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# Mono- and bimetallic complexes of the group 10 metals with *N*-heteroaryl phosphine ligands

Christian Sarcher<sup>a</sup>, Saeid Farsadpour<sup>b</sup>, Leila Taghizadeh Ghoochany<sup>b</sup>, Yu Sun<sup>b</sup>, Werner R. Thiel<sup>b,\*\*</sup>, Peter W. Roesky<sup>a,\*</sup>

<sup>a</sup> Institut für Anorganische Chemie, Karlsruher Institut für Technologie (KIT), Engesserstraße 15, Geb. 30.45, 76131 Karlsruhe, Germany <sup>b</sup> Fachbereich Chemie, TU Kaiserslautern, Erwin-Schrödinger-Str. 54, 67663 Kaiserslautern, Germany

#### A R T I C L E I N F O

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# ABSTRACT

Reaction of the recently synthesized ligands *N*-(diphenylphosphino)-4-(pyridin-2-yl)pyrimidin-2-amine (Hpypya) and *N*-(diphenylphosphino)-4-phenylpyrimidin-2-amine (Hphpya) with [M(COD)Cl<sub>2</sub>] (M = Pd, Pt) (COD = 1,5-cyclooctadiene) in hot DMSO resulted in the corresponding palladium and platinum complexes [(Hpypya)MCl<sub>2</sub>] (M = Pd (1), Pt (2)) and [(Hphpya)MCl<sub>2</sub>] (M = Pd (3), Pt (4)). All compounds were characterized by single crystal X-ray diffraction. In all compounds the metal atom is distorted square planar coordinated. The N–H function forms hydrogen bonds either to a polar solvent molecule or to another metal complex. Further reaction of the pyridyl derivative [(Hpypya)PdCl<sub>2</sub>] with [AuCl(tht)] (tht = tetrahydrothiophene) did not result in a bimetallic neutral complex but in the ionic bimetallic compound [(Hpypya)PdCl][AuCl<sub>2</sub>] (**5**). Due to the addition of [AuCl(tht)] the gold(1) ion abstracts one chlorine atom from the palladium atom to form a linear [AuCl<sub>2</sub>]<sup>–</sup> anion. To keep the preferred square planar coordination mode of the palladium ion the remaining [(Hpypya)PdCl]<sup>+</sup> cation rearranges in such a way that the Hpypya ligand binds in a tridendate *N*,*N*,*P* coordination mode.

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# 1. Introduction

Chelating ligands with phosphorus and nitrogen donor atoms are well established in organometallic chemistry [1]. They also play an important role in homogeneous catalysis [2–5]. These ligands can be modified in terms of the electronic and steric properties, as well as of the bite angle. Besides the influence of the modification on the coordination properties of the ligands, the rate and selectivity of a catalytic reaction can also be influenced [6].

Chelating *P*,*N* ligands are a well-established class of compounds in group 10 chemistry [7–21]. In this context some of us are working for some time on phosphine ligands having an aromatic *N*heterocycle bound to the phosphorus centre [22–25]. The *N*-heterocycle decreases the electron-density at the phosphorus atom. For square planar coordinate group 8 complexes these compounds may act as chelating ligands coordinating via the P and one N atom to the metal site [22] while in gold(I) chemistry mainly linear coordination of the gold atom to the phosphine function will be

E-mail address: roesky@kit.edu (P.W. Roesky).

http://dx.doi.org/10.1016/j.jorganchem.2014.02.003 0022-328X/© 2014 Elsevier B.V. All rights reserved. expected [26]. In case of N–H functions being present on the ligand scaffold, the formation of intramolecular hydrogen bonds may also result in dimeric or polymeric structures.

Herein we report our results on reactions of the recently synthesized ligands *N*-(diphenylphosphino)-4-(pyridin-2-yl)pyrimidin-2-amine (Hpypya) and *N*-(diphenylphosphino)-4-pheny lpyrimidin-2-amine (Hphya) with suitable palladium and platinum precursors giving new group 10 complexes.

# 2. Results and discussion

Reaction of Hpypya with  $[M(COD)Cl_2]$  (M = Pd, Pt) (COD = 1,5cyclooctadiene) in hot DMSO resulted in the palladium and platinum complexes  $[(Hpypya)MCl_2]$  (M = Pd (1), Pt (2)) (Scheme 1). In a similar way the corresponding phenyl functionalized Hphpya complexes  $[(Hphpya)MCl_2]$  (M = Pd (3), Pt (4)) were obtained (Scheme 1). All four new compounds have been characterized by standard analytical/spectroscopic techniques and their solid-state structures were established by single crystal X-ray diffraction.

The <sup>1</sup>H NMR spectra of all compounds show not very characteristic signals in the aromatic region and one broad peak at lower field for the N–H function. In contrast the <sup>31</sup>P{<sup>1</sup>H} NMR spectra of 1–4 show a very characteristic signal which is down-field shifted in







<sup>\*</sup> Corresponding author. Tel.: +49 721 6084 6117; fax: +49 721 6084 4854. \*\* Corresponding author.



Scheme 1. Synthesis of 1-4.

comparison to the non-coordinated ligands (Table 1). In general the shift is larger for the palladium complexes **1** and **3** (about 30–32 ppm) than for the platinum compounds **2** and **4** (about 6–12 ppm). Moreover, characteristic satellite signals of the <sup>1</sup>*J*<sub>PtP</sub>-coupling (3817 Hz (**2**), 3838 Hz (**4**)) are present in the <sup>31</sup>P{<sup>1</sup>H} NMR spectra. This coupling is also detected in the <sup>195</sup>Pt NMR spectra of **2** and **4** which shows the expected doublets at  $\delta = -3526$  ppm (**2**) and -3538 ppm (**4**). There is no hint for a second coordination isomer with the other N atom acting as a donor site in the NMR spectra. Furthermore Hpypya does not undergo bidentate *N*,*N* or tridentate *P*,*N*,*N* coordination under the given reaction conditions.

Single crystals of compounds 1-4 were obtained from hot DMSO. Single crystals of 2 were also grown by a slow diffusion of npentane into a concentrated solution of **2** in CH<sub>2</sub>Cl<sub>2</sub>. By using the latter method a lower amount of DMSO is co-crystallized in the unit cell. Compound **1** crystallizes in the monoclinic space group  $P2_1/n$ with four molecules of 1 and two molecules of DMSO in the unit cell (Fig. 1). One of those DMSO molecules is bound via a hydrogen bond to the amino function of 1. All hydrogen atoms of 1 but not those of the DMSO molecules could be localized in the difference Fourier map. As expected the palladium atom is distorted square planar coordinated by the Hpypya ligand and two chlorine atoms. All bond angles around palladium vary from 83.56(6)° to 93.71(6)° and thus are close to the expected ideal 90° bond angle. As a result of the coordination of the Hpypya ligand a five membered Pd-P-N-C-N metallacycle is formed. The two Pd-Cl bond distances vary significantly (Pd-Cl1 2.3864(10) Å, Pd-Cl2 2.2895(9) Å). This difference can be explained by the trans influence of the opposite coordinated phosphorous and nitrogen atoms. The Pd–P-distance is 2.1962(9) Å and the Pd–N2 bond length is 2.057(2) Å. Similar bond distances were observed in [(dppai)(PdCl<sub>2</sub>)] (dppai = Diphenyphosphino-7azaindol) (Pd-Cl1 2.3444(6) Å, Pd-Cl2 2.2875(7) Å, Pd-P 2.2144(6) Å, Pd–N 2.044(2) Å) [27].

The analogue platinum compound **2** crystallizes from hot DMSO in an isostructural setup as **1** with a distorted square planar coordinated platinum atom (Fig. 2). As observed for **1** the two Pt–Cl bond distances vary significantly (Pt–Cl1 2.3809(12) Å, Pt–Cl2 2.2938(12) Å) as a result of the *trans* influence of the opposite

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<sup>31</sup> P	{ <sup>1</sup> H} NN	/IR data	of 1–4 in	comparison	to the	non-coordinated	l ligand.

Table 1

	Non-coordinated ligand $\delta(^{31}P\{^{1}H\})$ [ppm]	[(L)PdCl <sub>2</sub> ] δ( <sup>31</sup> P{ <sup>1</sup> H}) [ppm]	[(L)PtCl <sub>2</sub> ] δ ( <sup>31</sup> P{ <sup>1</sup> H}) [ppm]
Hpypya	29.7	72.0	36.2
Hphpya	24.7	64.3	36.1

coordinated phosphorous and nitrogen atoms. Crystallizing 2 by a slow diffusion of *n*-pentane into a concentrated solution of **2** in CH<sub>2</sub>Cl<sub>2</sub> resulted in a different solid state structure. In this case compound 2 crystallizes in the triclinic space group P-1 with two molecules of 2 and one equivalent of DMSO in the asymmetric unit (Fig. 3). The DMSO molecule again coordinates via a hydrogen bond to the amino function (N1-H1). 2 dimerizes via a hydrogen bond between the nitrogen atom (N4) of the pyridine ring and the amino function (N5–H5A) of the second equivalent. The bonding parameters are in both independent molecules similar and will thus only be discussed for one molecule. As observed for 1 the Pt1-Cl bond distances differ (Pt1-Cl1 2.294(2) Å and Pt1-Cl2 2.370(2) Å) as a result of the *trans* influence of the ligand. They are in the range of [(dppai)(PtCl<sub>2</sub>)] (Pt-Cl1 2.3381(11) Å, Pt-Cl2 2.3068(11) Å, Pt-N 2.039(3) Å, Pt-P 2.1998(11) Å) [28]. As expected the platinum atom is square planar coordinated with a bite angle of the ligand of N2-Pt1-P1 83.7(2)°.



**Fig. 1.** Solid-state structure of **1**, omitting hydrogen atoms. Selected bond lengths [Å] and angles [°]: Pd–Cl1 2.3864(10), Pd–Cl2 2.2895(9), Pd–P 2.1962(9), Pd–N2 2.057(2), P–N1 1.678(2), P–C1 1.813(2), P–C7 1.807(2), N1–H1 0.78(3), O1–H1 1.94(4), N1–O1 2.715(3); Cl1–Pd–Cl2 93.58(3), Cl2–Pd–P 89.28(3), P–Pd–N2 83.56(6), N2–Pd–Cl1 93.71(6), Cl1–Pd–P 176.05(2), Cl2–Pd–N2 172.35(6), Pd–P–N1 100.89(8), Pd–P–C1 115.44(8), Pd–P–C7 123.78(9), Pd–N2–C13 117.88(15), N1–P–C1 107.06(11), N1–P–C7 104.50(12), C1–P-C7 103.62(11), N1–C13–N2 117.1(2) N1–H1–O1 176(4).



**Fig. 2.** Solid-state structure of **2** (monoclinic) omitting hydrogen atoms. Selected bond lengths [Å] and angles [°]: Pt–Cl1 2.3809(12), Pt–Cl2 2.2938(12), Pt–P 2.1878(12), Pd–N2 2.040(3), P–N1 1.674(3), P–C1 1.817(4), P–C7 1.811(4), N1–O1 2.723(4); Cl1–Pt–Cl2 90.92(4), Cl2–Pt–P 92.21(4), P–Pt–N2 84.01(9), N2–Pt–Cl1 92.95(9), Cl1–Pt–P 176.13(4), Cl2–Pt–N2 175.60(9), Pt–P–N1 100.89(12), Pt–P–C1 116.30(14), Pt–P-C7 123.28(15), Pt–N2–Cl3 117.7(3), N1–P–C1 106.8(2), N1–P–C7 104.6(2), C1–P–C7 103.3(2), N1–C13–N2 117.1(4).

Compounds **3** and **4** which crystallize in the monoclinic space group  $P_{2_1}/c$  with one complex molecule and one molecule of DMSO in the asymmetric unit are isostructural to each other (Figs. 3 and 4). As observed for **1** the DMSO molecule is bound via a hydrogen bond (N1–H1–O) to the N–H function of the Hphyya ligand. In contrast to **1** and **2** only the pyridine ring is substituted by a phenyl group in **3** and **4**. Since this group is remote from the metal centre it does not significantly influence the coordination of the Hphyya ligand in comparison to Hpypya. The bite angle of the Hphyya ligand is P–Pd–N2 83.71(2)° (**3**) and P–Pt–N2 83.85(13)°



**Fig. 3.** Solid-state structure of **2** (triclinic), omitting hydrogen atoms. Selected bond lengths [Å] and angles [°]: Pt1–Cl1 2.294(2), Pt2–Cl2 2.370(2), Pt1–P1 2.185(2), Pt1–N2 2.019(6), P1–N1 1.672(7), P1–C1 1.801(7), 1.807(8), Pt2–Cl3 2.291(2), Pt2–Cl4 2.360(2), Pt2–P2 2.189(2), Pt2–N6 2.031(6); Cl1–Pt1–Cl2 91.35(7), Cl2–Pt1–N2 93.5(2), N2–Pt1–P1 83.7(2), P1–Pt1–Cl1 91.91(7), P1–Pt1–Cl2 174.25(7), Cl1–Pt1–N2 173.1(2), Pt1–P1–N1 101.2(2), Pt1–P1–Cl 116.8(3), Pt1–N2–Cl3 119.1(5), N1–P1–Cl 106.9(4), Cl–Pt1–C7 106.1(3), N1–C13–N2 116.1(7), Cl3–Pt2–Cl4 89.97(8), Cl4–Pt2–N6 93.2(2), N6–Pt2–P2 83.9(2), P2–Pt2–Cl3 92.78(8), P2–Pt2–Cl4 176.25(7), Cl3–Pt–N6 176.2(2).



**Fig. 4.** Solid-state structure of **3**, omitting carbon bound hydrogen atoms. Selected bond lengths [Å] and angles [°]: Pd−Cl1 2.3594(8), Pd−Cl2 2.2976(7), Pd−P 2.1925(8), Pd−N2 2.043(2), P−N1 1.684(2), P−C1 1.805(2), P−C7 1.803(2) N1−H1 0.79(3), O−H1 1.96(3), N1−O 2.751(3); Cl1−Pd−Cl2 93.08(3), Cl2−Pd−P 89.11(3), P−Pd−N2 83.71(5), N2−Pd−Cl1 94.25(6), Cl1−Pd−P 174.76(2), Cl2−Pd−N2 172.53(5), Pd−P−N1 100.90(7), Pd−P-C1 115.41(8), Pd−P−C7 119.75(8), Pd−N2−C13 118.26(14), N1−P−C1 106.57(11), N1−P−C7 106.88(10), C1−P−C7 106.18(11), N1−C13−N2 117.0(2), N1−H1−O 173(3).

(**4**). As expected for both compounds a slightly distorted square planar arrangement of the ligands around the metal centre is observed.

Since the Hpypya ligand of **1** and **2** has a non-coordinating nitrogen atom in the pyridyl ring we desired to synthesize some heterobimetallic complexes by adding another metal source. Reaction of **1** with [AuCl(tht)] (tht = tetrahydrothiophene) did not result in a bimetallic neutral complex but in the ionic compound [(Hpypya)PdCl][AuCl<sub>2</sub>] (**5**) (Scheme 2). Due to the addition of [AuCl(tht)] the gold(I) ion abstracts one chlorido ligand from the palladium site to form a linear [AuCl<sub>2</sub>]<sup>-</sup> anion. To keep the preferred square planar coordination mode of the palladium ion the remaining [(Hpypya)PdCl]<sup>+</sup> cation rearranges in such a way that the Hpypya ligand now binds in a tridendate *N*,*N'*,*P* coordination mode.

In the <sup>1</sup>H NMR spectrum the expected set of signals are observed in the aromatic region. Additionally the NH signal is seen at low field ( $\delta = 9.04$  ppm) in a comparable range to **1** ( $\delta = 9.06$  ppm). More characteristic is the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum which shows one peak at  $\delta = 71.2$  ppm. This signal is down field shifted by almost 40 ppm in comparison to the non-coordinated ligand. In the ESI-MS spectrum the peak at m/z = 499.00 amu can be assigned to the [(Hpypya)PdCl]<sup>+</sup> cation.

Single crystals of compound **5** could be grown by slow diffusion of *n*-pentane into a saturated solution of **5** in CH<sub>2</sub>Cl<sub>2</sub>. **5** crystallizes in the monoclinic space group  $P_{21/c}$  (Fig. 6). Unfortunately, only crystals of low quality were obtained. Although, the X-ray data collected from **5** was poor, the connectivity of **5** and its composition could be deduced. However, further bonding parameters shall not be discussed. As can be seen from Fig. 6 the palladium atom in **5** is coordinated by two nitrogen atoms and the phosphorous atom of the Hpypya ligand as well as by one chlorido ligand. Thus, a distorted square planar coordination polyhedron is formed. The gold atom is linearly coordinated by two chlorido ligands.

Concentration of the reaction mixture which led to **5** resulted in a crop of different crystals which consists of [(Hpypya) PdCl]<sub>2</sub>[AuCl<sub>2</sub>]Cl (**5**') (Scheme 2) as byproduct which could not be obtained analytically pure. Although **5**' can only be isolated as a mixture together with **5** the solid state structure could be established by single crystal diffraction. **5**' crystallizes in the triclinic space group *P*-1 with two molecules in the unit cell (Fig. 7). In contrast to **5** two different anions are found in **5**'. These are [AuCl<sub>2</sub>]<sup>-</sup>



Scheme 2. Synthesis of 5 and 5'.

and Cl<sup>-</sup>. The chloride ion bridges two [(Hpypya)(PdCl)]<sup>+</sup> cations via hydrogen bonding N4-H4-Cl5-H8-N8. As observed for 5 the palladium atoms are coordinated in a distorted square planar fashion by two nitrogen atoms, the phosphorous atom of the Hpypya ligand, and one chlorido ligand. Since the two [(Hpypya)(PdCl)]<sup>+</sup> cations have almost the same bonding parameters only one cation is discussed in detail. The Pd1-Cl1 distance is 2.287(3) Å and the Pd1-P1 distance is 2.195(3) Å. The Pd1-N distances range from 1.981(8) Å (Pd1-N2) to 2.105(9) Å (Pd1-N1) showing that the palladium atom is closer located to the pyrimidine *N*-atom. The observed distances are in agreement with the literature, e.g. in  $[(dppemp)(PdCl)]^+$   $(dppemp = 1-\{2-(diphenylphos$ phino)ethyl}-4-methylpiperazine): Pd-Cl 2.2897(5) Å, Pd-P 2.2242(5) Å, Pd–N1 2.033(1) Å, Pd–N4 2.143(1) Å [29]. A distorted square planar arrangement around the palladium atom which is formed by N1, N2, P1 and Cl1 is observed. The bite angles of the ligand are P1-Pd1-N2 83.9(3)° and N1-Pd1-N2 79.2(3)°. The angles of the trans located atoms are Cl1-Pd1-N2 177.7(3)° and P1-Pd1-N1 162.9(3)°.

As expected the gold atom in the  $[AuCl_2]^-$  anion is almost linearly coordinated having a Cl3–Au–Cl4 angle of 179.6(2)° and Au–

**Fig. 5.** Solid-state structure of **4**, omitting carbon bound hydrogen atoms. Selected bond lengths [Å] and angles [°]: 2.3565(14), Pt–Cl2 2.2997(14), Pt–P 2.1788(15), Pt–N2 2.044(4), P–N1 1.678(5), P–C1 1.797(6), P–C7 1.797(6), N1–H1 0.98(7), O–H1 1.75(7), N1–H1 2.730(6); Cl1–Pt–Cl2 90.83(5), Cl2–Pt–P 91.75(5), P–Pt–N2 83.85(13), N2–Pt–Cl1 93.67(13), Cl1–Pt–P 175.02(5), Cl2–Pt–N2 175.33(12), Pt–P–N1 101.2(2), Pt–P–C1 116.2(2), Pt–P–C7 120.0(2), Pt–N2–C13 117.6(3), N1–P–C1 106.5(2), N1–P–C7

106.7(2), C1-P-C7 105.1(3), N1-C13-N2 117.5(4), N1-H1-O 175(5).

Cl distances of 2.234(5) Å and 2.240(5) Å. The observed data of the anion is in agreement with comparable structures such as [NMe<sub>4</sub>] [AuCl]<sub>2</sub> (Cl-Au-Cl: 180° and Au-Cl: 2.257(4) Å [30]).

### 3. Summary

In summary, we have synthesized palladium and platinum complexes with the multidentate ligands Hpypya and Hphpya. In all compounds the metal atom is coordinated in a distorted square planar fashion. The N–H function forms hydrogen bonds either to a polar solvent molecule or to another metal complex. Further reaction of the pyridyl derivative [(Hpypya)PdCl<sub>2</sub>] with [AuCl(tht)] did not result in a bimetallic neutral complex but in a rearrangement of the coordination geometry at the palladium site leading to the ionic bimetallic compound [(Hpypya)PdCl][AuCl<sub>2</sub>]. We are presently investigating this rearrangement caused by a soft Lewisacid in more details.

#### 4. Experimental section

Although all products are not very air-sensitive all manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either or in an argon-filled *MBraun* glove box. THF was distilled under nitrogen from potassium benzophenone ketyl prior



Fig. 6. Solid-state structure of 5, omitting hydrogen atoms.





**Fig. 7.** Solid-state structure of **5**′, omitting carbon bound hydrogen atoms. Selected bond lengths [Å] and angles [°]: Pd1–Cl1 2.287(3), Pd1–P1 2.195(3), Pd1–N1 2.105(9), Pd1–N2 1.981(8), P1–N4 1.691(9), P1–C1 1.813(13), P1–C7 1.793(13), Pd2–Cl2 2.287(3), Pd2–P2 2.196(3), Pd2–N5 2.096(9), Pd2–N6 1.965(9), Au–Cl3 2.240(5), Au–Cl4 2.234(5); Cl1–Pd1–P1 95.81(11), Cl1–Pd1–N1 101.1(3), P1–Pd1–N2 83.9(3), N1–Pd1–N2 79.2(3), Cl1–Pd1–N1 177.7(3), P1–Pd1–N1 162.9(3), Pd1–P1–A4 99.9(3), Pd1–P1–C1 114.9(4), Pd1–P1–C7 119.7(4), N4–P1–C1 106.5(5), N4–P1–C7 107.0(5), Cl1–Pd1–C7 107.6(6), N2–Cl3–N4 117.0(9), Cl2–Pd2–P2 94.89(12), Cl2–Pd2–N5 102.1(3), P2–Pd2–N6 84.0(3), N5–Pd2–N6 79.1(4), Cl2–Pd2–N6 178.4(3), P2–Pd2–N5 162.8(3), N4–Cl5–N8 147.9(3), Cl3–Au–Cl4 179.6(2).

to use. Hydrocarbon solvents (toluene and *n*-pentane) were dried using an MBraun solvent purification system (SPS-800). All solvents for vacuum line manipulations were stored in vacuo over LiAlH<sub>4</sub> in resealable flasks. Deuterated solvents were obtained from Aldrich (99 atom % D) and were degassed, dried, and stored in vacuo over Na/ K alloy in resealable flasks. NMR spectra were recorded on a Bruker Avance II 300 MHz and a Bruker Avance 500 MHz FT-NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. IR spectra were obtained on a Bruker Tensor 34. Raman spectra were carried out with a Bruker MultiRAM. Mass spectra were recorded at 70 eV on a Finnigan MAT 8200 and on an Ionspec FTIR spectrometer. Elemental analyses were carried out with an Elementar Vario Micro Cube. Dichloro(1,5-cyclooctadiene)palladium(II) and dichloro(1,5cyclooctadiene)platinum(II) were purchased from abcr GmbH & Co. KG. [(tht)AuCl] [31,32] (tht = tetrahydrothiophene) was prepared according to modified standard procedures. Hpypya and Hpypya were prepared according to literature procedures [26].

# 4.1. [(Hpypya)PdCl<sub>2</sub>] (1)

143 mg (0.50 mmol) of dichloro(1,5-cyclooctadiene)palladium(II) were dissolved in 5 ml of DMSO. 178 mg (0.50 mmol) of *N*-(diphenylphosphino)-4-(pyridin-2-yl)pyrimidin-2-amine were added under stirring. The yellow mixture was heated to 100 °C and stirred for 1 h. After cooling down to ambient temperature the product was obtained as vellow crystals. Yield: 165 mg (62%). Anal. Calcd C<sub>21</sub>H<sub>17</sub>Cl<sub>2</sub>N<sub>4</sub>PPd · 2C<sub>2</sub>H<sub>6</sub>OS, C 43.52, H 4.24, N 8.12, S 9.29, found C 43.80, H 4.26, N 7.95, S 9.09. <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 9.06 (s, br, 1H, NH), 8.40–8.26 (m, 6H, Ph, pyridine-3-H, pyridine-6-*H*), 8.15 (dd,  ${}^{3}J_{HH} = 13.6$ , 7.4 Hz, 1H, pyridine-5-*H*), 7.84 (s, br, 1H, pyrimidine-6-H), 7.63-7.45 (m, 8H, Ph, pyridine-4-H, pyrimidine-5-*H*). <sup>31</sup>P{<sup>1</sup>H} NMR (121.48 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 72.0. IR (ATR):  $\nu$  (cm<sup>-1</sup>) = 2921 (m), 2852 (w), 2807 (w), 2535 (w), 1593 (s), 1550 (s), 1495 (vs), 1465 (vs), 1436 (m), 1404 (m), 1328 (m), 1306 (m), 1285 (w), 1261 (w), 1219 (m), 1108 (s), 1047 (vs), 1017 (vs), 956 (s), 858 (s), 795 (s), 766 (s), 751 (m), 708 (m), 690 (s), 650 (w), 635 (m), 541 (vs), 510 (s). Raman (solid state):  $\nu$  (cm<sup>-1</sup>) = 3053 (s), 2994 (w), 2911 (m), 1592 (vs), 1495 (w), 1467 (w), 1409 (m), 1330 (vs), 1307 (w), 1269 (w), 1223 (w), 1108 (m), 1038 (s), 1020 (s), 997 (vs), 959 (w), 754 (w), 705 (m), 674 (s), 616 (w), 543 (w), 383 (w), 346 (m), 310 (w), 278 (w). FAB-MS: m/z (%) = 497 ([M - Cl]<sup>+</sup>, 100), 461 ([M - 2Cl]<sup>+</sup>, 16).

# 4.2. [(Hpypya)PtCl<sub>2</sub>] (**2**)

(a) The reaction was done in air. To 100 mg (0.27 mmol) of dichloro(1,5-cyclooctadiene)platinum(II) and 95.2 mg (0.27 mmol) of N-(diphenylphosphino)-4-(pyridin-2-yl)pyrimidin-2-amine 3 ml of DMSO were added. The mixture was heated with a heat gun and shacked for 2 min. until the educts were completely dissolved. After cooling to ambient temperature the product was obtained as vellow crystals. Yield: 110 mg (66%). Anal. Calcd C21H17Cl2N4PPt·3C2H6OS, C 37.85, H 4.12, N 6.54, S 11.23, found C 37.82, H 3.71, N 6.59, S 10.54.

(b) 18.7 mg (0.05 mmol) of dichloro(1,5-cyclooctadiene)platinum(II) were dissolved in 0.5 ml of DMSO. 17.8 mg (0.05 mmol) of *N*-(diphenylphosphino)-4-(pyridin-2-yl)pyrimidin-2-amine were added under stirring. The yellow mixture was heated to 100 °C, stirred for 1 h, evaporated and dried in vacuo. Single crystals of 2 were grown by a slow diffusion of *n*-pentane into a concentrated solution of **2** in CH<sub>2</sub>Cl<sub>2</sub>. Yield: 24.9 mg (80%). <sup>1</sup>H NMR (300.13 MHz, DMSO- $d_6$ ):  $\delta$  (ppm) = 8.81 (d,  ${}^{3}J_{PH}$  = 3.1, 1H, NH), 8.38 (d,  ${}^{3}J_{HH}$  = 7.9, 1H, pyridine-6-H), 8.01–7.88 (m, 6H, Ph), 7.77–7.57 (m, 9H, Ph). <sup>31</sup>P {<sup>1</sup>H} NMR (121.49 MHz, DMSO- $d_6$ ):  $\delta$  (ppm) = 36.2 (s), 36.2 (d,  ${}^{1}J_{\rm PtP} = 3817$  Hz). <sup>195</sup>Pt NMR(86.02 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  (ppm) = -3526 (d, <sup>1</sup>J<sub>PtP</sub> = 3817 Hz). IR (ATR):  $\nu$  (cm<sup>-1</sup>) = 2962 (m), 2924 (m), 2854 (w), 1733 (w), 1598 (m), 1539 (m), 1505 (w), 1426 (m), 1259 (s), 1089 (vs), 1011 (vs), 957 (w), 792 (vs), 710 (w), 689 (m), 666 (w), 649 (w), 544 (m). Raman (solid state): v  $(cm^{-1}) = 3058 (s), 2963 (m), 2906 (s), 1588 (vs), 1494 (w), 1436 (w),$ 1329 (m), 1107 (w), 1045 (m), 1026 (m), 999 (s), 708 (w), 617 (w), 492 (w), 346 (w), 289 (w), 232 (w), 205 (w).

# 4.3. [(Hphpya)PdCl<sub>2</sub>] (**3**)

143 mg (0.50 mmol) of dichloro(1,5-cyclooctadiene)palladium(II) were dissolved in 5 ml of DMSO. 178 mg (0.50 mmol) of *N*-(diphenylphosphino)-4-phenylpyrimidin-2-amine were added under stirring. The yellow mixture was heated to 100 °C and stirred for 1 h. After cooling down to ambient temperature the product was obtained as yellow crystals. Yield: 221 mg (83%). Anal. Calcd  $C_{22}H_{18}Cl_2N_3PPd\cdot C_2H_6OS,\ C$  47.19, H 3.96, N 6.88, S 5.25, found C 47.13, H 3.80, N 6.77, S 5.19. <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 9.63 (d, <sup>3</sup>J<sub>PH</sub> = 5.7 Hz, 1H, NH), 8.14–7.98 (m, 6H, Ph), 7.72–7.49 (m, 10H, Ph, pyrimidine-6-*H*), 7.38 (d,  ${}^{3}J_{HH} = 6.0$  Hz, 1H,  ${}^{31}P{1 H}$ pyrimidine-5-H). NMR (121.48 MHz. CDCl<sub>3</sub>):  $\delta$  (ppm) = 64.3. IR (ATR):  $\nu$  (cm<sup>-1</sup>) = 3004 (w), 2911 (w), 2782 (w), 2682 (w), 1595 (s), 1540 (m), 1483 (m), 1429 (vs), 1334 (m), 1282 (m), 1215 (m), 1143 (w), 1103 (m), 1013 (s), 951 (vs), 848 (w), 835 (w), 787 (w), 765 (s), 752 (m), 709 (m), 687 (vs), 652 (s), 615 (w), 540 (vs), 524 (s). Raman (solid state):  $\nu$  (cm<sup>-1</sup>) = 3058 (s), 3000 (w), 2913 (m), 1594 (vs), 1502 (m), 1370 (w), 1334 (s), 1282 (m), 1216 (w), 1191 (w), 1159 (w), 1144 (w), 1103 (m), 1029 (m), 1016 (m), 1000 (s), 952 (w), 748 (w), 708 (w), 671 (w), 617 (w), 542 (w), 332 (m), 311 (w), 270 (w), 232 (w). FAB-MS: m/z (%) = 495 ([M - C1]<sup>+</sup>, 30), 460 ([M - 2C1]<sup>+</sup>, 28).

# 4.4. [(Hphpya)PtCl<sub>2</sub>] (4)

93.5 mg (0.25 mmol) of dichloro(1,5-cyclooctadiene)platinum(II) were dissolved in 5 ml of DMSO. 88.8 mg (0.25 mmol) of *N*-(diphenylphosphino)-4-phenylpyrimidin-2-amine were added under stirring. The yellow mixture was heated to 100 °C and stirred for 1 h. After cooling down to ambient temperature the product was obtained as yellow crystals. Yield: 121 mg (78%). Anal. Calcd C<sub>22</sub>H<sub>18</sub>Cl<sub>2</sub>N<sub>3</sub>PPt·C<sub>2</sub>H<sub>6</sub>OS, C 41.21, H 3.46, N 6.01, S 4.58, found C 41.00, H 3.37, N 5.79, S 4.45. <sup>1</sup>H NMR (300.13 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  (ppm) = 9.06 (d, <sup>3</sup>J<sub>PH</sub> = 6.5 Hz, 1H, NH), 8.10 (d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2H,

Ph), 8.02 (d,  ${}^{3}J_{HH} = 7.2$  Hz, 2H, Ph), 7.98 (d,  ${}^{3}J_{HH} = 7.1$ , 2H, Ph), 7.66– 7.51 (m, 10H, Ph, pyrimidine-6-*H*), 7.35 (d,  ${}^{3}J_{HH} = 6.6$  Hz, 1H, pyrimidine-5-*H*).  ${}^{31}P{}^{1}H$  NMR (121.48 MHz, DMSO- $d_{6}$ ):  $\delta$  (ppm) = 36.1 (s), 36.1 (d,  ${}^{1}J_{PtP} = 3841$  Hz).  ${}^{195}Pt$  NMR (64.30 MHz, DMSO- $d_{6}$ ):  $\delta$  (ppm) = -3538 (d,  ${}^{1}J_{PtP} = 3841$  Hz). IR (ATR):  $\nu$  (cm<sup>-1</sup>) = 3027 (w), 2963 (w), 2908 (w), 2784 (w), 2699 (w), 1601 (s), 1540 (s), 1484 (m), 1431 (vs), 1334 (w), 1275(m), 1261 (m), 1217 (m), 1187 (w), 1146 (w), 1105 (s), 1013 (vs), 949 (s), 801 (m), 764 (s), 712 (s), 686 (vs), 655 (s), 616 (w), 546 (vs), 532 (vs). Raman (solid state):  $\nu$  (cm<sup>-1</sup>) = 3058 (m), 2999 (w), 2913 (m), 1597 (vs), 1505 (m), 1441 (w), 1375 (w), 1335 (s), 1284 (w), 1218 (w), 1192 (w), 1160 (w), 1147 (w), 1106 (w), 1088 (w), 1024 (m), 1001 (s), 951 (w), 748 (w), 705 (w), 671 (w), 617 (w), 340 (w), 287 (w), 214 (w). FAB-MS: m/z (%) = 584 ([M - CI]<sup>+</sup>, 2), 550 ([M - 2CI]<sup>+</sup>, 2).

## 4.5. [(Hpypya)PdCl][AuCl<sub>2</sub>] (5)

143 mg (0.50 mmol) of dichloro(1,5-cyclooctadiene)palladium(II) were dissolved in 5 ml of DMSO. 178 mg (0.50 mmol) of *N*-(diphenylphosphino)-4-(pyridin-2-yl)pyrimidin-2-amine were added under stirring. The yellow mixture was heated to 100  $^\circ\text{C}$  and stirred for 1 h. After cooling down to ambient temperature 160 mg (0.50 mmol) of chloro(tetrahydrothiophene)gold(I) were added. The yellow solution was heated to 100 °C and stirred for 15 min. After cooling down to ambient temperature the solution was evaporated. The remaining residue was subsequently dried in vacuo. The product was obtained as a yellow powder. Yield: 337 mg (88%). Anal. Calcd C<sub>21</sub>H<sub>17</sub>AuCl<sub>3</sub>N<sub>4</sub>PPd · C<sub>2</sub>H<sub>6</sub>OS, C 32.72, H 2.75, N 6.64, S 3.80, found C. 32.30, H 3.01, N 6.05, S 3.96. <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 9.04 (s, br, 1H, NH), 8.25–8.10 (m, 4H, Ph), 7.98–7.73 (m, 3H, pyridine-3-H, pyridine-5-H, pyridine-6-H), 7.71-7.37 (m, 9H, Ph, pyridine-4-H, pyrimidine-5-H, pyrimidine-6-H). <sup>31</sup>P{<sup>1</sup>H} NMR (121.48 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 71.2. IR (ATR):  $\nu$  (cm<sup>-1</sup>) = 3048 (w), 2963 (w), 1733 (w), 1645 (w), 1591 (m), 1550 (m), 1505 (s), 1464 (m), 1435 (m), 1419 (m), 1331 (m), 1297 (w), 1260 (m), 1216 (m), 1194 (m), 1142 (w), 1103 (s), 1009 (vs), 951 (s), 840 (m), 786 (s), 769 (m), 754 (m), 706 (m), 692 (vs), 636 (m), 536 (vs), 509 (m). Raman (solid state):  $\nu$  (cm<sup>-1</sup>) = 3057 (w), 2911 (w), 1587 (s), 1477 (m), 1329 (w), 1105 (w), 1037 (w), 1026 (w), 998 (m), 346 (w), 276 (s). ESI-MS (DCM): m/z = 499.00 ([(Hpypya)(PdCl)]<sup>+</sup>).

#### 4.6. X-ray crystallographic studies of 1-5'

Single crystals were grown as described in the synthetic procedures of each compound. Suitable crystals were covered in mineral oil (Aldrich) and mounted onto a glass fiber. Data were collected on diffractometer equipped with a STOE imaging plate detector system IPDS2 using MoK $\alpha$  radiation with graphite monochromatization ( $\lambda = 0.71073$  Å) at low temperatures. Subsequent computations were carried out on an Intel Core2Quad. Structure solution was performed by direct methods; full-matrix-least squares refinement against  $F^2$  using SHELXS-97 and SHELXL-97 software [33]. Figs. 1–6 were generated using the program Diamond 3.2 [34].

Crystal data for **1**: C<sub>21</sub>H<sub>17</sub>Cl<sub>2</sub>N<sub>4</sub>PPd·3(C<sub>2</sub>H<sub>6</sub>OS), M = 768.04, monoclinic, a = 12.3543(4) Å, b = 14.4318(4) Å, c = 18.9579(6) Å,  $\beta = 99.306(3)^{\circ}$ , V = 3335.6(2) Å<sup>3</sup>, T = 200(2) K, space group  $P2_1/n$ , Z = 4,  $\mu$ (MoK $\alpha$ ) = 0.987 mm<sup>-1</sup>, 35,578 reflections measured, 8979 independent reflections ( $R_{int} = 0.0520$ ). The final  $R_1$  values were 0.0328 ( $I > 2\sigma(I)$ ). The final  $wR(F^2)$  values were 0.0651 (all data). The goodness of fit on  $F^2$  was 0.842.

Crystal data for **2** (monoclinic)  $C_{21}H_{17}Cl_2N_4PPt \cdot 3(C_2H_6OS)$ , M = 856.73, monoclinic, a = 12.4080(5) Å, b = 14.4931(7) Å, c = 18.8990(8) Å,  $\beta = 99.050(3)^\circ$ , V = 3356.3(3) Å<sup>3</sup>, T = 200(2) K, space group  $P2_1/n$ , Z = 4,  $\mu$ (MoK $\alpha$ ) = 0.987 mm<sup>-1</sup>, 27,646 reflections measured, 6242 independent reflections ( $R_{int} = 0.0538$ ). The final  $R_1$  values were 0.0276 ( $I > 2\sigma(I)$ ). The final  $wR(F^2)$  values were 0.0491 (all data). The goodness of fit on  $F^2$  was 0.941.

Crystal data for **2** (triclinic)  $2(C_{21}H_{17}Cl_2N_4PPt) \cdot C_2H_6OS$ , M = 1322.82, triclinic, a = 10.3304(5) Å, b = 13.1342(6) Å, c = 17.7250(8) Å,  $\alpha = 89.259(4)^\circ$ ,  $\beta = 80.600(4)^\circ$ ,  $\gamma = 75.038(4)^\circ$ , V = 2291.14(18) Å<sup>3</sup>, T = 173(2) K, space group *P*-1, Z = 2,  $\mu$ (MoK $\alpha$ ) = 6.493 mm<sup>-1</sup>, 21,851 reflections measured, 8340 independent reflections ( $R_{int} = 0.0574$ ). The final  $R_1$  values were 0.0369 ( $I > 2\sigma(I)$ ). The final  $wR(F^2)$  values were 0.0928 (all data). The goodness of fit on  $F^2$  was 0.965.

Crystal data for **3**:  $C_{22}H_{18}Cl_2N_3PPd \cdot C_2H_6OS$ , M = 610.79, monoclinic, a = 10.2114(3) Å, b = 11.8759(3) Å, c = 21.8722(6) Å,  $\beta = 92.3231(23)^\circ$ , V = 2650.26(12) Å<sup>3</sup>, T = 150(2) K, space group  $P2_1/c$ , Z = 4,  $\mu(MOK\alpha) = 1.063$  mm<sup>-1</sup>, 21,773 reflections measured, 6091 independent reflections ( $R_{int} = 0.0432$ ). The final  $R_1$  values were 0.0299 ( $I > 2\sigma(I)$ ). The final  $wR(F^2)$  values were 0.0681 ( $I > 2\sigma(I)$ ). The goodness of fit on  $F^2$  was 1.009.

Crystal data for **4**:  $C_{22}H_{18}Cl_2N_3PPt \cdot C_2H_6OS$ , M = 699.48, monoclinic, a = 10.1398(3) Å, b = 11.7931(4) Å, c = 21.7884(8) Å,  $\beta = 92.618(3)^\circ$ , V = 2602.73(15) Å<sup>3</sup>, T = 200(2) K, space group  $P2_1/c$ , Z = 4,  $\mu$ (MoK $\alpha$ ) = 5.760 mm<sup>-1</sup>, 25,661 reflections measured, 6128 independent reflections ( $R_{int} = 0.0682$ ). The final  $R_1$  values were 0.0375 ( $I > 2\sigma(I)$ ). The final  $wR(F^2)$  values were 0.0986 (all data). The goodness of fit on  $F^2$  was 1.068.

Crystal data for **5**:  $2(C_{21}H_{17}AuCl_3N_4PPd) \cdot CH_2Cl_2$ , M = 1617.07, monoclinic, a = 20.545(4) Å, b = 17.5710(22) Å, c = 13.968(3) Å,  $\beta = 102.003(15)^\circ$ , V = 4931.9(15) Å<sup>3</sup>, T = 173(2) K, space group  $P2_1/c$ , Z = 4.

Crystal data for **5**':  $2(C_{21}H_{17}CIN_4PPd) \cdot AuCl_2 \cdot Cl$ , M = 1299.73, triclinic, a = 9.5170(5) Å, b = 15.2755(8) Å, c = 16.7857(9) Å,  $\alpha = 113.897(4)^{\circ}$ ,  $\beta = 91.011(4)^{\circ}$ ,  $\gamma = 90.754(4)^{\circ}$ , V = 2230.16(20) Å<sup>3</sup>, T = 200(2) K, space group *P*-1, Z = 2,  $\mu$ (MoK $\alpha$ ) = 4.492 mm<sup>-1</sup>, 21,987 reflections measured, 8105 independent reflections ( $R_{int} = 0.0906$ ). The final  $R_1$  values were 0.0706 ( $I > 2\sigma(I)$ ). The final  $wR(F^2)$  values were 0.2248 (all data). The goodness of fit on  $F^2$  was 1.068.

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#### Appendix A. Supplementary material

CCDC 970717 to 970721 and 973143 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

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