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Synthesis and molecular structures of palladium(II) metalated 2-phenylpyridine complexes [PdCl(pyC_6H_4)L] containing amino- or acetylamino-pyridine co-ligands

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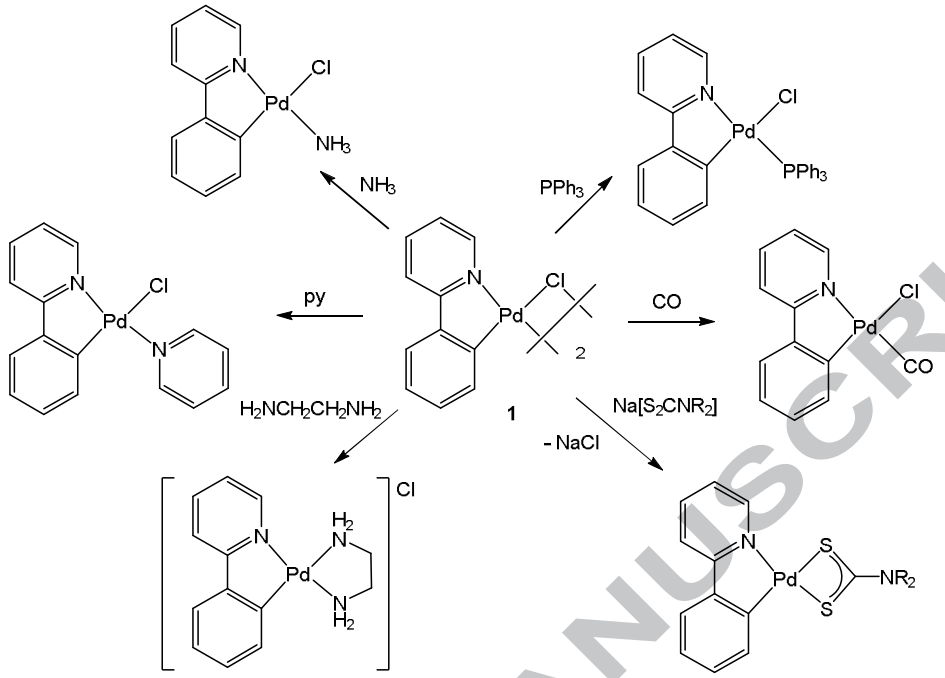
Abstract A number of cyclometalated palladium(II) complexes [PdCl(pyC_6H_4)(L)] containing amino-pyridine or acetylamino-pyridine co-ligands (L) have been prepared from the reaction of [Pd(pyC_6H_4)(μ-Cl)]$_2$ with two equivalents of these ligands. Crystal structures of four examples have been carried out, each showing a distorted square planer geometry around palladium with the amino- or acetylamino-pyridine ligand being coordinated *via* nitrogen atom and lying almost perpendicular to the square-plane. Similarly, [PdCl(pyC_6H_4)(κ^1-dppmO)] and [PdCl(pyC_6H_4)(κ^1-dppeO)] result from reactions of [Pd(C_6H_4py)(μ-Cl)]$_2$ with $Ph_2PCH_2P(O)PPh_2$ (dppmO) and $Ph_2PCH_2CH_2P(O)PPh_2$ (dppeO) respectively. Here the phosphine ligand is attached *via* only phosphorus, however, removal of the chloride upon addition of $AgNO_3$ lead to the formation of [Pd(pyC_6H_4)(κ^2-dppmO)][NO_3] and [Pd(pyC_6H_4)(κ^2-dppeO)][NO_3] in which the ligands are believed to bind in a chelate fashion.

Keywords: palladium, cyclometalated, crystal structure, 2-phenylpyridine, synthesis

1. Introduction

Organometallic palladium complexes containing cyclometalated ligands have attracted widespread interest for applications as anti-cancer treatments [**1-5**] and in catalysis [**6-11**], together with their novel physical properties [**12-17**]. The development of this chemistry stems in part from the ready availability of starting materials. Thus in 1968 reaction of 2-phenylpyridine with $Na_2[PdCl_4]$ was shown to afford a simple, high yielding route to the chloro-bridged dimer $[Pd(pyC_6H_4)(\mu\text{-}Cl)]_2$ (**1**) [**18**]. This has been used as a precursor towards the synthesis of a wide range of monomeric complexes of the type $[PdCl(pyC_6H_4)L]$ (Scheme 1). For example, addition of carbon monoxide affords $[PdCl(pyC_6H_4)(CO)]$ [**13**] and PPh_3 affords $[PdCl(pyC_6H_4)(PPh_3)]$ [**19**]. With monoanionic chelate ligands such as dithiocarbamates the chloride displacement is also facile affording neutral complexes $[Pd(pyC_6H_4)(S_2CNR_2)]$ [**20,21**], while with chelating neutral ligands (L_2) such as diphosphines and diamines, salts of the form $[Pd(pyC_6H_4)(L_2)][Cl]$ result [**13,22**].

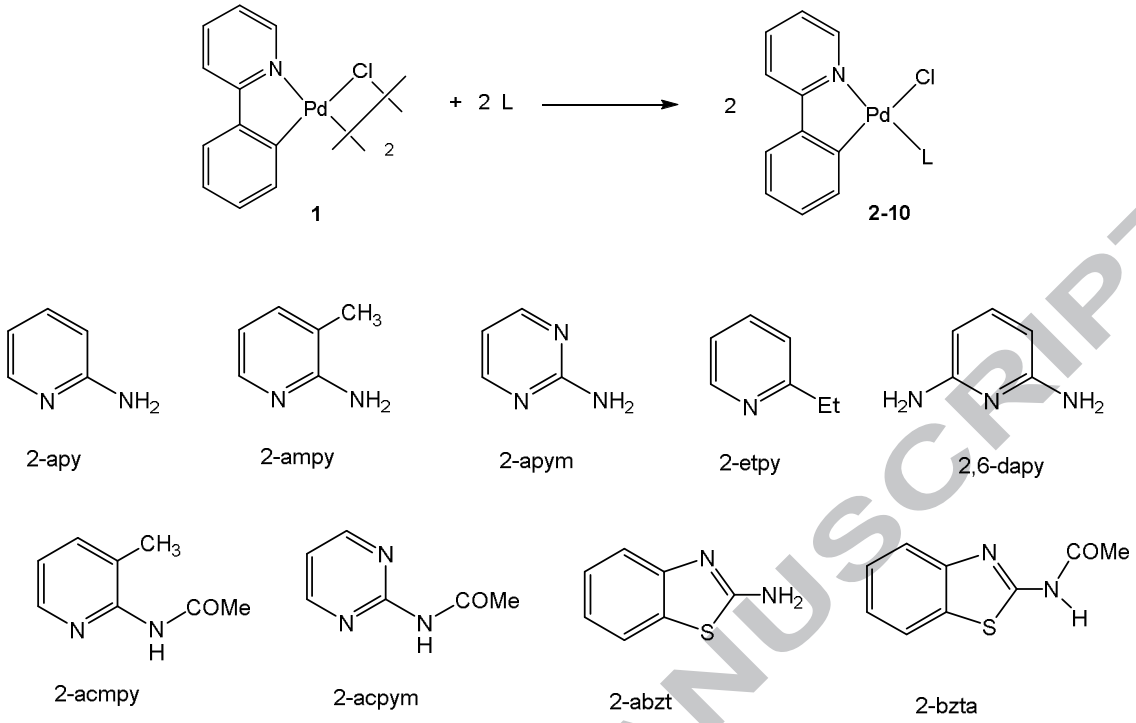
Palladium complexes containing heterocyclic nitrogen-containing ligands, such as derivatives of pyridine, quinoline, pyrazole, and 1,10-phenanthroline, especially the *trans* analogues with non-planar amine ligands, have been found to overcome multifactorial cisplatin resistance in human ovarian cell lines [**23,24**]. Given this, we were somewhat surprised to note that palladium complexes of the type $[PdCl(pyC_6H_4)L]$ containing simple pyridine-derived ligands were relatively rare. Thus, López and co-workers have reported the synthesis of $[PdCl(pyC_6H_4)(py)]$ upon reaction of **1** with pyridine in acetone, together with various related amine complexes $[PdCl(pyC_6H_4)(NH_3)]$ and $[PdCl(pyC_6H_4)(NH_2R)]$ ($R = Pr^i$, Bu^t) [**25**]. Pazderski and co-workers also reported the synthesis of $[PdCl(pyC_6H_4)(py)]$ together with a series of pyridine derivatives including the 2,4,6-trimethylpyridine complex which was crystallographically characterised [**26**]. Herein we report the related synthesis and characterisation of a series of amino- and acetylamino-pyridine complexes $[PdCl(pyC_6H_4)L]$. The aim of our work was to see if these ligands would act as mono- or bidentate ligands. In all cases the former is seen and this is confirmed by the crystal structures of four examples. In developing this idea further we also report the synthesis of diphosphine monoxide complexes, $[PdCl(pyC_6H_4)\{\kappa^1\text{-}Ph_2P(CH_2)_nPPh_2(O)\}]$ (n = 1,2), for which spectroscopic data strongly suggest a monodentate coordination through phosphorus. However, addition of silver nitrate to these complexes result in precipitation of AgCl and the formation of salts in which the ligand acts as a P,O-chelate.



Scheme 1.

2. Results and discussion

2.1 Synthesis and characterisation of [PdCl(pyC$_6$H$_4$)L] - Treatment of [Pd(pyC$_6$H$_4$)(μ-Cl)]$_2$ (**1**) with two equivalents of 2-aminopyridine in ethanol afforded after work-up the yellow mononuclear complex [PdCl(pyC$_6$H$_4$)(2-apy)] (**2**) in 78% yield. Similar reactions with 2-amino-3-methylpyridine (2-ampy), 2-aminopyrimidine (2-apym) and 2-ethylpyridine (2-etpy) also afforded related complexes **3-5** as yellow solids in 60-80% yields (Scheme 2). Spectroscopic and analytical data were in full accord with the proposed formulations. The ^{1}H NMR spectra (in d^6-dmso) were particularly informative with each showing a complex series of signals in the aromatic region of the spectrum over some 3 ppm. For example for **2**, eleven separate signals were observed between δ 9.43-6.23 consistent with the inequivalence of all aromatic protons, while the amine protons were observed as a singlet at δ 5.76.



Scheme 2.

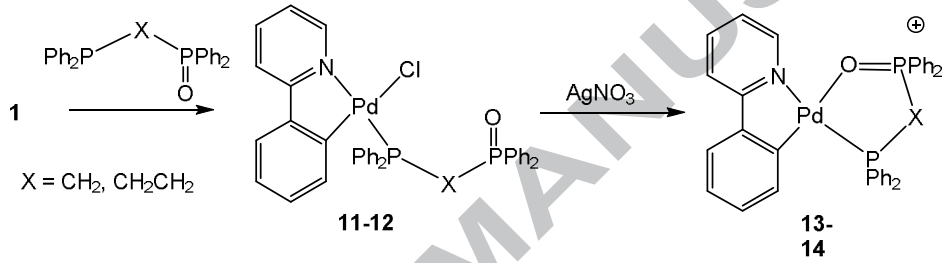
In order to confirm the above formulations, crystal structures were carried out on **2-4** the results of which are summarised in Figures 1-2 and Table 1. Each consists of discrete monomeric molecule with distorted square planer geometry around palladium. The metal atom is ligated to one nitrogen and ortho-carbon of phenyl-pyridine ligand, one chloride and the nitrogen of the introduced ligand. In all cases a regioselective N-*trans*-N bonding mode is observed. The Pd-C and Pd-N bond distances are in good agreement with the previously reported palladium compounds [**13**,**22**,**26-28**]. The two cyclic ligands are approximately at right angles to one another (see Figure 2b), dihedral angles between the two planes being 84.82°, 70.06º and 81.17º for **2-4** respectively. The Pd-Cl bond lengths are fall in the range 2.3697(11)-2.4251(7) Å.

Reaction of **1** with two equivalents of 2,6-diaminopyridine affords [PdCl(pyC_6H_4)(2,6-dapy)] (**6**) as a yellow solid in 88% yield. Characterisation was made on the basis of analytical and spectroscopic data. The ^{1}H NMR spectrum is as expected for coordination through the pyridine nitrogen atom, a singlet at δ 5.44 being assigned to the four NH_2 protons. Likewise reactions with N-(2-pyridyl)acetamide (2-acpy) and N-(2-pyrimidyl)acetamide (2-acpym)

afford [PdCl(pyC_6H_4)(2-acpy)] (**7**) and [PdCl(pyC_6H_4)(2-acpym)] (**8**) in *ca.* 60-70% yields. Addition of 2-aminobenzothiazole (2-abzt) and benzothiazolacetamide (2-bzta) also afford similar compounds [PdCl(pyC_6H_4)(2-abzt)] (**9**) and [PdCl(pyC_6H_4)(2-bzta)] (**10**) respectively (Scheme 2). To confirm the formation of **9** a crystal structure was carried out the results of which are summarised in Figure 3 and Table 1. Crystallographically the system is more complex with three independent molecules in the asymmetric unit. However there are only small differences between them and only one is shown. The molecular structure is very similar to those of **2-4** and the dihedral angle between the planes of the two cyclic ligands is 86.09º in the molecule shown.

2.2 Synthesis and characterisation of diphosphine-oxide complexes [PdCl(pyC_6H_4){κ^1-$Ph_2P(CH_2)_nP(O)Ph_2$}] and [Pd(pyC_6H_4){κ^2-$Ph_2P(CH_2)_nP(O)Ph_2$}][NO_3] (n = 1,2) - Complexes containing hemi-labile diphosphine monoxide ligands have been extensively described with some being found to be efficient catalysts for a range of processes [**29-34**]. Following the successful synthesis of the pyridyl and amino-pyridyl complexes described we attempted the preparation of $Ph_2PCH_2P(O)Ph_2$ (dppmO) and $Ph_2PCH_2CH_2P(O)Ph_2$ (dppeO) complexes. Heating a mixture of **1** and two equivalents of dppmO in dichloromethane for 2 h resulted in the slow formation of a yellow solution which after removal of solids, cooling to room temperature and slow evaporation of the solvent afforded [PdCl(pyC_6H_4)(κ^1-dppmO)] (**11**) in 82% yield as a yellow solid. A similar reaction with dppeO gave [PdCl(pyC_6H_4)(κ^1-dppeO)] (**12**) in 68% yield. Unfortunately we have been unable to obtain single crystals of either suitable for a structural study and thus assignment is based on analytical and spectroscopic data. Both show two resonances in the $^{31}P\{^1H\}$ NMR spectrum appearing at *ca.* 32.6 and 28.3 ppm in **11** and 46.4 and 36.2 ppm for **12**. In **12** the two signals are relatively sharp and appear as doublets (J_{PP} 52 Hz), but in **11** the signal at 32.6 ppm is very broad and no couplings can be extracted. This suggests that there is a fluxional process taking place on the NMR timescale, possibly rotation about the Pd-P bond. Room temperature ^1H NMR spectra of both display a series of sharp signals, the methylene protons of the dppm(O) ligand appearing as a triplet a δ 4.39 (J 12.0 Hz), while for **12** a multiplet at δ 2.59 integrating to four protons. These data are consistent with the formation of complexes in which the diphosphine is bound in a monodentate fashion through phosphorus (Scheme 3). Addition of $AgNO_3$ to CH_2Cl_2 solutions of **11-12** resulted in a significant darkening of the solutions, elimination of AgCl and formation of **13–14** respectively. The $^{31}P\{^1H\}$ chemical shifts of

these cationic complexes are displaced downfield with regard to free ligand corresponding to phosphorus-coordinated complexes, as reported previously for related complexes [**35-38**], and being attributed to binding of the electronegative oxygen to the metal centre. Thus in **13** a pair of doublets are observed at 54.3 and 28.2 ppm (J_{PP} 53 Hz), while **14** is characterised by two slightly broad singlets at 46.4 and 36.2 ppm. The methylene protons in **14** are now observed as a complex multiplet centred at δ 2.79, while in **13** a triplet is observed at δ 4.59 (J_{PH} 8.0 Hz). While we cannot fully ascertain which regioisomer is generated in each instance, in all cases the regioselectivity is high. We favour the isomers shown in Scheme 3 in which the phosphorus lies *trans* to the nitrogen of the 2-pyridylphenyl ligand.



Scheme 3

As far as we are aware diphosphine-oxide complexes of this type have not previously been reported. However, the proposed six-membered chelate in **14** is likely to be very similar to that recently reported for [Pd(C_6H_4py){κ^2-Ph_2P(o-C_6H_4)C(O)H}][OTf], prepared in a related two-step procedure upon reaction of *ortho*-(diphenylphosphino)benzaldehyde with [Pd(pyC_6H_4)(μ-Cl)]$_2$ (**1**) which initially affords [PdCl(C_6H_4py){κ^1-Ph_2P(o-C_6H_4)C(O)H}] and then converts to the chelate upon addition of silver triflate [**39**].

3. Experimental

3.1 General methods and materials

All reactions were carried out in air using standard bench reagents. NMR spectra were recorded at the Institut für Chemie, Martin-Luther-Universität, Halle-Wittenberg, Germany, or University of Zaragoza, Spain on Varian Unity 500 and Gemini 200 spectrometers, respectively. IR spectra were recorded on a Shimadzu FT-IR 8400 spectrophotometer using KBr discs in the range 400-4000 cm^{-1}. Elemental analyses were carried out at University

College London, Martin-Luther-Universität, Halle-Wittenberg, Germany and University of Zaragoza, Spain. Melting points were measured on Gallenkamp melting point apparatus and were uncorrected. $Na_2[PdCl_4]$, 2-phenylpyridine, 2-aminobenzothiazole (2-abzt), 2-aminopyridine (2-apy), 2-aminopyrimidine (2-apym), 2-amino-3-methylpyridine (2-ampy), 2,6-diaminopyridine (2,6-dapy) and 2-ethylpyridine (2-etpy) were purchased and used as supplied. Compounds $[Pd(pyC_6H_4)(\mu\text{-}Cl)]_2$ (**1**) [**40**], N-(2-pyridyl-3-methyl) acetamide (2-acmpy) [**41**], N-(2-pyridyl)acetamide (2-acpy) [**42**], benzothiazolacetamide (2-bzta) [**43**] were prepared by literature methods.

3.2 Synthesis of [PdCl(pyC$_6$H$_4$)(2-apy)] (**2**) - A solution of 2-apy (0.050 g, 0.1337 mmol) in acetone (5ml) was added to a yellow suspension of **1** (0.0395 g, 0.0668 mmol) in acetone (10 ml). The resulting yellow solution was stirred for 2 h, filtered and slow evaporation of the solvent at room temperature gave yellow prismatic crystals (0.041 g, 78 %). Anal. Calc. for $C_{16}H_{14}ClN_3Pd$, C, 49.1, H, 3.6, N, 10.7. Found: C, 49.0, H, 3.8, N, 10.8 %. IR (KBr) 3047-3299s, 3157-3068m, 1625vs, 1600s, 406m cm^{-1}. ^{1}H NMR (dmso-d^6) δ 9.43 (dd, 1H, J 3.9, 0.8), 8.40 (dd, 1H, J 5.7, 0.8), 7.82 (ddd, 1H, J 8.0, 7.7, 1.5), 7.66 (d, 1H, J 7.9), 7.50 (ddd, 1H, J 8.0, 7.7, 1.5), 7.45 (dd, 1H, J 7.5, 1.5), 7.17 (ddd, 1H, J 6.4, 5.6, 1.2), 7.09 (ddd, 1H, J 7.6, 7.5, 1.2), 6.91(ddd, 1H, J 7.4, 7.2, 1.2), 6.74-6.68 (m, 2H), 6.23 (dd, 1H, J 7.7, 1.2), 5.76 (s, 2H, NH_2). Mp 252-254 ^{o}C.

3.3 Synthesis of [PdCl(pyC$_6$H$_4$)(2-ampy)] (**3**) - A solution of 2-ampy (0.200 g, 1.337 mmol) in CH_2Cl_2 (5 ml) and five drops of NEt_3 was added to a yellow suspension of **1** (0.395 g, 0.668 mmol) in CH_2Cl_2 (10 ml). The resulting yellow solution was stirred a room temperature for 3h, filtered and left to evaporate at room temperature. The yellow cubic crystals formed were filtered off and dried under vacuum (0.040 g, 75 %). Anal. Calc. for $C_{17}H_{16}ClN_3Pd$, C, 50.5, H, 3.9, N, 10.4. Found: C, 50.4, H, 3.8, N, 10.4. IR (KBr) 3417-3305s, 3170-3062w, 2918w, 2852w, 1618s, 1598s, 406m cm^{-1}. ^{1}H NMR (dmso-d^6) δ 9.46 (d, 1H, J 7.9), 8.32 (d, 1H, J 7.9), 7.81 (ddd, 1H, J 8.0, 7.9, 4.0), 7.66 (d, 1H, J 7.9), 7.46 (d, 1H, J 7.9), 7.40 (d, 1H, J 3.9), 7.18 (dd, 1H, J 5.9, 4.0), 7.08 (dd, 1H, 5.9, 4.0), 6.93 (dd, 1H, J 8.0, 7.9), 6.70 (dd, 1H, J 6.0, 5.9), 6.17 (d, 1H, J 7.9), 5.66 (s, 2H, NH_2), 2.21 (s, 3H, CH_3). Mp 232-234 ^{o}C.

3.4 Synthesis of [PdCl(pyC$_6$H$_4$)(2-apym)] (**4**) - A solution of 2-apym (0.127 g, 1.337 mmol) in acetone (5 ml) was added to a yellow suspension of **1** (0.395 g, 0.668 mmol) in acetone (10 ml). The yellow solution was stirred for 3 h, filtered and left to evaporate at room

temperature. The yellow cubic crystals formed were filtered off and dried under vacuum (0.390 g, 74 %). Anal. Calc. for $C_{15}H_{13}ClN_4Pd$ C: 46.1, H, 3.4, N, 14.3. Found: C, 46.0, H, 3.4, N, 14.2 % IR (KBr) 3330s, 3170s, 3278s, 1649s, 1562s, 460s cm^{-1}. ^1H NMR (dmso-d^6) δ 9.22 (d, 1H, J 4.0), 8.62 (d, 1H, J 4.0), 8.48 (s,1H), 8.20 (d, 1H, J 4.0), 8.04 (s, 2H, NH_2), 7.69 (d, 1H, J 4.0), 7.39 (s, 1H), 7.10 (d, 1H, J 8.0), 6.90 (d, 1H, J 8.0), 6.78 (d, 1H, J 4.0), 6.53 (d, 1H, J 8.0), 6.20 (d, 1H, J 8.0). Mp 216-218 °C.

3.5 Synthesis of [PdCl(pyC$_6$H$_4$)(2-etpy)] (**5**) - 2-Ethylpyridine (2-etpy) (0.280 g, 0.267 mmol) was added to a yellow suspension of **1** (0.0791 g, 0.1337 mmol) in EtOH (10 ml). The mixture was stirred for 3 h at room temperature. The yellow solution was filtered and allowed to evaporate at room temperature to give yellow cubic crystals (0.062 g, 63 %). Anal. Calc. for $C_{18}H_{17}ClN_2Pd$, C, 53.5, H, 4.4, N, 7.1. Found: C, 53.4, H, 4.4, N, 7.1 % IR (KBr) 3056m, 2962m, 1683w, 1604s, 406s cm^{-1}. ^1H NMR (dmso-d^6) δ 9.47 (d, 1H, J 5.3), 8.80 (d, 2H, 6.3), 7.81 (ddd, 1H, J 8.5, 8.0, 1.6), 7.65 (d, 1H, J 7.9), 7.47 (dd, 1H, J 7.7, 1.2), 7.29 (d, 2H, J 6.7), 7.15 (ddd, 1H, J 7.2, 6.5, 1.6), 7.10 (ddd, 1H, J 7.5, 7.5, 1.2), 6.94 (ddd, 1H, J 7.6, 7.5, 1.6), 6.25 (dd, 1H, J 7.7, 1.2), 2.76 (q, 2H, CH_2, J 8.0), 1.32 (t, 3H, Me, 8.0). Mp 282 °C decomposed.

3.6 Synthesis of [PdCl(pyC$_6$H$_4$)(2,6-dapy)] (**6**) - A solution of 2,6-dapy (0.024 g, 0.2219 mmol) in EtOH (5 ml) was added to a suspension of **1** (0.065 g, 0.1109 mmol) in EtOH (10ml). The mixture was stirred for 4 h and the yellow solid formed was filtered and dried under vacuum. This was recrystallized from MeOH and benzene to give yellow microcrystalline solid (0.071 g, 88 %). Anal. Calc. for $C_{16}H_{15}ClN_4Pd$, C, 47.4, H, 3.7, N, 13.8. Found: C, 47.6, H, 3.5, N, 14.0 % IR (KBr) 3434-3402s, 3278s, 1602s, 487m cm^{-1}. ^1H NMR (dmso-d^6) δ 9.46 (d, 1H, J 3.9), 7.84 (ddd, 1H, J 7.8, 7.7, 1.6), 7.67 (d, 1H, J 7.9), 7.46 (d, 1H, J 7.5), 7.34 (dd, 1H, J 7.9 , 4.0), 7.20 (ddd, 1H, J 7.2, 7.1, 1.2), 7.10 (ddd, 1H, J 7.6, 7.5, 0.8), 6.95 (ddd, 1H, J 8.7, 7.6, 1.2), 6.32 (d, 1H, J 7.5), 6.04 (d, 2H, J 7.9), 5.44 (s, 4H, $2NH_2$). Mp 254-256 °C.

3.7 Synthesis of [PdCl(pyC$_6$H$_4$)(2-acmpy)] (**7**) - Prepared and isolated by a method similar to that used for **2** except that NEt_3 was not added. Yield, 61%. Anal. Calc. for $C_{19}H_{18}ClN_3OPdCl.0.25CH_2Cl_2$, C, 49.4, H, 3.9, N, 8.9. Found: C, 49.4, H, 3.6, N, 8.2 % IR (KBr) 3211- 3168s, 2923w, 1683vs, 1602s, 1581m 405m cm^{-1}. 1H NMR (dmso-d^6), δ 9.74 (s, 1H, NH), 9.35 (d, 1H, J 3.9), 8.65 (d, 1H, J 7.9), 7.84 (ddd, 1H, J 7.9), 7.79 (d, 1H, J 7.9), 7.67 (d, 1H, J 7.9), 7.43 (d, 1H, J 7.9), 7.28 (ddd, 1H, J 7.9), 7.19 (ddd, 1H, J 5.9), 7.08 (ddd,

1H, J 7.9), 6.89 (ddd, 1H, J 7.9), 6.10 (d, 1H, J 7.9), 2.38 (s, 3H, MeCO), 2.23 (s, 3H, Me). Mp 310℃ decomposes.

3.8 Synthesis of [PdCl(pyC$_6$H$_4$)(2-acpym)] (**8**) - A solution of 2-acpym (0.0184 g, 0.134 mmol) in CH_2Cl_2 (5 ml) containing three drops of NEt_3 was added to a yellow suspension of **1** (0.0395 g, 0.067 mmol) in CH_2Cl_2 (10 ml). The yellow solution was stirred for 3 h, filtered and slow evaporation at room temperature gave a yellow precipitate which was recrystallized from CH_2Cl_2 and MeOH to give a yellow powder (0.041g, 71 %). Anal. Calc. for $C_{17}H_{15}ClN_4OPd$, 47.1, H, 3.5, N, 12.9. Found: C, 47.3, H, 3.4, N, 13.2 % IR (KBr) 3330s, 3170s, 3278s, 1649s, 1562s, 460s cm^{-1}. ^{1}H NMR (dmso-d^6) δ 9.42 (d, 1H, J 4.0), 8.66 (d, 1H, J 4.0), 8.57 (s, 1H, NH), 8.47 (s, 1H), 7.84 (dd, 1H, J 7.9, 4.0), 7.67 (d, 1H, J 7.9), 7.47 (d, 1H, J 7.9), 7.19 (dd, 1H, J 4.0, 4.0), 7.13 (dd, 1H, J 7.9, 4.0), 6.97 (dd, 1H, J 7.9, 3.8), 6.78 (dd, 1H, J 4.0, 4.0), 6.31 (d, 1H, J 7.9), 1.63 (s, 3H). Mp 182-184 ºC.

3.9 Synthesis of [PdCl(pyC$_6$H$_4$)(2-abzt)] (**9**) - A solution of 2-abzt (0.200 g, 1.337 mmol) in EtOH (5 ml) was added to a yellow suspension of **1** (0.395 g, 0.668 mmol) in EtOH (10 ml). The yellow solution was stirred for 2 h at room temperature, filtered and left to evaporate at room temperature. The yellow cubic crystals formed were filtered and dried under vacuum (0.480 g, 81 %). Anal. Calc. for $C_{18}H_{14}N_3SPdCl$, C, 49.3, H, 3.9, N, 7.6. Found: C, 49.5, H, 3.7, N, 7.8 % IR (KBr) 3255s, 3085s, 1614s, 1541s, 420m cm^{-1}. ^{1}H NMR (dmso-d^6) δ 9.26 (d, 1H, J 7.9), 8.02 (d, 1H, J 7.9), 7.99 (d, 1H, J 7.9), 7.67 (d, 1H, J 7.9), 7.62 (d, 1H, J 7.9), 7.43 (s, 2H, NH_2), 7.31-7.28 (m, 3H), 7.20-7.13 (m, 2H), 6.82 (dd, 1H, J 7.9, 1.2), 6.13 (d, 1H, J 7.9). Mp 208-210℃.

3.10 Synthesis of [PdCl(pyC$_6$H$_4$)(2-bzta)] (**10**) - A solution of 2-bzta (0.0513 g, 0.267 mmol) in CH_2Cl_2 (5 ml) was added to yellow suspension of **1** (0.0395 g, 0.0668 mmol) in CH_2Cl_2 (10 ml). The yellow solution was stirred for 3 h, filtered and left to evaporate at room temperature. The yellow precipitate formed was recrystallized from CH_2Cl_2 and MeOH to give a yellow powder (0.078 g, 60 %). Anal. Calc. for $C_{20}H_{16}ClN_3OPdS.0.2CH_2Cl_2$, C, 48.0, H, 3.2, N, 8.3. Found: C, 48.3, H, 3.2, N, 8.1 % IR (KBr) 3136-3109m, 3045m, 2958-2923m, 1693s, 1602s, 1537vs, 437m cm^{-1}. ^{1}H NMR (dmso-d^6) δ 10.99 (s, 1H, NH), 9.42 (s, 1H), 8.34 (s, 1H), 7.88 (d, 1H, J 7.9), 7.82 (d, 1H, J 3.9), 7.70 (d, 1H, J 7.9), 7.45-7.37 (m, 3H), 7.23 (dd, 1H, J 3.9, 2.0), 7.05 (dd, 1H, J 7.9, 4.0), 6.73 (dd, 1H, J 7.9, 3.0), 5.82 (s, 1H), 2.39 (s, 3H, Me). Mp 264-266℃.

3.11 Synthesis of [PdCl(pyC$_6$H$_4$)(κ^1-dppmO)] (**11**) - A solution of dppmO (0.042 g, 0.10 mmol) in CH_2Cl_2 (4 ml) was added to a suspension of **1** (0.036 g, 0.10 mmol) in CH_2Cl_2 (5 ml). The mixture was heated under reflux for 2 h. The resulting yellow solution was filtered off and left to stand for slow evaporation for one day. The yellow solid formed was filtered off, dried and recrystallized from CH_2Cl_2/hexane to afford the product as yellow solid (0.0623 g, 82%). Anal. Calc. for $C_{36}H_{30}NOP_2PdCl$: C, 62.1; H, 4.3; N, 2.0. Found: C, 61.9; H, 4.3; N, 2.1 %. IR (KBr): 3051m, 2950w, 1649m, 1562m, 1431s, 1261s, 1186s, 1101s, 1018s, 800vs, 690m, 501m cm^{-1}. ^{1}H NMR (dmso-d^6): δ 9.27 (s, 1H), 8.16 (s,1H), 7.92-7.35 (m, 22H), 7.17 (d, 1H), 6.97 (t, 1H, J 8.0), 6.51 (t, 1H, J 7.5), 6.29 (t, 1H, J 7.6), 4.39 (t, 2H, J 12.0, CH_2). ^{31}P NMR (dmso-d^6): δ 32.6 (vbrs, Ph_2PO), 28.3 (s, Ph_2P) ppm. Mp 162-164 ^{o}C.

3.12 Synthesis of [PdCl(pyC$_6$H$_4$)(κ^1-dppeO)] (**12**) - This complex was prepared and isolated in a similar manner that used for **11** to afford **13** in 68% yield. Anal. Calc. for $C_{37}H_{32}NOP_2PdCl$: C, 62.6; H, 4.5; N, 2.0. Found: C, 62.5; H, 2.5; N, 2.0 %. IR (KBr): 3055m, 2916m, 2850w, 1731m, 1596m, 1566m, 1481m, 1434s, 1186vs, 1114m, 1016m, 730m, 692m, 513m, cm^{-1}. ^{1}H NMR (dmso-d^6): δ 9.45 (s, 1H), 8.12 (d, 1H, J 8.0), 7.91(d, 1H, J 7.4), 7.89(d, 1H, J 7.4), 7.75 (d, 1H, J 7.6), 7.61-7.45 (m, 20H), 6.96 (t, 1H, 7.9), 6.51 (t, 1H, J 7.9), 6.44 (t,1H, J 7.8), 2.59 (m, 4H, 2CH_2) ppm. ^{31}P NMR (dmso-d^6): δ 38.9 (d, J 52, Ph_2PO), 30.3 (d, J 52, Ph_2P) ppm. Mp 212-216 ^{o}C.

3.13 Synthesis of [Pd(pyC$_6$H$_4$)(κ^2-dppmO)]NO$_3$ (**13**) - A solution (5 ml) of silver nitrate $AgNO_3$ (0.052 g, 0.05 mmol) in a mixture of EtOH/H_2O (1:2) was added to a solution of **11** (0.041 g, 0.05 mmol) in CH_2Cl_2 (4 ml). The mixture was stirred in dark for 2 h, the mixture was filtered off to remove solid AgCl and the mother liquor was left for slow evaporation at room temperature to afford a yellow solid. This was filtered off, washed with water, dried and recrystallized from CH_2Cl_2 (0.0482 g, 88%). Anal. Calc. For $C_{36}H_{30}N_2O_4P_2Pd$: C, 59.8; H, 4.2; N, 3.9. Found: C, 59.6; H, 4.0; N, 3.3 %. IR (KBr): 3055m, 2923m, 1625m, 1558m, 1485w, 1436m, 1382s, 1132m, 740m, 692m, 509m cm$^{-1.}$ ^{1}H NMR (dmso-d^6): δ 9.06 (s, 1H), 8.25 (d, 1H, J 7.0), 7.86-7.44 (m, 22H), 7.07 (t, 1H, J 7.5), 6.63 (t, 1H, J 7.5), 6.38 (t, 1H, J 7.5), 4.59 (t, 2H, J 8.0, CH_2) ppm. ^{31}P NMR (dmso-d^6): δ 54.3 (d, J 53, Ph_2PO), 28.2 (d, J 53, Ph_2P) ppm. Mp 154-156 ^{o}C.

3.14 Synthesis of [Pd(pyC$_6$H$_4$)(κ^2-dppeO)]NO$_3$ (**14**) - This complex was prepared and isolated in a manner similar to that used for **13** to afford **14** in 92% yield. Anal. Calc. for $C_{37}H_{32}N_2O_4P_2Pd$: C, 60.2; H, 4.5; N, 3.8. Found: C, 60.4; H, 4.3 ; N, 3.7 %. IR (KBr):

3058w, 2920w, 1652m, 1600m, 1560m, 1481m, 1434m, 1380s, 1126m, 730s, 694s, 545m, 507m cm^{-1}. ^{1}H NMR (dmso-d^6): δ 8.95 (s, 1H), 8.25 (s, 1H), 7.93-7.47 (m, 22H), 7.03 (t, 1H, J 6.6), 6.96 (t, 1H, J 7.5), 6.38 (t, 1H, J 7.6), 2.83-2.75 (m, 4H, $2CH_2$) ppm. ^{31}P NMR (dmso-d^6): δ 46.4 (brs, Ph_2PO), 36.2 (brs, Ph_2P) ppm. Mp: 153-155 ^{o}C.

3.15 Crystallography

Single crystals of **2** and **3** were mounted on glass fibres and all geometric and intensity data were taken from these samples using a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 150 ± 2 K. Data collection, indexing and initial cell refinements were all done using SMART software. Data reduction were carried out with SAINT PLUS and absorption corrections applied using the programme SADABS [**44**]. Structures were solved by direct methods or Patterson methods and developed using alternating cycles of least-squares refinement and difference-Fourier synthesis. All non-hydrogen atoms were refined anisotropically. Hydrogens were placed in calculated positions (riding model). Structure solution used SHELXTL PLUS V6.10 program package [**45**].

Single crystals of **4** and **9** were mounted on a SuperNova, Dual Atlas diffractometer using a Nylon Loop. The crystals were kept at 150(1) K during data collection. Using Olex2 [**46**] the structure was solved using Direct Methods. The structures were refined with the ShelXL refinement package using Least Squares minimization [**47**]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms (except those directly bonded to metals) were included using a riding model.

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Supplementary data

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, 1417810 for **2**, 1417809 for **3,** 1417812 for **4** and 1417811 for **9**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1 EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.ac.uk).

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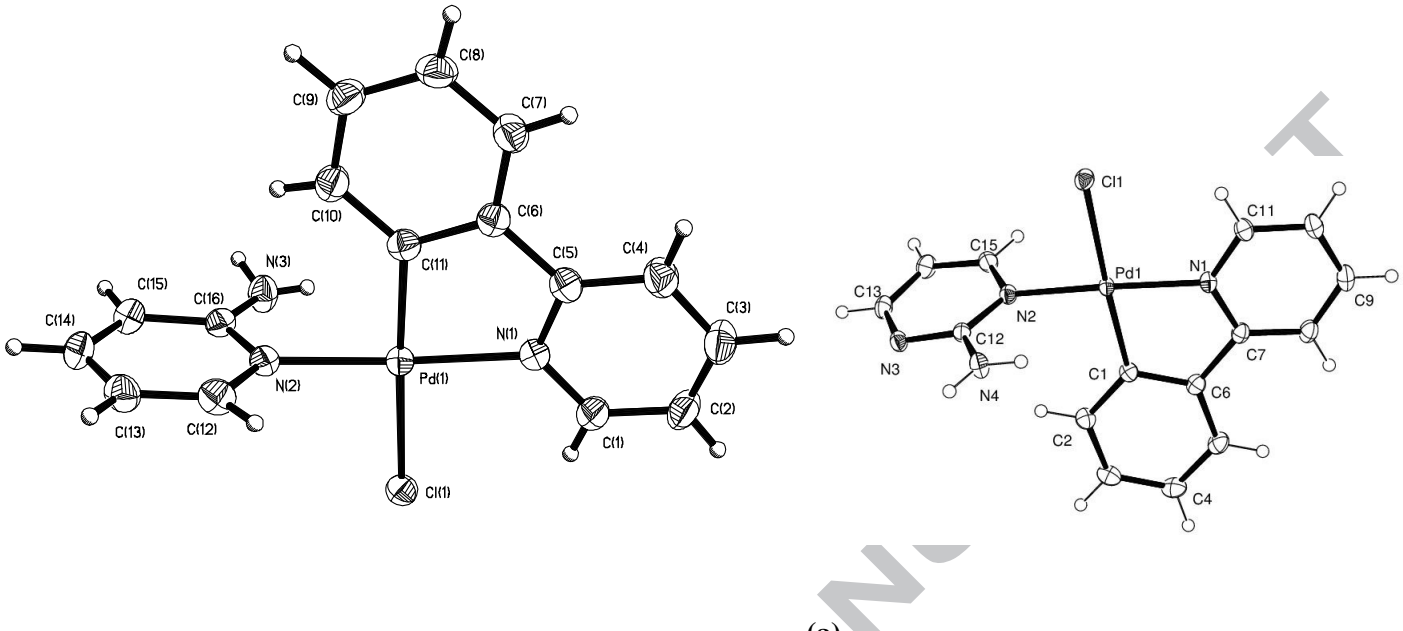
Table 1. Crystallographic data

Compound	**2**	**3**	**4**	**9**
Empirical formula	$C_{16}H_{14}ClN_3Pd$	$C_{17}H_{16}ClN_3Pd$	$C_{15}H_{13}ClN_4Pd$	$C_{54}H_{42}Cl_3N_9Pd_3S_3$
Formula weight (Å)	390.15	404.18	391.17	1338.80
Temperature (K)	150(2)	150(2)	150 (2)	150 (2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$
Unit cell dimensions				
a (Å)	11.345(3)	12.171(5)	9.1845(4)	7.1075(2)
b (Å)	7.112(2)	7.602(3)	9.2070(3)	32.6357(9)
c (Å)	17.798(5)	16.554(7)	17.6564(7)	22.3095(7)
α (°)	90	90	90	90
β (°)	96.626(4)	99.010(6)	104.926(5)	90.270(3)
γ (°)	90	90	90	90
Volume (Å^3)	1426.5(7)	1512.7(11)	1442.67(3)	5174.8(3)
Z	4	4	4	4
Density (calculated) (Mg/m^3)	1.817	1.775	1.8008	1.7183
Absorption coefficient (mm^{-1})	1.483	1.402	1.469	1.356
F(000)	776	808	772.8	2656.1
Crystal size (mm)	0.42 × 0.38 × 0.22	0.28 × 0.26 × 0.08	0.33 × 0.17 × 0.09	0.39 × 0.29 × 0.08
θ Range for data collection (°)	2.76 to 28.36	2.25 to 28.10	6.38 to 59.1	5.62 to 59.2
Index ranges	$-14 \le h \ge 14$ $-9 \le k \ge 9$ $-23 \le l \ge 23$	$-15 \le h \ge 16$ $-9 \le k \ge 9$ $-21 \le l \ge 21$	$-12 \le h \ge 12$ $-12 \le k \ge 9$ $-24 \le l \ge 23$	$-9 \le h \ge 7$ $-37 \le k \ge 41$ $-30 \le l \ge 21$
Reflections collected	10871	11390	9885	40206
Independent reflections [R_{int}]	3253 [R_{int} = 0.0299]	3402 [R_{int} = 0.0436]	3529 [R_{int} = 0.0445]	12564 [R_{int} = 0.0424]
Data / restraints / parameters	3253 / 0 / 246	3402 / 0 / 199	3529 / 0 /189	12564 / 0 / 648
Goodness-of-fit on F^2	0.969	0.944	1.039	1.058
Final R indices [I>2σ(I)]	R_1 = 0.0252, wR_2 = 0.0598	R_1 = 0.0363, wR_2 = 0.0832	R_1 = 0.0306, wR_2 = 0.0731	R_1 = 0.0403, wR_2 = 0.0795
R indices (all data)	R_1 = 0.0328, wR_2 = 0.0612	R_1 = 0.0513, wR_2 = 0.0857	R_1 = 0.0334, wR_2 = 0.0757	R_1 = 0.0498, wR_2 = 0.0847
Largest diff. peak and hole(e.Å^{-3})	0.473 and -0.469	1.301 and -1.301	1.07 and -0.86	1.20 and -0.99

Table 2. Selected bond lengths (Å) and angles (º)

2			
Pd(1)–N(1)	2.0140(19)	Pd(1)–Cl(1)	2.4042(8)
Pd(1)–N(2)	2.025(2)	Pd(1)–C(11)	1.954(2)
N(1)–Pd(1)–Cl(1)	96.40(6)	N(2)–Pd(1)–Cl(1)	91.16(6)
N(1)–Pd(1)–N(2)	170.09(8)	C(11)–Pd(1)–N(1)	81.37(9)
C(11)–Pd(1)–N(2)	91.36(9)	C(11)–Pd(1)–Cl(1)	176.54(7)
3			
Pd(1)–N(1)	2.009(3)	Pd(1)–Cl(1)	2.3697(11)
Pd(1)–N(2)	1.999(3)	Pd(1)–C(17)	1.951(3)
N(1)–Pd(1)–Cl(1)	88.96(9)	N(2)–Pd(1)–Cl(1)	95.71(9)
N(1)–Pd(1)–N(2)	175.31(11)	C(17)–Pd(1)–N(2)	81.88(13)
C(17)–Pd(1)–N(1)	93.43(13)	C(17)–Pd(1)–Cl(1)	176.07(10)
4			
Pd(1)–N(1)	2.0309(19)	Pd(1)–C(1)	1.987(2)
Pd(1)–N(2)	2.0453(19)	Pd(1)–Cl(1)	2.4200(6)
N(1)–Pd(1)–Cl(1)	95.76(6)	N(2)–Pd(1)–Cl(1)	90.02(6)
N(1)–Pd(1)–N(2)	171.46(8)	C(1)–Pd(1)–Cl(1)	175.95(7)
C(1)–Pd(1)–N(1)	81.26(9)	C(1)–Pd(1)–N(2)	93.25(9)
9			
Pd(1)–N(1)	2.032(2)	Pd(1)–C(1)	1.982(3)
Pd(1)–N(2)	2.029(2)	Pd(1)–Cl(1)	2.4251(7)
N(1)–Pd(1)–Cl(1)	97.90(7)	N(2)–Pd(1)–Cl(1)	88.37(7)
N(1)–Pd(1)–N(2)	171.83(9)	C(1)–Pd(1)–Cl(1)	172.54(8)
C(1)–Pd(1)–N(1)	81.26(11)	C(1)–Pd(1)–N(2)	93.20(11)



(a) **(b)**

Figure 1. The molecular structures of **(a)** [PdCl(pyC_6H_4)(2-apy)] (**2**) and **(b)** [PdCl(pyC_6H_4)(2-apym)] (**4**)

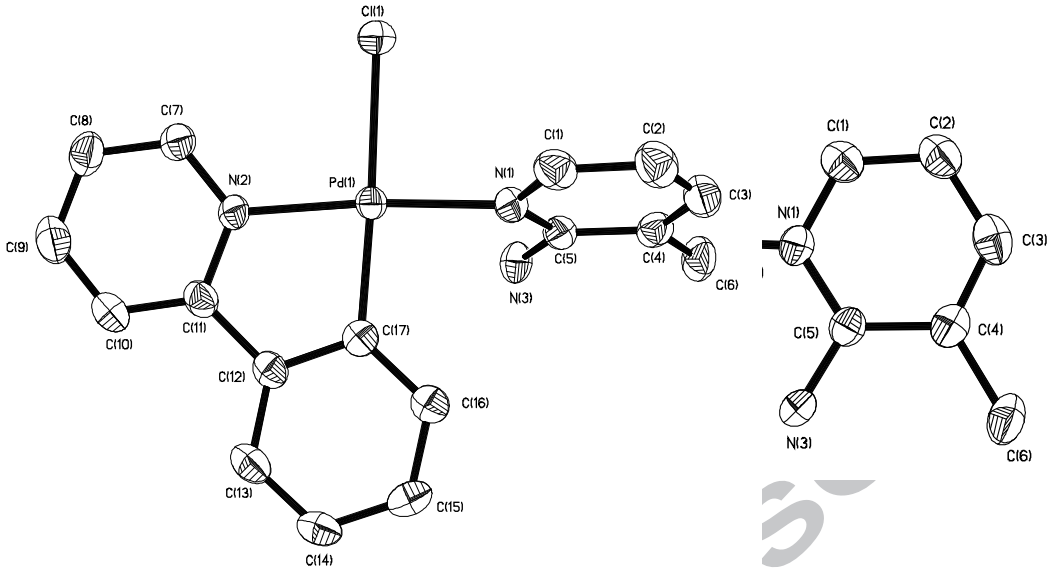


Figure 2. Two views of the molecular structure of [PdCl(pyC_6H_4)(2-ampy)] (**3**)

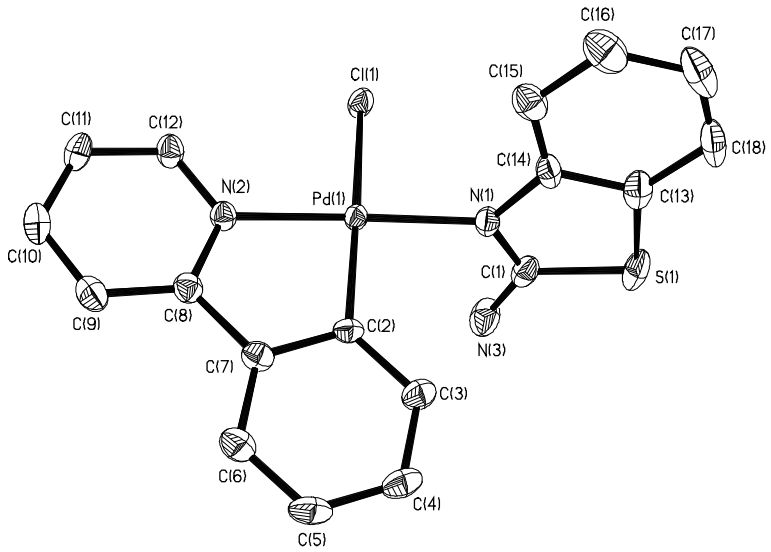
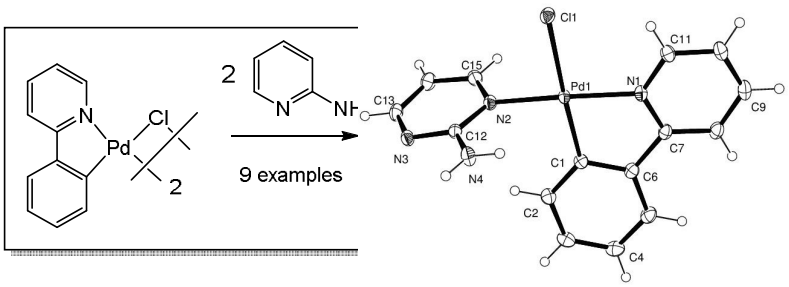


Figure 3. The molecular structure of one independent molecule of [PdCl(pyC_6H_4)(2-abzt)] (**9**)

Highlights

- Synthesis of cyclometalated palladium(II) complexes [PdCl(pyC_6H_4)(L)]
- Crystal structure of four examples
- Synthesis of chelate complexes [Pd(pyC_6H_4)(κ^2-diphospineO)]Cl

Graphic



Graphic abstract

Cyclometalated palladium(II) complexes, $[PdCl(pyC_6H_4)(L)]$, containing amino-pyridine, acetylamino-pyridine or diphosphine monoxide co-ligands (L) have been prepared and crystal structures of four examples are reported, each showing a distorted square planer geometry around palladium with the N-coordinated amino- or acetylamino-pyridine ligand lying almost perpendicular to the square-plane. Removal of the chloride from the diphosphine monoxide complexes upon addition of $AgNO_3$ lead to the formation of $[Pd(pyC_6H_4)(\kappa^2\text{-dppmO})][NO_3]$ and $[Pd(pyC_6H_4)(\kappa^2\text{-dppeO})][NO_3]$ in which the ligands are believed to bind in a chelate fashion.