
Cl1a
C9a
C10a
C11a
Cl3a
C15a
C14a
C13a
C12a
Cl2a
C16a
C17a
O1a
C18a
C18
C17
O1
C16
N2
Pd2
Cl1
C9
C8
N1
C2
C1
C6
C7
C3
C5
C4
Cl2
C12
C13
C14
C15
Cl3
C11
C10

Figure 9

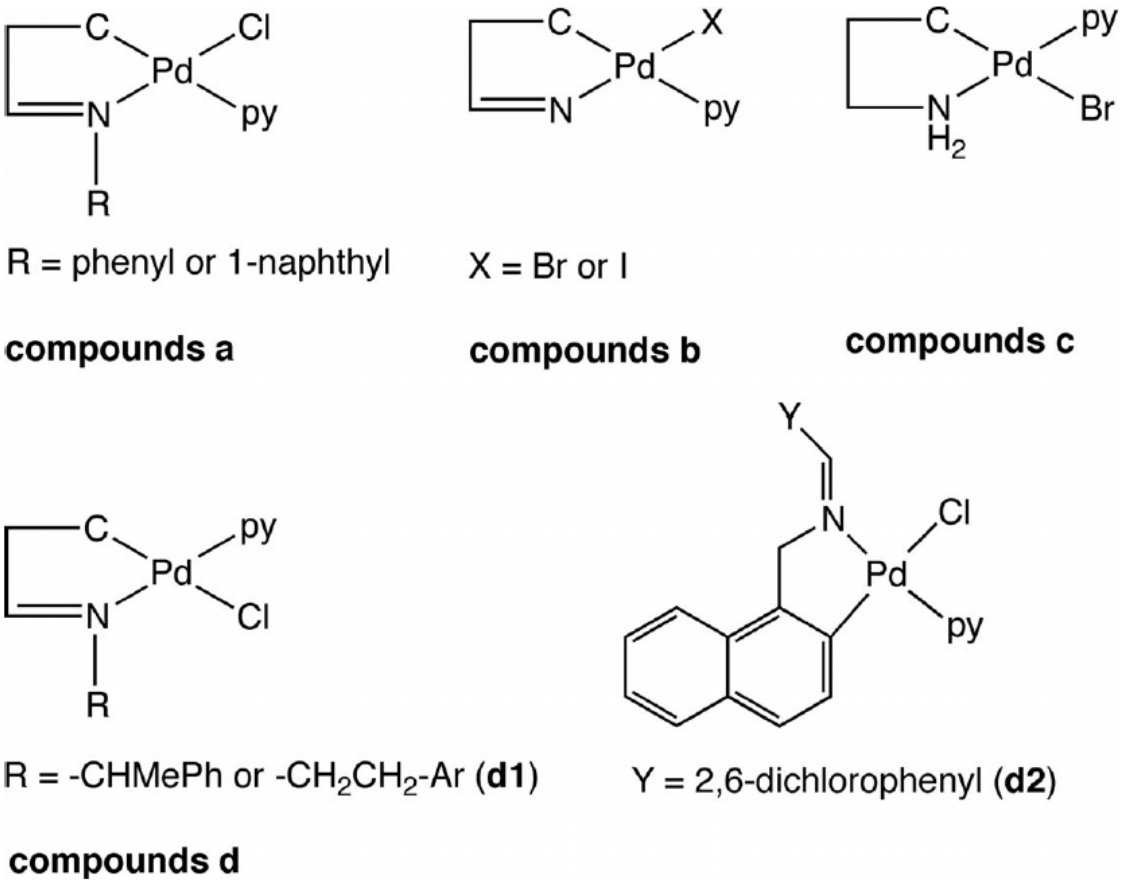
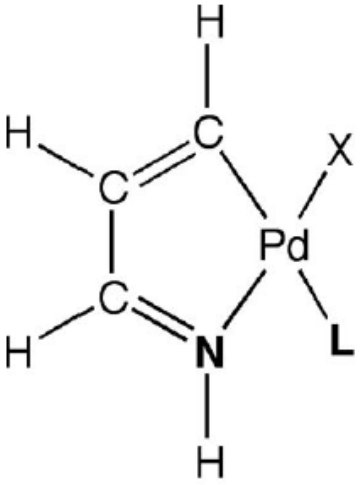
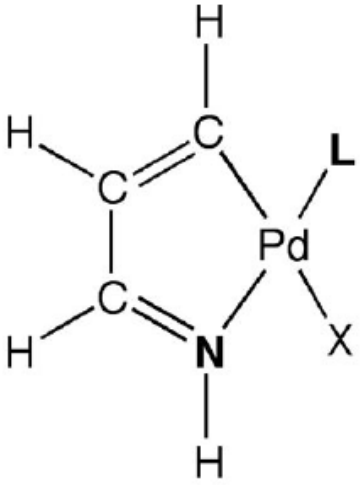

C
Cl
Pd
N
py
R
R = phenyl or 1-naphthyl
compounds a
C
X
Pd
N
py
X = Br or I
compounds b
C
py
Pd
N
H2
Br
compounds c
C
py
Pd
N
Cl
R
R = -CHMePh or -CH2CH2-Ar (d1)
compounds d
Y
N
Cl
Pd
py
Y = 2,6-dichlorophenyl (d2)

Figure 10



cis-***N***,***L*** stereoisomer



trans-***N***,***L*** stereoisomer