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Neutral mononuclear luminescent Pd(II) complexes with heterocyclic thiolate ligands and chelating phosphines. Structural and photophysical assignments.

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Abstract

Two heterocyclic thiolate ligands, namely pymt and py2S (pymt = pyrimidine2thiolate and py2S pyridine-2-thiolate) the diphosphines and = bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp), were used in the synthesis of three neutral Pd(II) complexes (cis-[Pd(dppm)(pymt)₂] (1), cis-[Pd(dppe)(pymt)₂] (2) and cis-[Pd(dppp)(pyrt)₂] (3)). Crystallographic analysis of the isolated complexes reveals their square planar arrangement and the coordination of the thiolate moieties through their exocyclic sulphur atom. The complexes absorb in the visible part of the spectrum through charge transfer transitions while after photoexcitation at 385 nm they appear to emit with a broad band located at 465 nm.

Keywords: Palladium, Thiolate ligands, Luminescence, DFT calculations.

1. Introduction

Heterocyclic thiones constitute an extended and very interesting class of multifunctional donor ligands [1] that combine soft and hard coordination sites thus being able to selectively bind various metal centers [2]. Further the ability of these ligands to coordinate in a monodentate or a bridging mode results in a high structural diversity of their complexes [1, 3-6]. As has been seen, extended structures also can be supported by the incorporation of bidentate P-donor molecules with small saturated carbon chains [7].

Due to the presence of the thioamide group in their skeleton, pyrimidine-type thiones and thiolates and their complexes with a variety of metals have been the subject of many studies related to model systems of sulphur-analogues of DNA-bases [4]. Based on this characteristic, research interest largely focused on the possibility of developing novel complexes with targeted properties, mainly anticarcinogenic [8-10]. As far it concerns the Pd(II) metal core, its d⁸-outershell electronic configuration imposes a square planar coordination environment and in conjunction to the implementation of the aforementioned ligands could lead to the development of new DNA intercalating metallodrugs [11]. It should be noted that the combination of heavy metals with S,N-donor atoms has already been recognized to result in interesting anticarcinogenic properties [4].

Besides the biological importance of sulphur-containing complexes, much research effort has been devoted to the exploitation of their redox and photophysical properties. In this respect, a large class of dithiolene complexes of group 10 metals (Ni, Pd, Pt) has been studied extensively owing to their intriguing spectroscopic behaviour [12-15]. Recently also, a series of coinage metal complexes incorporating heterocyclic thiones or thiolates in combination with aryl-phosphines or

phenanthroline revealed interesting photophysics [16-20]. The emission energy of these systems can be tuned through a thione-modification while their emitting state is readily assigned as MLCT or LMCT on the basis of both experimental and theoretical data. As far as it concerns the Pd(II) center, its coexistence with ligands of low energy π -acceptor orbitals can give rise to charge transfer bands resulting to luminescence in the visible part of the spectrum [21]. In the same framework, the spin-orbit coupling induced by the "heavy-atom" nature of this nucleus can promote an efficient intersystem crossing towards triplet states and which results to long-lived phosphorescence with possible applications in lighting technologies [22-24].

In the framework of our ongoing investigations on the molecular and photophysical properties of heteroleptic S,N,P-containing metal complexes, we herein explore the structural, electronic and spectroscopic characteristics of a series of neutral Pd(II) compounds bearing a diphosphine ligand combined with an heterocyclic S,N-thiolate moiety.

2. Results and Discussion

2.1. Synthesis and Spectroscopic Details

All of the presented complexes were synthesized under atmospheric conditions by reacting a methanolic solution of $PdCl_2$ with the respective diphosphine, followed by the addition of two equivalents of the deprotonated (with KOH in MeOH) thiol. The products were isolated as air stable orange to red microcrystalline solids, soluble in common organic solvents such as methanol, dichloromethane and chloroform, resulting in yellow to deep orange colored solutions.

For both sulfur containing ligands and with reference to their protonated neutral forms, a prototropic thiol-thione tautomerism occurs including a proton-

migration between the sulfur and an endocyclic nitrogen atom. As has been suggested, this atom transfer is incomplete [25] while in solution, the thione form of the neutral ligands is reported to prevail over the respective thiole form [26]. On the other hand no reports seem to exist on the charge localization and the relative stability of the deprotonated ligands. Scheme I comprises the structures of the anions of the two tautomers of each sulfur-ligand used and should not be merged with resonance structures as the negative charge refers to the σ -system of the molecular skeleton [27].



In both anionic forms of each S-ligand, coordination may occur either through the sulfur or/and the pyridine nitrogen atom(s) of the heterocyclic ring [28]. In the present case, X-ray crystallography reveals their monodentate interaction with the

metal center through the sulfur atom. This is somewhat expected as the precoordinated phosphines increase the soft character of the metal predisposing the binding of pymt and py2S through their soft-base site. Additionally and because of the stereochemical demands imposed by the bulky phosphines, the coordination of both anions through their sulfur atom should also be favored due to a longer metal-ligand bond which contributes to reduce steric repulsions within the coordination sphere. The complexes (1), (2) and (3) were all isolated as mononuclear species containing a chelating phosphine and two thiolate ligands coordinated on the metal core in a *cis*square planar arrangement (Scheme II).

Scheme II



The infrared spectra of the prepared complexes show the expected distinct and strong vibrational features attributed to the phosphine moieties. These bands appear as a set of sharp peaks located around 690 and 510 cm⁻¹ and reveal small shifts upon coordination to the metal center [29, 30]. In all cases, a strong band located in the region 1559-1565 cm⁻¹ for both pymt and py2S systems can be assigned to the stretching vibrations of the -C=N- and -C=C- bonds of the heterocyclic rings. Moreover, the spectra of the studied compounds lack both the characteristic stretching frequency of the -NH group in the 3150 cm⁻¹ region [31, 32] and the *v*(SH) bands at ca. 2500-2600 cm⁻¹ which verifies the presence of the sulfur-ligand in its deprotonated anionic form.

2.2. X-ray Structures

The molecular structures of the complexes (1), (2) and (3), (details of crystal and structure refinement are given bellow in Table 3) have been established by singlecrystal X-ray diffraction. Plots for the structures are presented in Figs. 1–3 and selected bond lengths and angles are given in the legends to the respective plots.



Fig. 1. A view of **1** with the atomic numbering schemes. Displacement ellipsoids are shown in the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) Pd1–S1 2.3267(9); Pd1–S2 2.3613(9); Pd1–P1 2.2895(8); Pd1–P2 2.2937(8); S1–C1 1.757(3); S2–C5 1.722(4) and bond angles (°) S1–Pd1–S2 80.56(3); S1–Pd1–P1 103.62(3); S2–Pd1–P1 174.55(3); S1–Pd1–P2 176.67(3); S2–Pd1–P2 102.73(3); P1–Pd1–P2 73.07(3); Pd1–S1–C1 113.80(11); Pd1–S2–C5 110.79(12).



Fig. 2. A view of **2** with the atomic numbering schemes. Displacement ellipsoids are shown in the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) Pd1–S1 2.3754(6); Pd1–S2 2.3773(6); Pd1–P1 2.2744(6); Pd1–P2 2.2724(6); S1–C1 1.734(3); S2–C5 1.739(2) and bond angles (°) S1–Pd1–S2 89.05(2); S1–Pd1–P1 90.85(2); S2–Pd1–P1 175.06(2); S1–Pd1–P2 172.92(2); S2–Pd1–P2 95.72(2); P1–Pd1–P2 84.85(2); Pd1–S1–C1 101.89(9); Pd1–S2–C5 97.62(8).



Fig. 3. A view of **3** with the atomic numbering schemes. Displacement ellipsoids are shown in the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) Pd1–S1 2.3835(5); Pd1–S2 2.3606(6); Pd1–P1 2.2598(5); Pd1–P2

2.2759(5); S1–C1 1.745(2); S2–C6 1.735(3) and bond angles (°) S1–Pd1–S2 91.13(2); S1–Pd1–P1 85.15(2); S2–Pd1–P1 176.27(2); S1–Pd1–P2 175.23(2); S2–Pd1–P2 91.63(2); P1–Pd1–P2 92.102(19); Pd1–S1–C1 100.63(8); Pd1–S2–C6 99.81(9).

All three complexes are four-coordinate monomers comprising the palladium(II) cation in a distorted square planar coordination environment generated by the S atoms of two thiolate moieties and two P atoms of the respective diphosphine. Within the central core of each complex, angular distortions from the ideal geometry can be certainly attributed to the bite angle of the chelating diphosphine. Thus, while the three complexes do not differ significantly from each other with regard to their S–Pd–P trans angles (ranging between 172.92° and 176.67°), there is a direct relation between each P–Pd–P bite angle and its respective opposite S–Pd–S angle. In fact, a small P–Pd–P bite angle of 73.03° in compound **1** is responsible for the narrowing of the S–Pd–S angle at a value of 80.56°, while a more wide P–Pd–P bite angle (84.85° and 92.102° in **2** and **3** respectively) is associated with the correspondingly widened S–Pd–S angle of 89.05° in **2** and 91.13° in **3**. Considering interbond distances involving the central metal ion, which are very close to those found in other related complexes [4, 28], there are no significant differences between the three complexes.

It is to note that a crystal structure of compound **2** has been already described by others [4]. Comparing the two structures together, one can notice a marked conformational difference that concerns the orientation of the two pyrimidine rings. Thus, in the earlier described structure the two pyrimidine rings are nearly perpendicular to each other, each of them directed parallel to a phenyl ring of the phosphine ligand with a distance of 3.907 Å between their respective centroids. In the

actual structure of **2**, however, the dihedral angle between the planes of the two pyrimidine rings is only 72.45°, consequently only one of these rings is allowed to participate in such a π -stacking interaction, however at the clearly shorter distance of 3.618 Å. Finally, in addition to this π -stacking interaction, intramolecular hydrogen bonding C24–H ^{...} N2 (C ^{...} N = 3.518 Å, H ^{...} N = 2.586 Å, < C–H–N = 165.49°) appears to contribute both to the orientation of the pyrimidine rings and to the overall stabilization of the molecule in the solid state.

2.3. Photophysical Studies

The electronic spectra of the three complexes in dichloromethane display a strong absorption in the ultraviolet region (290-315 nm) with ε values ranging from ca. 17000 to 35000 M⁻¹cm⁻¹ (Figure 4). This band is assigned to intraligand $\pi - \pi^*$ transitions of the aromatic rings of the phosphines with contributions from high energy electronic excitations located in the heterocyclic rings of the thiolate ligands. In the case of (1) and (3), a low intensity shoulder ($\varepsilon \sim 4000 \text{ M}^{-1}\text{cm}^{-1}$) appears at ca 350 nm followed by an absorption tail extending up to 430 nm (Table 1). For (2) a clear absorption band appears at 410 nm ($\varepsilon \sim 3000 \text{ M}^{-1} \text{cm}^{-1}$) extending up to 460 nm. According to literature data [23, 33] and the results of theoretical calculations (vide infra) the latter absorptions are assigned as a mixture of charge transfer transitions comprising the metal core and both type of ligands (MLCT/LLCT). Additionally and because of the spin-orbit coupling induced by the presence of the Pd-heavy nucleus, a participation of excitations from the ground state towards low lying triplets $(S_0 \rightarrow T_n)$ of the complexes could also be expected. Such transitions would be of a very low intensity and potently contribute in the tails of the lowest energy absorptions appearing in the electronic spectra of the compounds.



Fig. 4. Absorption spectra of [Pd(dppm)(pymt)₂] (1) (red curve), [Pd(dppe)(pymt)₂]
(2) (blue curve) and [Pd(dppp)(py2S)₂] (3) (green curve) in dichloromethane.

Table 1. Photophysical data of the synthesized Pd(II) complexes in fluid solution.

Compound	λ_{abs}, nm^{a} ($\epsilon_{abs}, M^{-1}cm^{-1}$)	λ_{em} , nm ^{b,c}
$[Pd(dppm)(pymt)_2](1)$	359 (sh, 3754)	458
$[Pd(dppe)(pymt)_2](2)$	408 (3015)	472
[Pd(dppp)(py2S) ₂] (3)	356 (sh, 3902)	471

^arefers to the longest wavelength absorption in dichloromethane ${}^{b}\lambda_{exc} = 385 \text{ nm}, \text{ }^{c}\text{dichloromethane solution}$

All of the prepared complexes were tested for their ability to emit in fluid solution. After excitation at 385 nm of an optically diluted sample of each complex in dichloromethane, a broad peak maximizing around 465 nm is detected (Figure 5). The selected photoexcitation cannot directly populate any pure phosphine-residing (intraligand, IL) π - π^* singlet excited state because of their expected higher lying energies, thus the observed luminescence can be readily assigned to the lowest lying state being a ³LLCT/³MLCT/³IL [24]. The triplet character of the emitting state is supported by a heavy atom effect [22-24, 33-35] induced by the Pd-nucleus while the participation of the metal center orbitals is indicated by the unstructured profile of the emission band [36a]. The relatively large Stokes shift of the emission (ca. 80 nm) also

agrees with its triplet nature. At this point it should be mentioned that mixed-ligand complexes of Pd(II) bearing dithiolate moieties appear to be in general non luminescent due to strong interactions with the solvent and/or non-totally symmetric distortions [36b].



Fig. 5. Normalized emission spectra of [Pd(dppm)(pymt)₂] (1) (red curve), [Pd(dppe)(pymt)₂] (2) (blue curve) and [Pd(dppp)(py2S)₂] (3) (green curve) in dichloromethane after photoexcitation at 385 nm.

2.4. Theoretical Results

In order to unravel some marked structural and electronic features of the synthesized compounds we performed DFT and TD-DFT calculations on (**2**) as representative case. The PBE1PBE [37] functional along with the LANL2DZ [38] basis set for the metal core and the 6-31G(d,p) [39] basis sets for the light atoms were selected for the calculations. The structure of the neutral complex was optimized in a dichloromethane environment. The obtained geometrical parameters are presented in Table S1. In the optimized structure (Figure S1), the complex retains its square planar configuration with two slightly unequivalent Pd-P and two also slightly varying Pd-S bond lengths. The metal-sulfur bonds appear to be somewhat longer than the two Pd-P bonds (ca. 2.40 and 2.31 Å, respectively) while the bond angles within the

chromophoric PdP_2S_2 unit deviate from the ideal value of 90° with the P-Pd-S bond angles been larger than the P-Pd-P and S-Pd-S angles. All of the theoretically resulting geometrical features are in good agreement with the crystallographically determined values for the complex.



Fig. 6. Frontier MOs of [Pd(dppe)(pymt)2] (**2**) as they resulted from geometry optimization in dichloromethane.

The electronic structure of (2) was further probed by inspecting the symmetry and localization of the frontier MOs of the system obtained from DFT calculations. As can be seen in Figure 6, the highest occupied orbital (HOMO) mainly locates in

the π -system of the heterocyclic thiolate ligands with a partial d- σ antibonding character between the metal core and the phosphorus atoms. The same holds for HOMO-1 with the difference of a bonding character for the Pd-P interactions. HOMO-2 bears large contributions from the d AOs of the metal center along with a smaller participation of the thiolates' ring system and the exocyclic sulfur atoms. On the other hand, the lowest unoccupied orbital (LUMO) is of a d- σ antibonding nature extending in the region of the PdP₂S₂ chromophore with a negligible contribution from the π -system of the phosphine phenyl rings. The sulfur atoms of the thiolates do not participate in LUMO+1 which mainly localizes on the Pd-phosphine region while LUMO+2 mainly locates in the phosphine moiety with a small participation of the thiolates' heterocyclic π -system. In Figure 7, a simulation of the experimentally obtained light absorption of the complex under study through TD-DFT calculations is presented. The computed eigenvectors offer a very good representation of the recorded spectrum. According to the shape of the involved MOs, the nature of the electronic transitions (Figure 8 and Table 2) contributing to the visible-part absorption band of the complex is assigned as thiolate to phoshine charge transfer with large contributions from the metal core in the donor orbitals (LLCT/MLCT). Higher energy excitations bear either an IL or MLCT character. The results are in agreement with the nature of the emissive state of the complex, as discussed above.



Fig. 7. Experimental absorption spectrum of $[Pd(dppe)(pymt)_2]$ (2) along with the calculated excitation energies appearing as vertical lines.

Table 2. Selected principal singlet-singlet electronic transitions of the complex [Pd(dppe)(pymt)₂] (2) calculated at the PBE1PBE/6-31G(d,p),LANL2DZ level of theory.

Excitation	E/eV	λ/nm	Orbital Nature	Character	OS, f
$HOMO \rightarrow LUMO$	2.833	437.7	$d-\sigma^*/\pi_{pymt} \rightarrow d-\sigma^*/\pi_{PPh3}$	MLCT/LLCT	0.0194
HOMO-1 \rightarrow LUMO	2.853	434.6	d - $\sigma/\pi_{pymt} \rightarrow d$ - σ^*/π_{PPh3}	MLCT/LLCT	0.0236
HOMO-2 \rightarrow LUMO	3.205	386.8	$4d_{Pd}/\pi_{pymt} \rightarrow d-\sigma^*/\pi_{PPh3}$	MLCT/LLCT	0.0186
HOMO \rightarrow LUMO+1	3.980	311.5	d - $\sigma^*/\pi_{pymt} \rightarrow d$ - σ^*/π_{PPh3}	MLCT/LLCT	0.0144
HOMO-1 \rightarrow LUMO+1	4.096	302.7	$d-\sigma^*/\pi_{pymt} \rightarrow \pi_{PPh3}$	MLCT/LLCT	0.0591
HOMO-3 \rightarrow LUMO	4.144	299.2	$\pi_{\text{PPh3}}/\sigma_{\text{pymt}} \rightarrow d - \sigma^*/\pi_{\text{PPh3}}$	LLCT/IL	0.1679
HOMO \rightarrow LUMO+2	4.168	297.5	d - $\sigma^*/\pi_{pymt} \rightarrow \pi_{PPh3}/\pi_{pymt}$	MLCT/LLCT/IL	0.1205
HOMO-4 → LUMO HOMO-14 → LUMO	4.196	295.5	$4d_{Pd}/\pi_{PPh3} \rightarrow d$ - σ/π_{PPh3}	MLCT/IL	0.1354
HOMO-4 → LUMO HOMO-2 → LUMO+4	4.336	285.9	$4d_{Pd}/\pi_{PPh3}/\pi_{pymt} \rightarrow d\text{-}\sigma^*/\pi_{PPh3}/\pi_{pymt}$	MLCT/LLCT/IL	0.1949



Fig. 8. Predicted electronic transitions and participating MOs with the higher CI coefficients for the $[Pd(dppe)(pymt)_2]$ (2).

3. Conclusions

Three Pd(II) neutral complexes bearing two heterocyclic thiolate units and a chelating diphosphine moiety were synthesized and characterized. As revealed by crystallographic data, the complexes adopt in all cases a square planar arrangement in accordance to the d⁸-character of the metal core. Further, coordination of the deprotonated thiolates to the Pd(II) ion takes place through their exocyclic sulphur atom while no interaction with the heterocyclic nitrogen atoms is detected. In

solution, the complexes absorb in the visible part of the spectrum with the lowest energy transitions described as MLCT/LLCT according to DFT results. Further the complexes are emissive in a dichloromethane solution after photoexcitation in their CT-bands.

4. Experimental

4.1. Materials and Measurements

The starting materials PdCl₂, bis(diphenylphosphino)methane, 1,2bis(diphenylphosphino)ethane, 1,3-bis(diphenylphosphino)propane), pyrimidine-2thione and pyridine-2-thione were used as received. Solvents of reagent grade were also used without any prior purification or drying process. Elemental analyses for C, H and N were performed with a Perkin-Elmer 240B elemental analyzer. Infrared spectra were recorded in KBr pellets on a Nicolet FT-IR 6700 spectrophotometer. Electronic absorption spectra were recorded in 1 cm cuvettes on a Shimadzu 160A spectrophotometer. Emission studies in dichloromethane were performed on a Hitachi F-7000 Fluorometer.

4.2. Computational Details

The geometry of (2) was optimized with DFT theory assuming a dichloromethane medium and without symmetry constraints with the PBE1PBE [37] functional. The obtained crystallographic data were used for the description of the initial geometry. The 6-31G(d,p) [39] and LanL2DZ [38] basis sets were selected respectively for the light elements and the metal core. TD-DFT calculations in the aforementioned solvent system were performed on the same level of theory and with the same basis sets. In all cases computations were executed with the Gaussian 03W

[40] package using the PCM [41] algorithm implemented in it. Vibrational frequencies calculations ensured that the obtained geometry is real minimum in the potential energy hypersurface. Visualization of the obtained structure and MOs was performed with GaussView 5.0.

4.3. Crystal Structure Determination

Single crystals of *cis*-[Pd(ddpm)(pymt)₂] (1), *cis*-[Pd(ddpe)(pymt)₂] (2) and *cis*-[Pd(ddpp)(py2S)₂] (3), suitable for crystal structure analysis were obtained by slow evaporation of their mother liquids at room temperature. For the structure determination single crystals of the compounds were mounted on a Bruker Kappa APEX II diffractometer equipped with a triumph monochromator. The collected frames were integrated with the Bruker SAINT software package [42] using a narrow-frame algorithm. Data were corrected for absorption effects using the numerical method from crystal dimensions (SADABS) [43]. The structures were solved using SUPERFLIP package [44] and refined by full–matrix least-squares method on F^2 using the CRYSTALS package version 14.48 [45]. All non hydrogen atoms have been refined anisotropically. All hydrogen atoms were found at expected positioned using riding constraints. By the end of the refinement they were positioned using riding constraints. The crystal data and some details of the data collection and structure refinement for all compounds are given in Table 3. Illustrations were generated with CAMERON [46].

Compound	1	2	3
Formula	$C_{33}H_{28}N_4P_2Pd_1S_2$	$C_{34}H_{30}N_4P_2Pd_1S_2$	$C_{37}H_{34}N_2P_2Pd_1S_2$
Formula weight	713.09	727.12	739.17
Crystal system	Monoclinic	Monoclinic	Monoclinic
Temperature (K)	295	295	295
Space group	C2/c	$P2_1/c$	$P2_1/c$
Unit cell dimensions	a = 22.9567(7) Å b = 8.8667(3) Å c = 30.5007(9) Å $\alpha = 90^{\circ}$ $\beta = 102.751(2)^{\circ}$ $\gamma = 90^{\circ}$	a = 8.5459(3) Å b = 10.5547(3) Å c = 35.2540(11) Å $\alpha = 90^{\circ}$ $\beta = 90.528(2)^{\circ}$ $\gamma = 90^{\circ}$	a = 17.6938(5) Å b = 8.6339(2) Å c = 21.7762(6) Å $\alpha = 90^{\circ}$ $\beta = 92.156(2)^{\circ}$ $\gamma = 90^{\circ}$
Ζ	8	4	4
Absorption coefficient $(\mu) \text{ (mm}^{-1})$	0.888	0.847	0.810
Density (calculated) (Mg/m ³)	1.629	1.52	1.48
Theta range for data collection (°)	1.819 to 27.449	1.155 to 27.205	1.152 to 35.538
F(000)	2896	1480	1512
Reflections collected	77202	35711	112840
Independent reflections	6852	6960	15101
Completeness up to	99.6% (theta =	98.1% (theta =	99.2% (theta =
theta	27.4489°)	27.205 °)	35.538°)
Data / restraints / parameters	6052/0/379	6720/0/388	10512/0/397
Goodness-of-fit on F ²	1.000	1.000	1.000
Final R indices	$R_1=0.044,$	$R_1 = 0.033,$	$R_1 = 0.039,$
[I>2σ(I)]	$wR_1 = 0.069$	wR ₁ =0.052	$wR_1 = 0.067$
Largest diff. peak and hole ($e^{\text{Å}^{-3}}$)	0.61, -1.70	0.78, -0.39	1.06, -0.60

Table 3. Crystal data and structure refinement details for compounds 1, 2 and 3

4.4. Synthesis of the complexes

All the complexes were prepared according to the following general procedure. In a solution of $PdCl_2$ (0.5 mmol) in 20 mL of methanol, the appropriate amount of the respective solid diphosphine is added (0.5 mmol). After stirring for 30 min, 1 mmol of the selected thiole, deprotonated with KOH in 20 mL of methanol, is

added and the reaction mixture is stirred for 48 h under moderate heating (60 °C). The resulting solution is filtrated for the removal of any residual solids and the filtrate is left to stand in air after the addition of a small amount of a 1:1 mixture of $CH_2Cl_2/CHCl_3$. Slow evaporation of the solvent gave the products in the form of crystals which were filtered off and dried under vacuum.

$[Pd(dppm)(pymt)_2](1)$

Red solid. Yield 92 % (0.46 mmol, 0.33 g). Elemental Analysis: Calcd for $C_{33}H_{28}N_4P_2PdS_2$: C, 55.58; H, 3.96; N, 7.86. Found: C, 55.50; H, 4.01; N, 7.78. IR (KBr, cm⁻¹): 3054 (w, =C-H), 2953 (w, -C-H), 1560 (s, -C=N-), 1536 (s, -C=C-), 1434 (s), 1371 (s), 1175 (s), 1097 (m), 744 (s), 691 (s), 505 (s).

[Pd(dppe)(pymt)₂] (2)

Orange solid. Yield 94 % (0.47 mmol, 0.34 g). Elemental Analysis: Calcd for $C_{34}H_{30}N_4P_2PdS_2$: C, 56.16; H, 4.16; N, 7.71. Found: C, 56.31; H, 4.12; N, 7.70. IR (KBr, cm⁻¹): 3048 (w, =C-H), 2970 (w, -C-H), 1561 (s, -C=N-), 1531 (s, -C=C-), 1434 (s), 1371 (s), 1174 (s), 1099 (m), 740 (s), 687 (s), 521 (s).

$[Pd(dppp)(py2S)_2](3)$

Orange solid. Yield 93 % (0.46 mmol, 0.34 g). Elemental Analysis: Calcd for $C_{37}H_{34}N_2P_2PdS_2$: C, 60.12; H, 4.64; N, 3.79. Found: C, 60.32; H, 4.72; N, 3.82. IR (KBr, cm⁻¹): 3051 (w, =C-H), 2912 (w, -C-H), 1569 (s, -C=N-), 1542 (s, -C=C-), 1442 (s), 1435 (s), 1403 (s), 1175 (s), 1121 (m), 748 (s), 691 (s), 512 (s).

5. Appendix. Crystallographic data

Crystallographic data (without structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication no. CCDC-1042948 (1), CCDC-1042949 (2) and CCDC-1042950 (3). Copies of the data can be obtained free of charge from the CCDC (12 Union Road, Cambridge CB2 1EZ, UK; Tel.: +44-1223-336408; Fax: +44-1223-336033; e-mail: <u>deposit@ccdc.cam.ac.uk</u>; Web site: <u>http://www.ccdc.ca.ac.uk</u>).

6. Supplementary Materials

Electronic Supplementary Information (ESI) available: Optimized geometry of the [Pd(dppe)(pymt)₂] (**2**) (Figure S1), structural data for the optimized geometry of the complex in dichloromethane (Table S1).

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The present study comprises the synthesis and photophysical investigation of three new square planar palladium (II) compounds, each bearing two thiolate units and a chelating diphosphine. DFT calculations are performed in order to rationalize their spectroscopic behavior in solution.