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Montoya García, Vanessa; Pons Picart, Josefina; García-Antón, Jordi; [et al.]. «New 3-Allylpalladium Complexes with Pyridylpyrazole Ligands : Synthesis, Characterization and Study of the Influence of N1 Substituents on the Apparent Allyl Rotation». Organometallics, Vol. 26, Issue 13 (June 2007), p. 3183-3190. DOI 10.1021/om070093u

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# New $\eta^3$-Allylpalladium Complexes with Pyridylpyrazole Ligands: Synthesis, Characterization and Study of the Influence of N1 Substituents on the Apparent Allyl Rotation.

**Vanessa MONTOYA[a], Josefina PONS[a*], Jordi GARCÍA-ANTÓN[a], Xavier SOLANS[b], Mercè FONT-BARDIA[b], Josep ROS[a*]**

[a]*Departament de Química, Unitat de Química Inorgànica, Universitat Autònoma de Barcelona, 08193-Bellaterra, Barcelona, Spain*

[b]*Cristal.lografia, Mineralogia i Dipòsits Minerals, Universitat de Barcelona, Martí i Franquès s/n, 08028-Barcelona, Spain*

*Keywords*: pyridylpyrazole ligands; allyl ligand; fluxionality; palladium.

## Abstract

Allylpalladium [Pd($\eta^3$-$C_3H_5$)(L)]($BF_4$) (L = $\mathbf{L}^1$ (**1**), $\mathbf{L}^2$ (**2**), $\mathbf{L}^3$ (**3**), $\mathbf{L}^4$ (**4**)) complexes with pyridylpyrazole ligands 2-(5-phenyl-*1H*-pyrazol-3-yl)pyridine ($\mathbf{L}^1$), 2-(1-ethyl-5-phenyl-*1H*-pyrazol-3-yl)pyridine ($\mathbf{L}^2$), 2-(1-octyl-5-phenyl)-*1H*-pyrazol-3-yl)pyridine ($\mathbf{L}^3$) and 2-(5-phenyl-3-pyridin-2-yl-pyrazol-1-yl)ethanol ($\mathbf{L}^4$) were synthesized from the appropriate pyridylpyrazole ligand and [Pd($\eta^3$-$C_3H_5$)Cl]$_2$ in the presence of $AgBF_4$. The cationic complex **1** was converted into neutral complex **5** under basic conditions. These complexes were characterized and the crystal and molecular structure of [Pd($\eta^3$-$C_3H_5$)($L^2$)]($BF_4$) (**2**) was resolved by X-ray diffraction. Also, we have studied the apparent allyl rotation observed as $H_{syn}$-$H_{syn}$ and $H_{anti}$-$H_{anti}$ interconversions. The influence of the solvent, the traces of water and the N1-substituent have also been studied.

## Introduction

In recent years, nitrogen binding ligands have received a great deal of attention due to their promising properties in applied sciences, mostly due to their high efficiency in homogenous catalysis [1-3]. To date, a number of N-ligand derivatives have found practical applications and the search for new, more effective and/or selective species is still in progress. Chelating bi- or tridentate N-coordinating ligands such as diazabutanes, bis(oxazolinyl)pyrroles, dipyridylamides and their prospective applications have been recently reported [4]. The relevance of N-donors in organometallic chemistry has been exhaustively discussed. In these complexes, ligands affect the metal centre electronically and sterically.

Allylpalladium chemistry is one of the most successful and innovative areas of organometallic catalysis [5,6]. The most general coordination for allyl ligands is the $\eta^3$ bonding mode. The fluxional behavior of these systems directly related to the allyl group or to the ancillary ligands has also attracted much attention [7]. One process frequently encountered in allylpalladium complexes is the mutual exchange of *syn* and *anti* groups. This process is believed to occur through an $\eta^3$- $\eta^1$- $\eta^3$ isomerization in ($\eta^3$-allyl)palladium complexes [8]. A second dynamic process that is frequently observed in complexes with N-donor ligands is the apparent rotation of the allyl group. The apparent rotation is observed as a *syn-syn*, *anti-anti* exchange and/or isomerization process, depending on the molecular symmetry. Two main mechanisms have been proposed for the apparent allyl rotation: a) associative mechanism that involves five-coordinated intermediates (coordination of the solvent, the anion or other molecules) that can undergo allyl pseudorotation [9-11] and b) dissociative mechanisms with formation of T-shape three-coordinated intermediates after dissociation of monodentate

or didentate (partial dissociation) ligands [12,13]. Consequently, one scope of this work is to determine whether the apparent allyl rotation in derivatives with N-donor ligands involves Pd-N bond breaking or not.

Pyrazoles are known as both monodentate and exodidentate ligands, and their nitrogen atoms can coordinate to metal centers as either anionic or neutral donor groups. Pyrazole ligands having a 2-pyridyl group [14] could be good candidates for the production of both cationic and neutral $\eta^3$-allylpalladium complexes. They could also be helpful to study the apparent allyl rotation in the complexes obtained.

## Results and discussion

### Synthesis and spectroscopic properties

Allylpalladium complexes with four different pyridylpyrazole ligands have been prepared: 2-(5-phenyl-*1H*-pyrazol-3-yl)-pyridine ($\mathbf{L}^1$) [15], 2-(1-ethyl-5-phenyl-*1H*-pyrazol-3-yl)-pyridine ($\mathbf{L}^2$) [15], 2-(1-octyl-5-phenyl)-*1H*-pyrazol-3-yl)-pyridine ($\mathbf{L}^3$) [16] and 2-(5-phenyl-3-pyridin-2-yl-pyrazol-1-yl)ethanol ($\mathbf{L}^4$). These ligands differ in the substituent in the N1 position and were prepared following an efficient method published in the literature[15,16] .The reaction of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ with these ligands in the presence of $AgBF_4$ in dichloromethane and at room temperature gave the new allylpalladium complexes $[Pd(\eta^3\text{-}C_3H_5)(L)](BF_4)$ (L = $\mathbf{L}^1$ (**1**), $\mathbf{L}^2$ (**2**), $\mathbf{L}^3$ (**3**), $\mathbf{L}^4$ (**4**)) as pale yellow powders in quantitative yield. Treatment of **1** in a mixture of $CH_2Cl_2/CH_3OH$ (1:1) with sodium methoxide produced the neutral $\eta^3$-allylpalladium complex **5** (Figure 1).

**Insert Figure 1**

The complexes have been fully characterized by elemental analysis, conductivity measurements, IR, $^1$H NMR and $^{13}C\{^1H\}$ NMR spectroscopy, and mass spectrometry.

For the majority of these complexes, HMQC experiments were also performed and in some cases NOESY experiments were carried out.

Elemental analysis and conductivity measurements confirm the stoichiometries proposed for the compounds. To confirm the existence of complexes **1-5**, electrospray mass spectra were recorded. The positive ionization spectra of **1-4** gave peaks with *m/z* values of 368, 396, 480, and 412, respectively (molecular peak of the cation). For complex **5,** *m/z* value is 368 and corresponds to $[Pd(\eta^3\text{-}C_3H_5)(L^1)+H)]^+$. Conductivity measurements of $10^{-3}$ M samples in acetone for complexes **1**-**4** (between 104-134 $\Omega^{-1}cm^2mol^{-1}$) are in agreement with 1:1 electrolytes, whereas for the complex **5** in acetonitrile the value is 29 $\Omega^{-1}cm^2mol^{-1}$, in agreement with the non-electrolytic nature of the complex [17,18].

The $^1$H NMR spectroscopic data for complexes **1-5** in acetonitrile-$d_3$ are collected in Table 1. The assignment of each proton was made on the basis of a previous publication of the free ligands [16]. In these complexes, the $H_1$ chemical shift of the pyridyl group and the signal of the pyrazolyl proton are consistent with the coordination of both nitrogens to Pd(II). The chemical shifts are observed towards higher frequencies for all the complexes with respect to the free ligands [16]. The same behavior is observed in other Pd(II) complexes with the same ligands ($[PdCl_2(L)]$) (L = **L**$^1$-**L**$^4$) [15,19,20] Concerning the allyl group, a single doublet resonance is observed at room temperature for the $H_{syn}$ and also for the $H_{anti}$ protons for complexes **1-4**. This observation is not in accordance with a static behavior of the complexes, where two non equivalents $H_{syn}$ and two non equivalents $H_{anti}$ would be expected, due to the asymmetry of the nitrogen ligands. This constitutes a clear indication of a dynamic situation that involves a *syn-syn*, *anti-anti* interconversion, such as an apparent allyl rotation process. This apparent allyl

rotation is not observed in complex **5**, which shows a doublet for each $H_{syn}$ and also for each $H_{anti.}$

The $^{13}C\{^{1}H\}$ NMR spectra were recorded in acetonitrile-$d_3$ for **1** and **4** and in dichloromethane-$d_2$ for **2**, **3** and **5**, due to the low solubility of the complexes. Spectroscopic data are gathered in the Experimental Section. The assignment for each carbon was made on the basis of the literature data and HMQC experiments. In a similar way to the $^{1}H$ NMR spectra a single broad signal was observed for the terminal carbons of the allyl moieties in complexes **1** and **4**. This again reflects the apparent allyl rotation. However, two different signals (one for each terminal carbon) were observed for the spectra recorded in dichloromethane-$d_2$ (complexes **2**, **3**, and **5**). This observation indicates that the apparent allyl rotation is dependent on the solvent, and was further studied by NMR, in a number of different solvents.

**NMR studies in different solvents**

In order to analyze the dynamic behavior of the complexes, we performed $^{1}H$ NMR spectra of **1**-**5** in different solvents, acetonitrile-$d_3$ (Table 1), dichloromethane-$d_2$ (Table 2), and acetone-$d_6$ (Table 3), at room temperature. It was not possible to perform $^{1}H$ NMR spectra of complexes **1** and **5** in dichloromethane-$d_2$ and acetone-$d_6$ respectively, due to their low solubility in these solvents.

**Insert Table 1**

**Table 2**

**Table 3**

**Figure 2**

**Table 4**

As an example, Figure 2 shows the $^{1}$H NMR spectra in different solvents for complex **2**. In this study, the most significant variations in the spectra are found for the allylic signals (see Table 4). For complexes **1**-**4,** in acetonitrile-$d_3$ (a coordinating solvent) only one signal for the *anti* hydrogens and only one signal for the *syn* hydrogens are observed. This does not occur for complex **5**, where two signals for each kind of proton are found. To confirm the data obtained for acetonitrile-$d_3$, an additional $^{1}$H NMR experiment was performed for **4** in dimethylsulfoxide-$d_6$. This $^{1}$H NMR spectrum is similar to that found in acetonitrile-$d_3$ (only one signal for $H_{syn}$ and only one signal for $H_{anti}$).

However, when a non-coordinating solvent is used (dichloromethane-$d_2$), different spectra, depending on the complex, were obtained. For complexes **2**, **3** and **5**, two $H_{anti}$ signals are observed, whereas for $H_{syn}$, two signals are observed for **3** and **5** and only one signal is observed for **2**. On the other hand, complex **4** presents broad signals for both $H_{syn}$ and $H_{anti}$.

When the $^{1}$H NMR spectra were recorded in acetone-$d^6$ for **1**-**4**, only one doublet was observed for both $H_{syn}$ and a broad band was observed for both $H_{anti}$.

These experiments indicate that the apparent allyl rotation is dependent on the solvent. Consequently, this process would involve an associative mechanism with the coordination of a molecule of solvent (coordination 4→5→4 on Pd(II)).

In order to see if there is any kind of interaction with a solvent like acetone-$d_6$, NOESY experiments were performed and they show NOE interaction between the $H_{syn}$ and $H_2O$ molecules in the solvent (commercial grade deuterated solvents were used). This observation could indicate that, in this case, the apparent allyl rotation involves the coordination of a water molecule. Scheme 1 shows the proposed mechanism for this process: a five-coordinated Pd(II) intermediate is obtained by the coordination of X (X

= water or coordinating solvent), followed by a pseudo rotation of the allyl group which interchanges the two allyl terminal hydrogen. The decoordination of the X group leads to the final product in which the observed $H_{syn}$-$H_{syn}$ $H_{anti}$-$H_{anti}$ interchange has taken place.

**Insert Scheme 1**

One special case is observed for complex **4** in dichloromethane-$d_2$. In this case, we observed the presence of broad bands for both $H_{syn}$ and $H_{anti}$. Similar behavior is observed for complexes **1-4** in coordinating solvent or solvents containing $H_2O$ molecules. This would indicate that the hydroxyethyl group of the pyridylpyrazole ligand interacts with the palladium atom, forming an intermediate similar to that found with $H_2O$ or a molecule of coordinating solvent. Therefore, for complex **4** in dichloromethane-$d_2$, the process would take place through an intramolecular associative mechanism (Scheme 2).

**Insert Scheme 2**

**Variable temperature NMR studies**

Variable temperature $^1$H NMR studies under different solvents (acetonitrile-$d_3$, acetone-$d_6$, and dichloromethane-$d_2$) were performed in order to obtain more information about the dynamic behavior of complexes **1-4** and the influence of the N1-substituent in the apparent allyl rotation. The study of the apparent allyl rotation was not performed at different temperatures with complex **5** because this complex presents a static situation in all the solvents.

As an example, Figure 3 shows the variable temperature $^1$H NMR spectra of **2** in acetone-$d_6$.

**Insert Table 5**

For complexes **1**-**4**, at low temperatures, two $H_{anti}$ and two $H_{syn}$ signals were observed, as is expected for a static situation. Posterior increase of the temperature allowed the determination of the corresponding coalescence temperatures. These coalescence temperatures ($T_c$) and the separation of the two doublet signals allowed us to calculate the $\Delta G^{\ddagger}$ of the processes [21] (see Table 5). In some cases it was not possible to determine the $\Delta G^{\ddagger}$ values because either the signals were not fully split at the minimum experimental temperature or the $T_c$ was not reached at the maximum temperature allowed by the solvent. For complexes **1**-**4**, the values of $\Delta G^{\ddagger}$ in acetonitrile-$d_3$ or acetone-$d_6$ solvents are similar, and are independent of the N1-substituent. In contrast, in dichloromethane-$d_2$, for complexes **2** and **3** the exact values could not be obtained as $T_c$ was not reached at 305 K (maximum temperature allowed for this solvent). We have calculated the $\Delta G^{\ddagger}$ values for this temperature, and we can only suppose that the real values are higher than those obtained for 305 K, and also higher than the values obtained for acetonitrile-$d_3$ and acetone-$d_6$. For complex **4** in dichloromethane-$d_2$, we could obtain exact $\Delta G^{\ddagger}$ values, because the $T_c$ is 298 K, due to the fact that the hydroxyethyl moiety favors an intramolecular associative mechanism of the apparent allyl rotation.

**Crystal and molecular structures of $[Pd(\eta^3\text{-}C_3H_5)(L^2)](BF_4)$ (2)**

The crystal structure of complex **2** consists of $[Pd(\eta^3\text{-}C_3H_5)(L^2)]^+$ cations, $BF_4^-$ anions held by Coulomb forces. The cation $[Pd(\eta^3\text{-}C_3H_5)(L^2)]^+$ is shown in Figure 4.

The metal atom is coordinated to a $\mathbf{L^2}$ ligand via one pyrazole nitrogen, one pyridine nitrogen, and one allyl ligand in a $\eta^3$-coordination. The two terminal allyl carbons are 0.282(3) Å and 0.169(3) Å from the plane defined by

PdNpyNpzC(17)C(18)C(19) atoms. The central carbon (C(18)) is -0.403(3) Å out of this plane. **L²** behaves as a bidentate ligand forming a five-membered metallocycle.

The [Pd($\eta^3$-$C_3H_5$)(Npy)(Npz)] *core* (containing pyrazole and pyridine nitrogen atoms and a $\eta^3$-bonded allyl ligand) is found in one complex described in the literature [22].

The bond distance Pd-Npy is almost identical to Pd-Npz (2.115(3) Å and 2.117(3) Å, respectively). The Pd-C bond lengths of the allyl group are in the range expected for these types of complexes [23]. The distance measured for the Pd-C(terminal) in *trans* disposition to Npy (2.114(3) Å) is of the same order than the distance found for the other Pd-C(terminal) and Pd-C(central) bonds (2.101(4) Å and 2.108(3) Å, respectively).

The Pd-Npy, Pd-Npz and Pd-C bond lengths in **2** are in the range of bond distances found in the literature for complexes containing N,N'-ligands *trans* to an allyl-palladium fragment [24-26].

Selected bond distances and angles for this complex are gathered on Table 6.

**Insert Table 6**

The allyl group has deviated from the ideal geometry (C-C distances of 1.36 Å and C-C-C angles of 120º): it presents two types of C-C distances 1.373(8) Å and 1.402(6) Å and a C-C-C angle of 118.3(4)º. Similar distorted allyl groups have also been described in other complexes containing the [Pd($\eta^3$-$C_3H_5$)]$^+$ fragment [27-29]. The dihedral angle between the allylic plane and the palladium coordination plane is 66.90(9)º.

The N(1)-Pd-N(2) bite angle is 77.68(10)º**.** This angle is smaller than those found in the literature, with 2-(5-phenyl-*1H*-pyrazol-3-yl)pyridine (**L¹**), [$PdCl_2$($L^1$)] [15],

79.16 (14)º, 2-(1-ethyl-5-phenyl-*1H*-pyrazol-3-yl)pyridine (**L**$^2$) [$PdCl_2(L^2)$] [20], 78.83(9)º and 2-(1-octyl-5-phenyl-*1H*-pyrazol-3-yl)pyridine (**L**$^3$) [$PdCl_2(L^3)$] [20], 79.39(13)º.

The **L**$^2$ ligand is not planar. The pyridyl and phenyl groups are twisted with respect to the pyrazole ring. The py-pz dihedral angle is 7.05(17)º and the ph-pz is 18.09(18)º. The py-pz dihedral angles are bigger than those found in complexes [$PdCl_2(L^1)$] (py-pz 1.43(4)º) [15], [$PdCl_2(L^3)$] [19] (py-pz 1.5(2)º) and [$PtCl_2(L^2)$] [20] (py-pz 3.4(4)º), whereas the ph-pz angle is smaller than those found in the complexes [$PdCl_2(L^3)$] (69.2(3)º), [$PtCl_2(L^2)$] [20] (54.0(4º)) but bigger than that found for [$PdCl_2(L^1)$] [15] (0.48(3)º).

The n-alkyl group, which is bonded to the N(3) atom, moves away from the chelating plane giving a torsion angle N(2)-N(3)-C(15)-C(16) of 89.5(3)º.

## Conclusions

Five new allylpalladium derivatives containing N-donor ligands have been prepared and their fluxional behavior studied. The apparent allyl rotation has been studied in detail. This process presents low $\Delta G^{\ddagger}$ values and is favored by coordinating solvents (or eventually traces of water present in the solvent), meaning that the apparent allyl rotation takes place through an isomerization of the square-planar geometry by an associative mechanism. The process is also favored for complex **4**, which contains a hydroxyethyl moiety. This group takes the role of the coordinating solvent when dichloromethane-$d_2$ is used. Therefore, in this case the process would take place through an intramolecular associative mechanism. The low $\Delta G^{\ddagger}$ values indicate that the process takes place without Pd-N bond rupture. On the other hand, the process does not occur in

the neutral complex, probably due to the steric hindrance provoked in the rotation by the free pair of electrons of the pyrazolyl group.

## Experimental Section

### General Methods

Standard Schlenk techniques were employed throughout the synthesis using a double manifold vacuum line with high purity dry nitrogen. All reagents were commercial grade materials and were used without further purification. All solvents were dried and distilled by standard methods. The elemental analyses (C, H, N) were carried out by the staff of the Chemical Analyses Service of the Universitat Autònoma de Barcelona on a Carlo Erba CHNS EA-1108 instrument. Conductivity measurements were performed at room temperature (r.t.) in $10^{-3}$ M acetone and acetonitrile samples employing a Crison, micro CM 2200 conductimeter. Infrared spectra were performed on a Perkin-Elmer FT spectrophotometer series 2000 $cm^{-1}$ as KBr pellets in the range 4000-400 $cm^{-1}$ under a nitrogen atmosphere. The $^{1}H$ NMR, $^{13}C\{^{1}H\}$ NMR, HMQC, and NOESY spectra were run on a NMR-FT Bruker 250 MHz instrument. $^{1}H$ NMR and $^{13}C\{^{1}H\}$ NMR chemical shifts (δ) were determined relative to internal TMS and are given in ppm. Liquid chromatography/Electrospray mass spectrometry experiments were performed by the Scientific Services of the Universitat de Barcelona on a Shimadzu AD VP chromatography instrument and API 150 (Applied Biosystems) mass spectrometer. The carrier was $CH_3CN$ at a 0.2 ml $min^{-1}$ flow rate. The samples were dissolved in $CH_3CN$ at a concentration of 0.4 mg $ml^{-1}$ and 5 μl of each solution injected on line. In the case of electrospray interface, whole flow was introduced in the capillary source and nebulized AT a 12 (arbitrary units) nitrogen flow. The auxiliary gas was nitrogen at 7000 cc $min^{-1}$ flow rate. The main electrical conditions were: positive

electrospray capillary at 4200 V; potentials DP = 20 V; FP = 200 V; EP = -10 V, the mass range measured was between 100 and 950 a.m.u., in full scan mode, cycle time was 2 s and the source temperature was 200 ºC.

Compounds 2-(5-phenyl-*1H*-pyrazol-3-yl)pyridine (**L**$^1$) [15], 2-(1-ethyl-5-phenyl-*1H*-pyrazol-3-yl)pyridine (**L**$^2$) [15], 2-(1-octyl-5-phenyl)-*1H*-pyrazol-3-yl)pyridine (**L**$^3$) [16] and 2-(5-phenyl-3-pyridin-2-yl-pyrazol-1-yl)ethanol (**L**$^4$), were prepared according to the published methods (Figure 1). Samples of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ were prepared as described in the literature [30].

**Synthesis of the complexes**

*Complexes [Pd($\eta^3$-$C_3H_5$)(L)]$BF_4$ (L = **L$^1$(1), L$^2$(2), L$^3$(3), L$^4$(4)**)*

0.37 mmol of the corresponding ligand (**L**$^1$, 0.083 g; **L**$^2$, 0.092 g; **L**$^3$, 0.123 g; **L**$^4$, 0.098 g) were added to a mixture of $AgBF_4$ (0.37 mmol, 0.070 g) and the $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.18 mmol, 0.066 g) dissolved in dry dichloromethane (40 ml) at 0ºC. After stirring the mixture, light protected and at room temperature for 1.5 h, methanol (40 mL) was added. The yellow solution was then filtered through a pad of celite. The solution was stirred for 1 h and then most of the solvent was removed under vacuum, and diethyl ether (5 ml) was then added dropwise to induce precipitation. The yellow solid was filtered off, rinsed twice with 5 ml of diethyl ether and dried under vacuum.

**1:** Yield: 87 % (0.147 g). **$C_{17}H_{16}BF_4N_3Pd$** (455.6). *Anal. Calc.* C, 44.82, H, 3.54, N, 9.22. Found: C, 44.90, H, 3.62, N, 8.99 %. **Conductivity** ($\Omega^{-1}cm^2mol^{-1}$, $9.1x10^{-4}$ M in acetone): 132. **IR**: (KBr, $cm^{-1}$) 3416 ν(N-H), 3020 $\nu(C\text{-}H)_{ar}$, 2960 $\nu(C\text{-}H)_{al}$, 1616 $\nu((C{=}C), \nu(C{=}N))_{ar}$, 1454 $\delta((C{=}C), \delta(C{=}N))_{ar}$, 1084 ν(B-F), 768 $\delta(C\text{-}H)_{oop}$. **$^{13}C\{^1H\}$ NMR** (acetonitrile-$d_3$ solution, 63 MHz, 298 K) δ: 154.4 ($C_1$), 153.8 ($C_{15}$), 150.6 ($C_{14}$),

147.8 ($C_{16}$), 141.4 ($C_3$), 130.7 ($C_{11}$), 130.0 ($C_{10,}$ $C_{12}$), 127.4 ($C_{17}$), 126.6 ($C_{9,}$ $C_{13}$), 126.6 ($C_2$), 122.7 ($C_4$), 118.7 ($C_6$), 102.01 ($C_5$), 62.0 ($C_7$, $C_8$) ppm. **ES(+) MS** *m/z* **(%) =** 368 (100%) $[Pd(\eta^3\text{-}C_3H_5)(L^1)]^+$, 222 (3%) $[L^1+H]^+$

**2:** Yield: 85 % (0.152 g). **$C_{19}H_{20}BF_4N_3Pd$** (483.6). *Anal. Calc.* C, 47.19, H, 4.17, N, 8.69. Found: C, 46.90, H, 4.05, N, 8.38 %. **Conductivity** ($\Omega^{-1}cm^2mol^{-1}$, $9.2x10^{-4}$ M in acetone): 113. **IR**: (KBr, $cm^{-1}$) 3066 $\nu(C\text{-}H)_{ar}$, 2924 $\nu(C\text{-}H)_{al}$, 1610 $\nu((C=C)$, $\nu(C=N))_{ar}$, 1465 $\delta((C=C)$, $\delta(C=N))_{ar}$, 1083 $\nu(B\text{-}F)$,768 $\delta(C\text{-}H)_{oop}$. **$^{13}C\{^1H\}$ NMR** (dichloromethane-$d_2$ solution, 63 MHz, 298 K) δ: 154.0 ($C_1$), 151.8 ($C_{15}$), 150.9 ($C_{14}$), 148.2 ($C_{16}$), 141.3 ($C_3$), 130.8 ($C_{11}$), 129.7 ($C_{10,}$ $C_{12}$), 129.3 ($C_9$, $C_{13}$), 128.4 ($C_{17}$), 126.6 ($C_2$), 122.4 ($C_4$), 118.4 ($C_6$), 105.7 ($C_5$), 65.8 ($C_7$ or $C_8$), 59.4 ($C_7$ or $C_8$), 46.9 (N-$CH_2CH_3$), 16.4 (N-$CH_2CH_3$) ppm. **ES(+) MS** *m/z* **(%) =** 396 (100%) $[Pd(\eta^3\text{-}C_3H_5)(L^2)]^+$, 250 (13%) $[L^2+H]^+$

**3:** Yield: 80 % (0.168 g). **$C_{25}H_{32}BF_4N_3Pd$** (567.8). *Anal. Calc.* C, 52.89, H, 5.68, N, 7.40. Found: C, 52.92, H, 5.59, N, 7.36 %. **Conductivity** ($\Omega^{-1}cm^2mol^{-1}$, $1.0x10^{-3}$ M in acetone): 104. **IR**: (KBr, $cm^{-1}$) 3099 $\nu(C\text{-}H)_{ar}$, 2952 $\nu(C\text{-}H)_{al}$, 1615 $\nu((C=C)$, $\nu(C=N))_{ar}$, 1465 $\delta((C=C)$, $\delta(C=N))_{ar}$, 1057 $\nu(B\text{-}F)$, 765 $\delta(C\text{-}H)_{oop}$. **$^{13}C\{^1H\}$ NMR** (dichloromethane-$d_2$ solution, 63 MHz, 298 K) δ: 154.0 ($C_1$), 151.8 ($C_{15}$), 150.9 ($C_{14}$), 148.7 ($C_{16}$), 141.3 ($C_3$), 130.8 ($C_{11}$), 129.7 ($C_{10,}$ $C_{12}$), 129.4 ($C_9$, $C_{13}$), 128.5 ($C_{17}$), 126.6 ($C_2$), 122.4 ($C_4$), 118.4 ($C_6$), 105.7 ($C_5$), 65.9 ($C_7$ or $C_8$), 59.2 ($C_7$ or $C_8$), 51.7 (N-$CH_2$-$(CH_2)_6$-$CH_3$), 32.0-22.9 (N-$CH_2$-$(CH_2)_6$-$CH_3$), 14.2 (N-$CH_2$-$(CH_2)_6$-$CH_3$) ppm. **ES(+)MS m/z (%) =** 480 (100%) $[Pd(\eta^3\text{-}C_3H_5)(L^3)]^+$

**4:** Yield: 78 % (0.144 g). **$C_{19}H_{20}BF_4N_3OPd$** (499.6). *Anal. Calc.* C, 45.68, H, 4.03, N, 8.41. Found: C, 45.90, H, 3.96, N, 8.23 %. **Conductivity** ($\Omega^{-1}cm^2mol^{-1}$, $1.0x10^{-3}$ M in acetone): 134. **IR**: (KBr, $cm^{-1}$) 3467 ν(O-H), 3050 $\nu(C-H)_{ar}$, 2924 $\nu(C-H)_{al}$, 1616 $\nu((C=C), \nu(C=N))_{ar}$, 1464 $\delta((C=C), \delta(C=N))_{ar}$, 1060 ν(B-F), 767 δ(C-H)oop. **$^{13}C\{^1H\}$ NMR** (acetonitrile-$d_3$ solution, 63 MHz, 298 K) δ: 153.8 ($C_1$), 151.7 ($C_{15}$), 151.1 ($C_{14}$), 149.5 ($C_{16}$), 141.1 ($C_3$), 130.7 ($C_{11}$), 129.7 ($C_{10}$, $C_{12}$), 129.6 ($C_9$, $C_{13}$), 128.5 ($C_{17}$), 126.3 ($C_2$), 122.4 ($C_4$), 118.5 ($C_6$), 105.7 ($C_5$), 61.4 (N-$CH_2$-$CH_2$OH), 59.2 ($C_7$,$C_8$), 51.7 (N-$CH_2$-$(CH_2)_6$-$CH_3$), 32.0-22.9 (N-$CH_2$-$(CH_2)_6$-$CH_3$). **ES(+) MS** ***m/z*** **(%)** = 412 (100%) $[Pd(\eta^3\text{-}C_3H_5)(L^4)]^+$.

* The values of $^1$H NMR spectra in acetonitrile-$d_3$, dichloromethane-$d_2$, and acetone-$d_6$ are presented in Table 1, Table 2, and Table 3, respectively, except for the complex **1** in dichloromethane-$d_2$, due to its low solubility in this solvent.

*Complex $[Pd(\eta^3\text{-}C_3H_5)(L^1)]$ (**5**)*

To a mixture of **1** (0.20 mmol, 0.091 g) and sodium methoxide (0.20 mmol, 0.011 g) were added dichloromethane (0.25 ml) and methanol (0.25 ml) at room temperature. The mixture was stirred under sonication for 5 min. The solvent was evaporated. The yellow solid was rinsed with 5 ml of diethyl ether and dried under vacuum.

**5:** Yield: 60 % (0.044 g). **$C_{17}H_{15}N_3Pd$** (367.7). *Anal. Calc.* C, 55.52, H, 4.11, N, 11.43. Found: C, 55.49, H, 3.89, N, 11.55 %. **Conductivity** ($\Omega^{-1}cm^2mol^{-1}$, $1.1x10^{-3}$ M in acetonitrile-$d_3$): 29. **IR**: (KBr, $cm^{-1}$) 3025 $\nu(C-H)_{ar}$, 2962 $\nu(C-H)_{al}$, 1603 $\nu((C=C), \nu(C=N))_{ar}$, 1450 $\delta((C=C), \delta(C=N))_{ar}$, 761 δ(C-H)oop. **$^{13}C\{^1H\}$ NMR** (dichloromethane-$d_2$ solution, 63 MHz, 298 K) δ: 163.0 ($C_{14}$), 157.6 ($C_{15}$), 155.2 ($C_{16}$),

153.1 ($C_1$), 139.7 ($C_3$), 135.9 ($C_{17}$), 128.7 ($C_{10,}$ $C_{12}$), 126.5 ($C_{11}$), 125.4 ($C_{9,}$ $C_{13}$), 121.9 ($C_2$), 119.2 ($C_4$), 116.4 ($C_6$), 99.3 ($C_5$), 60.2 ($C_7$ or $C_8$), 56.2 ($C_7$ or $C_8$) ppm. **ES(+) MS** *m/z* **(%) =** 390 (7%) $[Pd(\eta^3\text{-}C_3H_5)(L^1)+Na]^+$, 368 (100%) $[Pd(\eta^3\text{-}C_3H_5)(L^1)+H]^+$

*The values of the $^1$H NMR spectra in acetonitrile-$d_3$, and dichloromethane-$d_2$, are presented in Table 1 and Table 2, respectively.

**X-ray crystal structure analyses of complex $[Pd(\eta^3\text{-}C_3H_5)(L^2)](BF_4)$**

Suitable crystals for X-ray diffraction of compounds $[Pd(\eta^3\text{-}C_3H_5)(L^2)](BF_4)$ were obtained through crystallization from dichloromethane. Data were collected on a MAR345 diffractometer with a image plate detector. Intensities were collected with graphite monochromatized Mo Kα radiation. Unit-cell parameters were determined from 3888 reflections ($3 < \theta < 31$) and refined by least-squares method. 14739 reflections were assumed in the range $2.55 \leq \theta \leq 29.99$. 4418 of which were non-equivalent by symmetry (Rint (on I) = 0.035). 3902 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. Lorentz-polarization but no absorption corrections were made.

The structure was solved by direct methods, using SHELXS97 computer program [31] and refined by full-matrix least-squares method by SHELXL97 computer program [32] using 14739 reflections (very negative intensities were not assumed). The function minimized was $\Sigma w \left| \left| F_O \right|^2 - \left| F_C \right|^2 \right|^2$, where $w = [\sigma^2(I) + (0.0623P)^2 + 0.6986P]^{-1}$ and $P = (\left| F_O \right|^2 + 2 \left| F_C \right|^2) / 3$. 18 H atoms were located from a difference synthesis and refined with overall isotropic temperature factor and 2H 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, which are linked. The final R(*F*) factor and

R($F^2$) values as well as the number of parameters and other details concerning the refinement of the crystal structures are gathered in Table 7.

**Insert Table 7**

CCDC-628754 contains 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.


## Acknowledgement

Support by the Spanish Ministerio de Educación y Cultura (project BQU2003-03582) is gratefully acknowledged.


## Supporting Information Available

Synthesis and characterization of ligand 2-(5-phenyl-3-pyridin-2-yl-pyrazol-1-yl)ethanol (**L$^4$**). This material is available free of charge via the Internet at http://pubs.acs.org.

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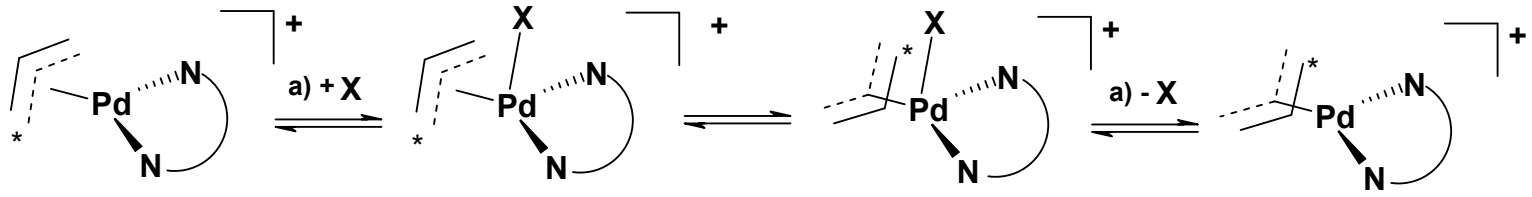
**Scheme 1.**



**Scheme 2.**

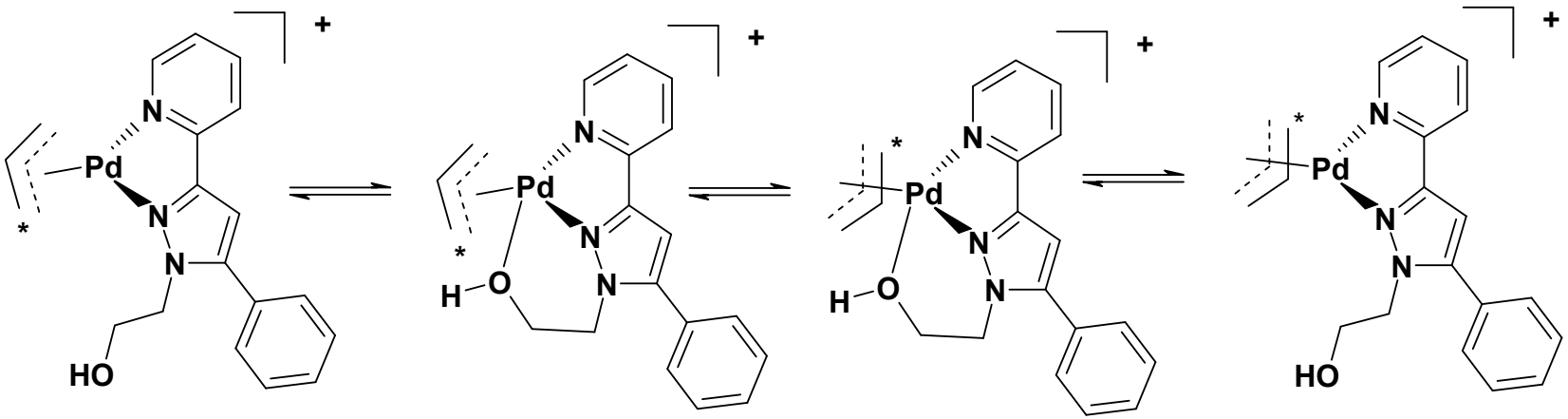


**Table 1.** $^{1}$H NMR (250 MHz, 298 K) spectroscopic data for complexes **1-5** in acetonitrile-$d_3$

| **chem. shifts in ppm (coupling constants in Hz)** | | | | | |
|---|---|---|---|---|---|
| | **1** | **2** | **3** | **4** | **5** |
| N-H | 13.21 (br) | | | | |
| $H_1$ | 8.75 (ddd, 5.4, 1.6, 0.9) | 8.75 (d, 5.5) | 8.74 (ddd, 5.7, 1.4, 0.6) | 8.75 (dd, 5.4, 1.6) | 8.59 (ddd, 5.4, 2.0, 0.9) |
| $H_3$ | 8.21 (td, 8.1, 1.6) | 8.20 (td, 7.7, 1.4) | 8.19 (td, 8.5,1.49) | 8.20 (td, 7.7, 1.6) | 7.96 (td, 7.5, 2.0) |
| $H_4$ | 8.09 (ddd, 8.1, 1.4, 0.9) | 8.06 (d, 7.7) | 8.04 (d, 8.5) | 8.08 (d, 7.7) | 7.78 (ddd, 7.2, 1.3, 0.9) |
| $H_{ph}$ | 7.85-7.81 (m) | 7.65-7.56 (m) | 7.63-7.55 (m) | 7.67-7.52 (m) | 7.86 (d, 7.2), 7.40 (t, 7.2), 7.29-7.30 (m) |
| $H_{ph,}$ $H_2$ | 7.63-7.54 (m) | | | | |
| $H_5$ | 7.41 (s) | 7.15 (s) | 7.17 (s) | 7.17 (s) | 7.04 (s) |
| $H_6$ | 5.92 (m) | 5.98 (m) | 5.95 (m) | 5.96 (m) | 5.77 (m) |
| $H_{7,}$ $H_8$ syn | 4.56 (d, 7.0) | 4.50 (d, 7.0) | 4.46 (d, 7.2) | 4.47 (d, 7.2) | 4.17 (d, 7.0), 4.04 (d, 6.8) |
| $H_{7,}$ $H_8$ anti | 3.51 (d, 12.4) | 3.58 (d, 12.5) | 3.54 (d, 12.2) | 3.55 (d, 12.4) | 3.31 (d, 12.2), 3.16 (d, 12.6) |
| N-C$H_2$ | | 4.33 (q, 7.2) | 4.29 (t, 7.2) | 4.39 (t, 5.4) | |
| N-$(CH_2)_x$-C$H_3$ | | 1.41 (t, 7.2) | 0.84 (t, 6.6) | | |
| N-$CH_2$-$CH_2$- | | | 1.78-1.74 (m) | 3.87 (m) | |
| N-$CH_2$-$CH_2$-$(CH_2)_5$-$CH_3$ | | | 1.32-1.02 (m) | | |

**Table 2.** $^{1}$H NMR (250 MHz, 298 K) spectroscopic data for complexes **2-5** in dichloromethane-$d_2$

| **chem. shifts in ppm (coupling constants in Hz)** | | | | |
|---|---|---|---|---|
| | **2** | **3** | **4** | **5** |
| $H_1$ | 8.72 (ddd, 5.4, 1.4, 0.9) | 8.73 (ddd, 5.4, 1.4, 0.7) | 8.69 (dd, 5.4, 1.6) | 8.53 (dt, 5.4, 1.1, 1.1) |
| $H_4$ | 7.99 (ddd, 7.9, 1.2, 0.9) | 8.00 (ddd, 7.8, 1.2, 0.7) | 7.98 (d, 7.7) | 7.70 (dt, 8.0, 0.9) |
| $H_3$ | 8.18 (td, 7.9, 1.4) | 8.18 (td, 7.9,1.6) | 8.15 (td, 7.7, 1.6) | 7.92-7.85 (m), 7.40 (m), |
| $H_{ph}$ | 7.65-7.60 (m) | 7.63-7.60 (m) | 7.65-7.52 (m) | 7.25 (tt, 7.7, 1.1) |
| $H_2$ | 7.57-7.52 (m) | 7.55-7.51 (m) | | 7.16 (ddd, 7.4, 5.4, 1.4) |
| $H_5$ | 7.00 (s) | 7.00 (s) | 7.00 (s) | 6.96 (s) |
| $H_6$ | 5.99 (m) | 5.98(m) | 5.99 (m) | 5.74 (m) |
| $H_7$, $H_8$ syn | 4.48 (d, 7.2) | 4.50, 4.45 (d, 7.0) | 4.57 (br) | 4.32 (d, 7.0), 3.93 (d, 6.9) |
| $H_7$, $H_8$ anti | 3.81 (d, 11.7), 3.39 (d, 12.2) | 3.76 (d, 12.5), 3.38 (d, 12.5) | 4.10 (br) | 3.27 (d, 12.5), 3.24 (d, 12.4) |
| N-C*H*$_2$ | 4.34 (q, 7.3) | 4.29 (t, 7.9) | 4.44 (t, 5.4) | |
| N-(CH$_2$)$_x$-C*H*$_3$ | 1.47 (t, 7.3) | 0.89 (t, 6.4) | | |
| N-CH$_2$-*CH*$_2$- | | 1.81-1.71 (m) | 3.98 (m) | |
| N-CH$_2$-CH$_2$-(C*H*$_2$)$_5$-CH$_3$ | | 1.32-1.16 (m) | | |

**Table 3.** $^{1}$H NMR (250 MHz, 298 K) spectroscopic data for complexes **1-4** in acetone-$d_6$

| **chem. shifts in ppm (coupling constants in Hz)** | | | | |
|---|---|---|---|---|
| | **1** | **2** | **3** | **4** |
| N-H | 13.30 (br) | | | |
| $H_1$ | 8.83 (d, 5.5) | 8.84 (d, 5.3) | 8.85 (d, 5.6) | 8.85 (d, 5.5) |
| $H_3$ | 8.31 (td, 8.1, 1.6) | 8.32 (td, 7.6, 1.5) | 8.29 (td, 8.4,1.4) | 8.20 (td, 7.6, 1.5) |
| $H_4$ | 8.09 (d, 8.1) | 8.07 (d, 7.6) | 8.03 (d, 8.5) | 8.06 (d, 7.7) |
| $H_{ph,}$ $H_2$ | 7.85-7.5 (m) | 7.73-7.62 (m) | 7.73-7.65 (m) | 7.77-7.62 (m) |
| $H_5$ | 7.52 (s) | 7.45 (s) | 7.51 (s) | 7.40 (s) |
| $H_6$ | 6.05 (m) | 6.04 (m) | 6.19 (m) | 5.96 (m) |
| $H_{7,}$ $H_8$ syn | 4.65 (d, 6.8) | 4.72 (d, 7.2) | 4.69 (d, 7.2) | 4.69 (d, 7.0) |
| $H_{7,}$ $H_8$ anti | 3.62 (br) | 3.76 (br) | 3.76 (br) | 3.72 (br) |
| N-C$H_2$ | | 4.48 (q, 7.1) | 4.29 (t, 7.2) | 4.35 (t, 5.4) |
| N-$(CH_2)_x$-C$H_3$ | | 1.43 (t, 7.3) | 0.87 (t, 6.7) | |
| N-$CH_2$-$CH_2$- | | | 1.82-1.76 (m) | 3.87 (m) |
| N-$CH_2$-$CH_2$-$(CH_2)_5$-$CH_3$ | | | 1.45-1.00 (m) | |

**Table 4.** $^{1}$H NMR (250 MHz, 298 K) spectroscopic data for complexes **1-5**

| Complex | Solvent | $H_7/H_8$ *syn* | $H_7/H_8$ *anti* |
|---|---|---|---|
| **1** | $CD_3CN$ | 4.56 (d, 7.0 Hz) | 3.51 (d, 12.4 Hz) |
| **1** | $(CD_3)_2CO$ | 4.65 (d, 6.8 Hz) | 3.62 (br) |
| **1** | $CD_2Cl_2$ | -* | -* |
| **2** | $CD_3CN$ | 4.50 (d, 7.0 Hz) | 3.58 (d, 12.5 Hz) |
| **2** | $(CD_3)_2CO$ | 4.72 (d, 7.2 Hz) | 3.76 (br) |
| **2** | $CD_2Cl_2$ | 4.48 (d, 7.2 Hz) | 3.81 (d, 11.7 Hz), 3.39 (d, 12.2 Hz) |
| **3** | $CD_3CN$ | 4.46 (d, 7.2 Hz) | 3.54 (d, 12.2 Hz) |
| **3** | $(CD_3)_2CO$ | 4.69 (d, 6.8 Hz) | 3.76 (br) |
| **3** | $CD_2Cl_2$ | 4.50 (d, 7.0 Hz), 4.45 (d, 7.0 Hz) | 3.76 (d, 12.5 Hz), 3.38 (d, 12.5 Hz) |
| **4** | $CD_3CN$ | 4.47 (d, 7.2 Hz) | 3.55 (d, 12.4 Hz) |
| **4** | $(CD_3)_2CO$ | 4.69 (d, 7.0 Hz) | 3.72 (br) |
| **4** | $CD_2Cl_2$ | 4.57 (br), | 4.10 (br) |
| **4** | DMSO | 4.57 (d, 7.0 Hz) | 3.61 (d, 12.5 Hz) |
| **5** | $CD_3CN$ | 4.18 (d, 7.0 Hz), 4.04 (d, 6.8 Hz) | 3.31 (d, 12.2 Hz), 3.16 (d, 12.5 Hz) |
| **5** | $(CD_3)_2CO$ | -* | -* |
| **5** | $CD_2Cl_2$ | 4.32 (d, 7.0 Hz), 3.93 (d, 7.00 Hz) | 3.27 (d, 12.5 Hz), 3.24 (d, 12.4 Hz) |

* $^{1}$H NMR spectra of complex **1** in $CD_2Cl_2$ and complex **5** in $(CD_3)_2CO$ could not be recorded due to the insolubility of these complexes in these solvents.

**Table 5.** ν (Hz), $T_c$ and $\Delta G^{\ddagger}$ data for complexes **1-4**

| **Complex** | **Solvent** | **Interchaging groups** | **$T_c$ (K)** | **Δν (Hz)** | **$\Delta G^{\ddagger}$ (KJ $mol^{-1}$)** |
|---|---|---|---|---|---|
| **1** | acetonitrile-$d_3$ | $H_{syn}$-$H_{syn}$ | 248 | ----- | ------ |
| | | $H_{anti}$-$H_{anti}$ | 298 | 18.2 | 63.8 |
| | acetone-$d_6$ | $H_{syn}$-$H_{syn}$ | 233 | 11.6 | 50.3 |
| | | $H_{anti}$-$H_{anti}$ | 298 | 69.8 | 60.5 |
| **2** | acetonitrile-$d_3$ | $H_{syn}$-$H_{syn}$ | -- | | |
| | | $H_{anti}$-$H_{anti}$ | -- | | |
| | acetone-$d_6$ | $H_{syn}$-$H_{syn}$ | -- | | |
| | | $H_{anti}$-$H_{anti}$ | 298 | 64.5 | 60.7 |
| | dichloromethane-$d_2$ | $H_{syn}$-$H_{syn}$ | | | |
| | | $H_{anti}$-$H_{anti}$ | > 305 | 100 | > 61 |
| **3** | acetonitrile-$d_3$ | $H_{syn}$-$H_{syn}$ | -- | | |
| | | $H_{anti}$-$H_{anti}$ | -- | | |
| | acetone-$d_6$ | $H_{syn}$-$H_{syn}$ | 213 | 10.6 | 46.0 |
| | | $H_{anti}$-$H_{anti}$ | 298 | 61.0 | 60.8 |
| | dichloromethane-$d_2$ | $H_{syn}$-$H_{syn}$ | > 305 | 12.5 | > 66 |
| | | $H_{anti}$-$H_{anti}$ | > 305 | 95.0 | > 61 |
| **4** | acetonitrile-$d_3$ | $H_{syn}$-$H_{syn}$ | | | |
| | | $H_{anti}$-$H_{anti}$ | | | |
| **4** | acetone-$d_6$ | $H_{syn}$-$H_{syn}$ | 233 | 15.6 | 49.7 |
| | | $H_{anti}$-$H_{anti}$ | -- | | |
| | dichloromethane-$d_2$ | $H_{syn}$-$H_{syn}$ | 298 | 18.2 | 63.8 |
| | | $H_{anti}$-$H_{anti}$ | 298 | 70.5 | 60.5 |

**Table 6.** Selected bond lengths (Å) and bond angles (º) for [Pd($\eta^3$-$C_3H_5$)($L^2$)]($BF_4$) **(2)** with estimated standard deviations (e.s.d.s) in parentheses

| | | | |
|---|---|---|---|
| Pd-N(1) | 2.115(3) | Pd-C(19) | 2.144(3) |
| Pd-N(2) | 2.117(3) | C(17)-C(18) | 1.373(8) |
| Pd-C(17) | 2.101(4) | C(18)-C(19) | 1.402(6) |
| Pd-C(18) | 2.108(3) | | |
| | | | |
| N(1)-Pd-N(2) | 77.68(10) | N(2)-Pd-C(19) | 110.82(13) |
| N(1)-Pd-C(17) | 102.78(18) | C(17)-Pd-C(19) | 68.23(19) |
| N(1)-Pd-C(18) | 134.61(18) | C(17)-Pd-C(18) | 38.1(2) |
| N(1)-Pd-C(19) | 170.71 (14) | C(18)-Pd-C(19) | 38.48(18) |
| N(2)-Pd-C(17) | 171.11(17) | C(17)-C(18)-C(19) | 118.3(4) |
| N(2)-Pd-C(18) | 145.13(18) | | |

**Table 7.** Crystallographic data for $[Pd(\eta^3\text{-}C_3H_5)(L^2)](BF_4)$ **(2)**

| | |
|---|---|
| Formula | $C_{19}H_{20}BF_4N_3Pd$ |
| *M* | 483.59 |
| Temperature (K) | 293(2) |
| Crystal System | monoclinic |
| Space group | $P2_1/c$ |
| Unit cell dimensions | |
| *a* (Å) | 8.028(5) |
| *b* (Å) | 10.519(4) |
| *c* (Å) | 23.157(10) |
| $\alpha$ (º) | 90 |
| $\beta$ (º) | 95.14(2) |
| $\gamma$ (º) | 90 |
| U (Å$^3$) | 1947.7(17) |
| Z | 4 |
| $D_{calc}$ (g.cm$^{-3}$) | 1.649 |
| $\mu$ (mm$^{-1}$) | 0.999 |
| *F*(000) | 968 |
| Crystal size | 0.2 x 0.1 x 0.1 |
| θ range (º) | 2.55 to 29.99 |
| Index range | -9<h<10, 0<k<14, 0<l<32 |
| Reflexions collected/ unique | 14739 / 4418 [R(int) = 0.0351] |
| Data/restraints/parameters | 4418 / 20 / 295 |
| Goodness-of-fit | 1.134 |
| Final $R_1$, ω$R_2$ | 0.0384, 0.1104 |
| $R_1$ (all data), ω$R_2$ | 0.0449, 0.1171 |
| Residual electron density (e Å$^{-3}$) | 0.468 and – 0.647 |

**Figure captions**

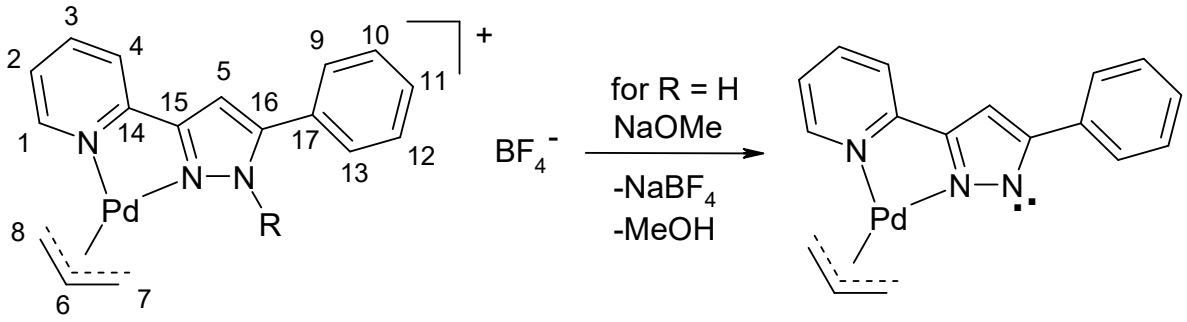
**Figure 1.** Numbering Scheme and reaction for the obtaining of complex **5**

**Figure 2.** $^{1}H$ NMR spectra (250 MHz, 298 K) of complex **2** in acetone-$d_6$ (a), acetonitrile-$d_3$ (b), and dichloromethane-$d_2$ (c)

**Figure 3.** $^{1}H$ NMR spectra (250 MHz) of complex **2** in acetone-$d_6$ at variable temperatures (233-298 K)

**Figure 4.** ORTEP drawing of the cation $[Pd(\eta^3\text{-}C_3H_5)(L^2)]^+$ (ellipsoids are shown at the 50% probability level)

**Figure 1.**




**(1)** R = H

**(2)** R = ethyl

**(3)** R = octyl

**(4)** R = $CH_2CH_2OH$

**(5)**

**Figure 2.**

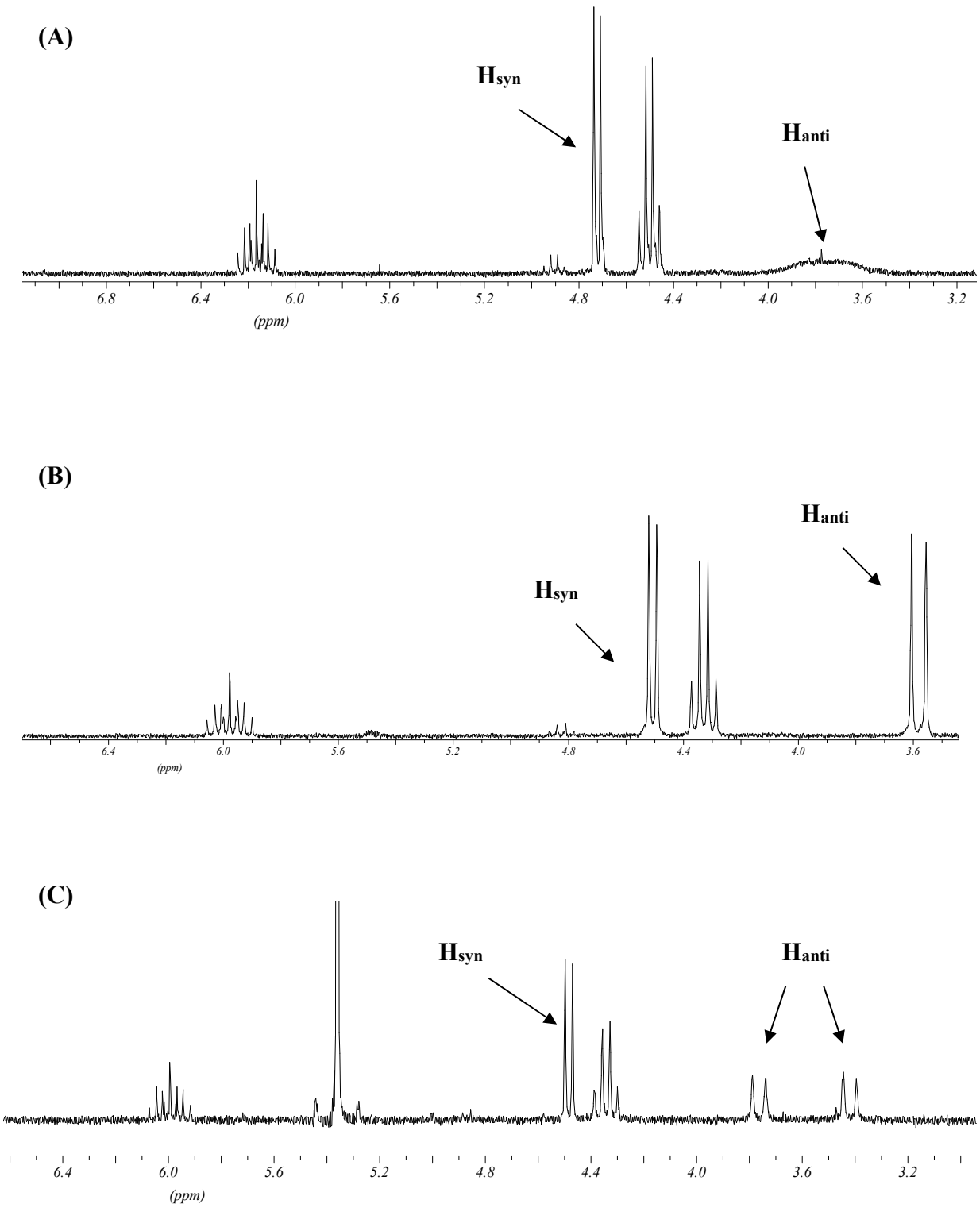

(A)
Hsyn
Hanti
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
(ppm)
(B)
Hanti
Hsyn
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
(ppm)
(C)
Hsyn
Hanti
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
(ppm)

**Figure 3.**

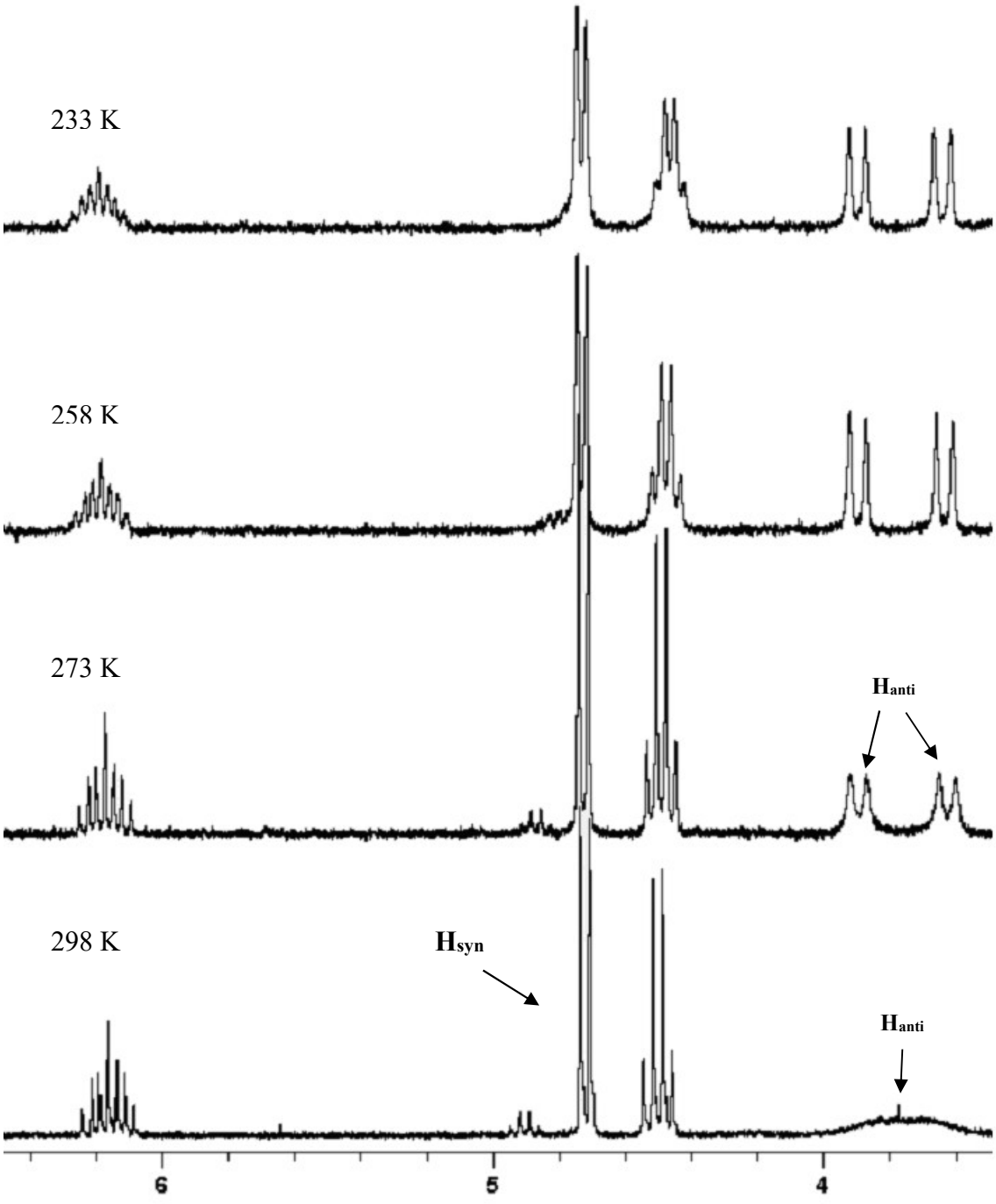
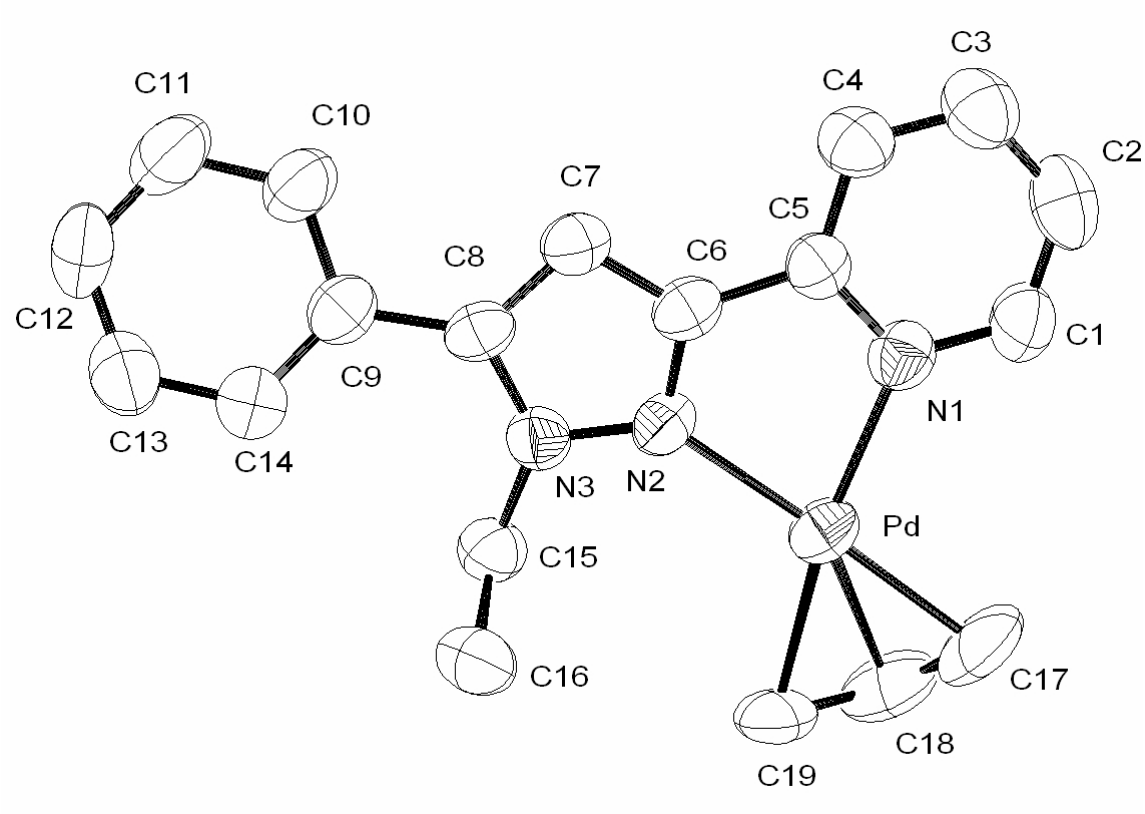


**Figure 4.**


C11
C10
C3
C4
C2
C7
C5
C8
C6
C12
C1
C9
N1
C13
C14
N3
N2
Pd
C15
C16
C17
C18
C19