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PII: S0022-328X(13)00690-6

DOI: 10.1016/j.jorganchem.2013.09.022

Reference: JOM 18268

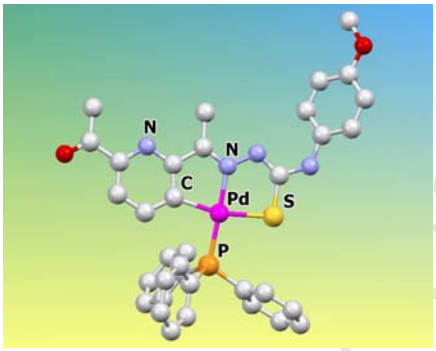
To appear in: *Journal of Organometallic Chemistry*

Received Date: 28 May 2013

Revised Date: 13 September 2013

Accepted Date: 16 September 2013

Please cite this article as: A.I. Matesanz, C. Henández, P. Souza, A new organometallic palladium(II) compound derived of 2,6-diacetylpyridine mono(thiosemicarbazone): synthesis, spectroscopic properties and crystal structure of two solvatomorphic forms, *Journal of Organometallic Chemistry* (2013), doi: 10.1016/j.jorganchem.2013.09.022.



A new organometallic palladium(II) compound derived of 2,6-diacetylpyridine mono(thiosemicarbazone) has been synthesized and structurally characterized by single crystal X-ray diffraction. The molecular structure shows that ~~The~~ the diacetylpyridine ring undergoes an interesting and unexpected C-H bond activation.

Highlights

- A new 2,6-diacetylpyridine mono(4-methoxyphenyl-thiosemicarbazone) cyclopalladated ~~diacetylpyridine/thiosemicarbazone~~ compound ~~with~~ has been prepared

- Cyclopalladation occurs at the~~The~~ diacetylpyridine ring which undergoes an interesting and unexpected C-H bond activation

- Two solvatomorphic forms, ~~of~~ [PdL(PPh_3)] and [PdL(PPh_3)]·DMSO, have been studied by X-ray crystallography

A new organometallic palladium(II) compound derived of 2,6-diacetylpyridine mono(thiosemicarbazone): synthesis, spectroscopic properties and crystal structure of two solvatomorphic forms

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Keywords: Cyclopalladated, 2,6-diacetylpyridine, solvatomorph, thiosemicarbazone, X-ray.

Summary

Preparation and characterization of a novel 2,6-diacetylpyridine mono(4-methoxyphenyl-thiosemicarbazone), H_2L, is described. Treatment of H_2L with $PdCl_2(PPh_3)_2$ gave the neutral mononuclear complex $[PdL(PPh_3)]$. Both compounds have been characterized by elemental analysis and FAB^+ spectrometry and by IR and ^1H NMR spectroscopy. Recrystallization of $[PdL(PPh_3)]$ in DMSO led to the isolation of two solvatomorphic forms of this compound which were studied by X-ray crystallography. In each solvatomorph, the thiosemicarbazone ligand acts as dianionic [CNS] tridentate donor coordinating to the palladium(II) ion in a square planar geometry through the iminic nitrogen atom, the sulfur atom and one *ortho* carbon atom of the pyridine ring and the fourth site is occupied by P atom from the PPh_3 coligand. The overall molecular conformation of the two solvatomorphs is very similar and the largest difference lies in the orientation of the methyl group of the 4-methoxyphenyl substituent with respect to the sulfur atom.

1. Introduction

Metal mediated activation of aromatic C-H bonds represents an active research area in organometallic chemistry due to the numerous applications that the resulting cyclometallated compounds have found in organic synthesis, catalysis, material sciences and as biologically active compounds [1-4]. The cyclometallation process occurs quite readily with platinum group metals and consists of two consecutive steps: initial coordination of the metal center via a donor group such as N, O, P, S, etc; and subsequent intramolecular activation of the C-H bond, which closes the metallacycle [5-8].

Thiosemicarbazones (Scheme 1, left) are important and versatile N/S donor ligands. They may exist as thione/thiol tautomeric forms owing to the intramolecular proton transfer and thus can bind to a metal center *via* a variety of coordination modes in both neutral and anionic forms. Usually the thiosemicarbazone moiety coordinates to the metal ion through the sulfur atom and the azomethine nitrogen atom forming five membered chelate rings [9,10]. The coordination capacity of thiosemicarbazones can be further increased, if the parent aldehyde or ketone contains, at R_1, an additional donor atom in position suitable for chelation (Scheme 1, right).

Scheme 1.

In this regard, heterocyclic thiosemicarbazone coordination compounds have been studied extensively and it is well established that both, the nature of the ligand

substituents, the metal ion, the type of anion, co-ligands and solvents have high influence in the bonding and nuclearity of the resulting complexes [11-15].

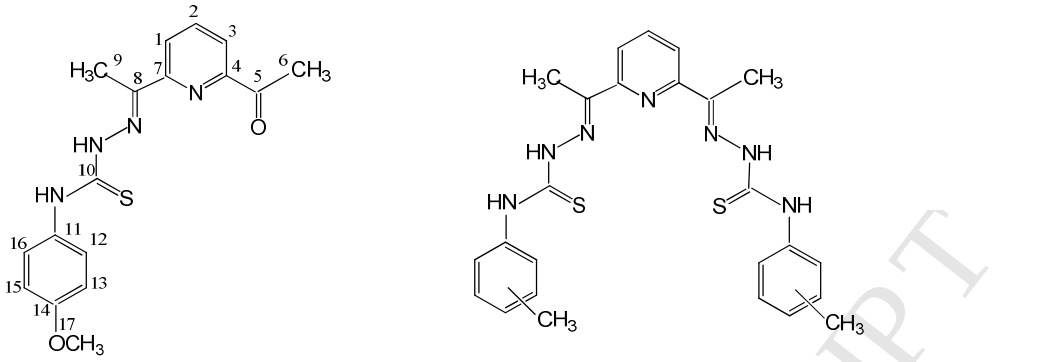
Cyclopalladated compounds with tridentate thiosemicarbazones prepared via C-H activation of an aryl group have also been previously described [16-20] and the cyclometallation has been attributed to the steric effect of R_2 substituents. However, there are limited reports concerning the C(sp^2)-H bond activation in electron-deficient aromatic systems such as in pyridines since α-(N)-heterocyclic thiosemicarbazones usually give rise to chelate complexes [1, 21-22].

As part of our systematic investigation on the chemistry of thiosemicarbazone derivatives, we have reported both cyclopalladated and coordination palladium(II) complexes derived of α-diphenyletanodione bis(thiosemicarbazones) [23-25] as well as numerous coordination palladium(II) complexes derived from different α-(N)-heterocyclic bis(thiosemicarbazones) [26-28].

Recently, we have prepared a series of palladium(II) and platinum(II) complexes derived from 2,6-diacetylpyridine bis(^{4}N-tolyl-thiosemicarbazones) and structural study revealed the mononuclear neutral nature of the complexes and the dianionic [SNNN] tetradentate behavior of the α-(N)-heterocyclic bis(thiosemicarbazone) ligands [29].

To extend the knowledge in this research field, in this study we report on the synthesis and chemical characterization of the new 2,6-diacetylpyridine mono(4-methoxyphenyl-thiosemicarbazone) ligand, H_2L (Scheme 2), and its cyclopalladated complex [PdL(PPh_3)].

In principle, the new ligand could give rise to [SNNO] or [SNN] donor sites forming, by reaction with palladium(II) salts, square planar coordination complexes in a similar manner to the related 2,6-diacetylpyridine bis(^{4}N-tolyl-thiosemicarbazones).



Scheme 2. Structural drawings of 2,6-diacetylpyridine mono(4-methoxyphenyl-thiosemicarbazone), H_2L (left) and 2,6-diacetylpyridine bis(^{4}N-tolyl-thiosemicarbazone) (right) ligands

However we found that 2,6-diacetylpyridine mono(4-methoxyphenyl-thiosemicarbazone) ligand undergoes an unexpected and interesting C-H bond activation of the pyridine ring leading to the formation of an orthopalladated compound.

2. Experimental

2.1. Measurements

Elemental analyses were performed on a LECO CHN-932 microanalyzer. Fast atom bombardment (FAB) mass spectra were performed on a VG AutoSpec spectrometer (nitrobenzyl alcohol matrix). Nuclear Magnetic Resonance (NMR) spectra were recorded on a BRUKER AMX-300 spectrometer. All cited physical measurements were obtained out by the Servicio Interdepartamental de Investigación (SIdI) of the Universidad Autónoma de Madrid.

Melting points were determined with a Stuart Scientific SMP3 apparatus. Infrared spectra (KBr pellets) were recorded on a Bomen–Michelson spectrophotometer (4000–400 cm^{-1}).

2.2. Materials

Solvents were purified and dried according to standard procedures. Hydrazine hydrate, 2,6-diacetylpyridine, 4-methoxyphenyl isothiocyanate, $PdCl_2(PPh_3)_2$ were commercially available.

2.3. Synthesis of compounds

2,6-Diacetylpyridine mono(4-methoxyphenyl-thiosemicarbazone), H_2L. An ethanolic solution of hydrazine hydrate (0.250 g, 5 mmol) was added dropwise with constant stirring to an ethanolic solution of 4-methoxyphenyl isothiocyanate (0.826 g, 5 mmol). The reaction mixture was stirred for one more hour and then the white product 4-methoxyphenyl-thiosemicarbazide formed was filtered, washed with cold ethanol and diethyl ether, dried *in vacuo* and recrystallized from ethanol. An ethanolic solution of the 4-methoxyphenyl-thiosemicarbazide (0.346 g, 1 mmol) was then stirred with 2,6-diacetylpyridine (0.163 g, 1 mmol) for 5 h. The resulting solution was reduced to half volume and the pale yellow solid formed was filtered, washed several times with hot water, diethyl ether and finally dried *in vacuo*.

Yield (55%), mp 196 ºC (decomposes). Elemental analysis found, C, 56.6; H, 5.5, N, 16.0; $C_{17}H_{18}N_4O_2S{\cdot}H_2O$ requires C, 56.5; H, 5.5, N, 15.5 %. MS (FAB^+ with *m*NBA matrix) *m*/*z* 343.1 for $[H_2L+H]^+$. IR (KBr pellet): *n*/cm^{-1} 3192, 3114 (s, NH); 1690 (s, CO); 1590 (s, CN); 1518 (s, CN-thioamide I); 805 (w, CS-thioamide IV). ^{1}H NMR (300.14 MHz, DMSO-d_6): δ (ppm) 10.60 (s, ^{2}NH); 10.15 (s, ^{4}NH); 8.70 (m, H12, H16); 8.25 (m, H13, H15); 7.90 (m, H2); 7.40 (d, H1); 6.90 (d, H3); 3.80 (s, H17); 2.50 and 2.30 (s, H6 and H9).

2,6-Diacetylpyridine mono(4-methoxyphenyl-thiosemicarbazonato-κ^3CNS)triphenylphosphinepalladium(II), [Pd(L)(PPh_3)]. The reaction of H_2L ligand with $PdCl_2(PPh_3)_2$, in toluene, in presence of Et_3N, in 1:1 molar ratios over 2 h at room temperature led to the formation of an orange solution which was filtered and left to stand at ambient temperature for two days. The solid formed was filtered, washed several times with hot water, recrystallizated from DMSO and finally dried in *vacuo*.

Yield (35%), mp >250 ºC. Elemental analysis found, C, 56.7; H, 4.6, N, 7.1; $C_{35}H_{31}N_4O_2SPPd$·DMSO requires C, 56.5; H, 4.7, N, 7.1 %. IR (KBr pellet): *n*/cm^{-1} 3418 (s, NH); 3048 (w, PPh_3); 1685 (s, CO); 1591 (s, CN); 1537 (s, CN-thioamide I); 1076 (w, PPh_3); 798 (vw, CS-thioamide IV). ^{1}H NMR (300.14 MHz, DMSO-d_6): δ (ppm) 9.40 (s, ^{4}NH), 7.65-7.45 (m, H12, H13, H15, H16 and -PPh_3 aromatic protons); 7.00 (d, H2); 6.85 (d, H3); 3.70 (s, H17); 2.55 and 2.50 (s, H6 and H9).

Rerystallization from DMSO led to the isolation of two types of crystals: (I) clear yellow plates and (II) clear yellow prismatic. The molecular structures of both crystals were determined by single crystal X-ray diffraction.

Crystallography

Data were collected on a Bruker X8 APEX II CCD. Crystallographic data and selected interatomic distances and angles are listed in Tables 1 and 2. The software package SHELXTL was used for space group determination, structure solution, and refinement [30]. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with anisotropic displacement parameters.

CCDC 940829 and 940830 contain the supplementary crystallographic data. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

3. Results and discussion

3.1. Synthesis and spectroscopic characterization

A new multidentate ligand, H_2L, was synthesized as a platform for metal arrangement. Complexation with $PdCl_2(PPh_3)_2$ led to the isolation of an orange solid. The new palladium(II) complex obtained which is stable to air and moisture was characterized by elemental analysis, IR and ^{1}H NMR spectroscopy and single crystal X-ray diffraction. It is noteworthy that only two reports on structural properties of mono(thiosemicarbazone) complexes derived of a (N)-hetrocyclic diketones have been found in literature [31-32].

Analytical data suggests $[PdL(PPh_3)]$ stoichiometry and this requires that a dideprotonate tridentate ligand behavior. The ^{1}HNMR spectroscopy was used to confirm the dideprotonation. Thus while the spectrum of the ligand shows two peaks at low field assigned to the hydrazinic and thioamidic protons (10.60 and 10.15 ppm respectively) and three signals assigned to the three pyridinic protons of the ligand, in the spectrum of the complex the absence of N^{2}H proton signal and the presence of only two signals assigned to pyridinic protons supported the dideprotonation.

The infrared spectral bands most useful for determining the mode of coordination of the ligand are the ν(C=O), ν(C=N) iminic and ν(C=S) thioamide IV vibrations. In the IR spectrum of palladium(II) complex, the ν(C=O) band appears at 1685 cm^{-1} indicating the no participation of the carbonyl oxygen in coordination. On the other hand, the shift of ν(C=S) thioamide IV to lower wavenumbers suggests coordination of the sulfur atom. Moreover, the presence of the triphenylphosphine ligand is confirmed by the existence of the characteristic bands around 3050 and 1070 cm^{-1} for ν(C-H) and ν(P-C), with no significant change when compared to the precursor $PdCl_2(PPh_3)_2$.

Thus analytical and spectroscopic findings point to an unexpected dianionic CNS tridentate behavior of the ligand ~~in complex~~ which could be confirmed from the structure of the complex determined by single-crystal X-ray diffraction techniques.

Lobana *et al.* [21] prepared a series of palladium thiosemicarbazone compounds containing both metallated thiophene or phenyl rings and the corresponding chelated derivatives. Thus, they demonstrated that the nature of R_2 thiosemicarbazone substituents (see Scheme 1) might induce cyclopalladation by changing electronic and steric properties. Similarly we achieved the activation of C-H bond of the aromatic pyridine ring and this unusual cyclopalladation can be tentatively attributed to the steric effect of acetyl group at R_2 which drives to R_1 substituent closer to palladium atom.

3.2. Crystallographic characterization of two polymorphs of [Pd(L)(PPh_3)]

Recrystallization of [Pd(L)(PPh_3)] compound in DMSO led to the isolation, from the same crystallization vial, of two types of clear yellow crystals (designated here as forms I and II) which differing in shape: I is plate and II is prismatic. The molecular structures of both crystals were determined by single crystal X-ray diffraction and the ORTEP view together with the atomic numbering scheme is shown in Fig. 1 and Fig. S1 (Supporting Information).

Interestingly, both forms, I and II, contain [Pd(L)(PPh_3)] molecules but while the first is DMSO solvated, the second do not contain any crystallization solvent molecules. Crystallographic data is shown in Table 1 and selected bond lengths are listed in Table 2.

Insert Figure 1

Insert Table 1

Insert Table 2

Both solvatomorphs crystallize in the same space group but show different lattice parameters. In each molecule, the palladium(II) ion is tetracoordinated, bound to the N_{iminic} and the S atoms from the thiosemicarbazone moiety, one *ortho* C atom of the pyridine ring and the P atom from the PPh_3 coligand. Therefore the thiosemicarbazone ligand behaves as dianionic [CNS] tridentate after metallation through C(1) carbon of pyridine ring and deprotonation of N(2).

It is important to note that upon coordination, the deprotonated thiosemicarbazone ligand undergoes significant evolution from the thione to the thiol form which is reflected in a C–S distance of 1.765(3) Å (form I) and 1.764(4) Å (form II). The C–N and N–N bond distances (Table 2) are intermediate between formal single and double bonds, pointing to extensive delocalization over the entire thiosemicarbazone skeleton.

The Pd–C 2.038(3) Å, Pd-N 2.025(2) Å, Pd–S 2.3249(7) Å and Pd–P 2.2469(7) Å (form I) and Pd–C 2.042(4) Å, Pd-N 2.036(3) Å, Pd–S 2.3222(11) Å and Pd–P 2.2484(10) Å (form II) bond distances are comparable with those reported for Pd(II) thiosemicarbazones [18,33]. The overall molecular conformation of the two polymorphs is very similar and the largest difference lies in the orientation of the methyl group of the 4-methoxyphenyl substituent with respect to the sulfur atom, namely *syn* (form II) or *anti* (form I) [34].

The bond angle data indicate that the stereochemistry around the palladium (II) ion is almost planar. The angles deviate slightly from that expected for a regular square–planar geometry, this distortion may be attributed to the restricted bite angle of the tridentate moieties. Coordination results in the formation of two five membered chelate

rings with bite angles C(1)-Pd(1)-N(3) = 81.66(10)º and N(3)-Pd(1)-S(1) = 82.87(7)º (form I) and C(1)-Pd(1)-N(3) = 81.47(15)º and N(3)-Pd(1)-S(1) = 83.12(10)º (form II).

In both polymorph supramolecular association patterns are basically characterized by π-π stacking interactions (Fig. 2 and S2) however in the I-polymorph DMSO solvent molecules are involved in intermolecular hydrogen bond with the ^{4}N-H atoms as is common in the crystal structures of thiosemicarbazones [21,24].

Figure 2

Acknowledgments

We are grateful to Ministerio de Economía y Competitividad, Instituto de Salud Carlos III of Spain (PI1100659) for financial support.

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Table 1 Crystal data and structure refinement for **I** and **II**.

	I	**II**
Molecular formula	$C_{37}H_{37}N_4O_3PPdS_2$	$C_{35}H_{31}N_4O_2PPdS$
Formula weight	787.20	709.07
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a(Å)	16.9191(11)	9.1218(10)
b(Å)	9.4437(6)	14.8577(17)
c(Å)	22.6259(12)	23.660(3)
α/°	90	90
β/°	102.292(3)	99.302(5)
γ/°	90	90
Volume(Å^3)	3532.3(4)	3164(6)
Z	4	4
Density (calculated) (g/cm^3)	1.480	1.488
Absorption coefficient (mm^{-1})	0.731	0.742
F(000)	1616	1448
Crystal size (mm^3)	0.05 x 0.40 x 0.40	0.08 x 0.10 x 0.25
Index ranges	-21≤h≤21, -11≤k≤11, -28≤l≤28	-10≤h≤10, -17≤k≤17, -28≤l≤28
Reflections collected	68535	55369
Independent reflections	7487 [R(int) = 0.0442]	5776 [R(int) = 0.0890]
Data / restraints / parameters	7487 /0 /438	5776 /1 /400
Goodness-of-fit on F^2	1.006	1.002
Final R indices [$I>2\sigma(I)$]	R1 = 0.0336, wR2 = 0.0952	R1 = 0.0373, wR2 = 0.1027
R indices (all data)	R1 = 0.0455, wR2 = 0.1127	R1 = 0.0610, wR2 = 0.1297
Largest diff. peak and hole, e.Å^{-3}	2.182 and -0.716	0.591 and -0.876

Table 2. Selected bond distances (Å) and angles (º) for **I** and **II**.

	I	**II**
S(1)-C(10)	1.765(3)	1.764(4)
C(8)-N(2)	1.295(4)	1.301(5)
C(10)-N(3)	1.312(4)	1.305(5)
C(10)-N(4)	1.361(4)	1.367(5)
Pd(1)-C(1)	2.038(3)	2.042(4)
Pd(1)-N(2)	2.025(2)	2.036(3)
Pd(1)-S(1)	2.3249(7)	2.3222(11)
Pd(1)-P(1)	2.2469(7)	2.2484(10)
N(2)-Pd(1)-C(1)	81.66(10)	81.47(15)
N(2)-Pd(1)-P(1)	174.08(7)	176.78(9)
N(2)-Pd(1)-S(1)	82.87(7)	83.12(10)
C(1)-Pd(1)-P(1)	97.69(8)	104.4(5)
C(1)-Pd(1)-S(1)	164.39(8)	164.46(12)
P(1)-Pd(1)-S(1)	97.49(3)	97.61(4)

Captions

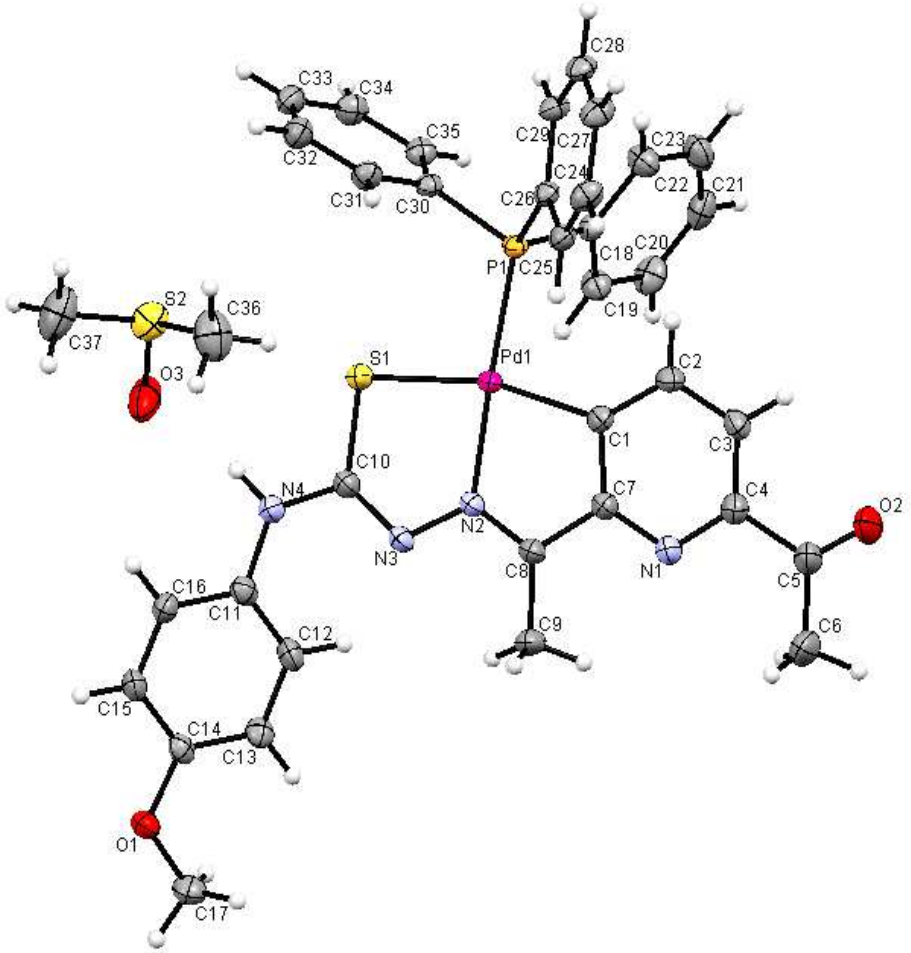
Scheme 1. General structure of thiosemicarbazones.

Scheme 2. General structure of diacetylpyridine mono and bis(thiosemicarbazone) ligands.

Figure 1. Molecular structure of **I**.

Figure 2. Crystal packing view of **I** along a axis.

Figure 1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C19
S2
C36
C37
S1
Pd1
C2
O3
C1
C3
C10
N4
C7
C4
O2
N2
N3
C8
N1
C5
C16
C11
C12
C9
C6
C15
C14
C13
O1
C17

Figure 2

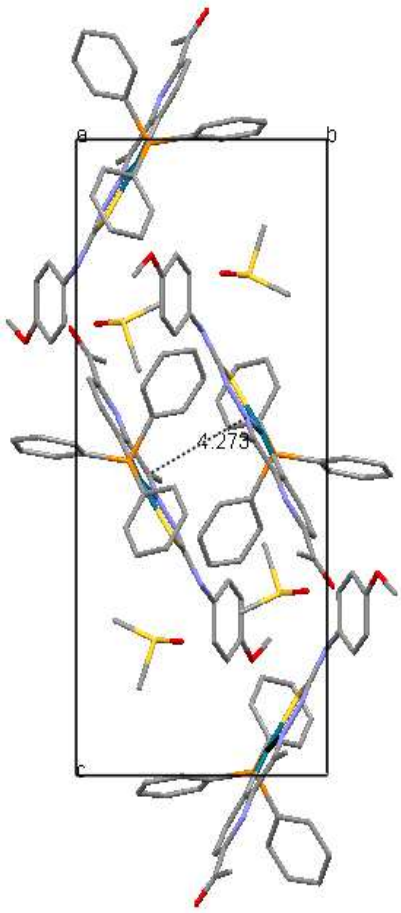

Figure S1

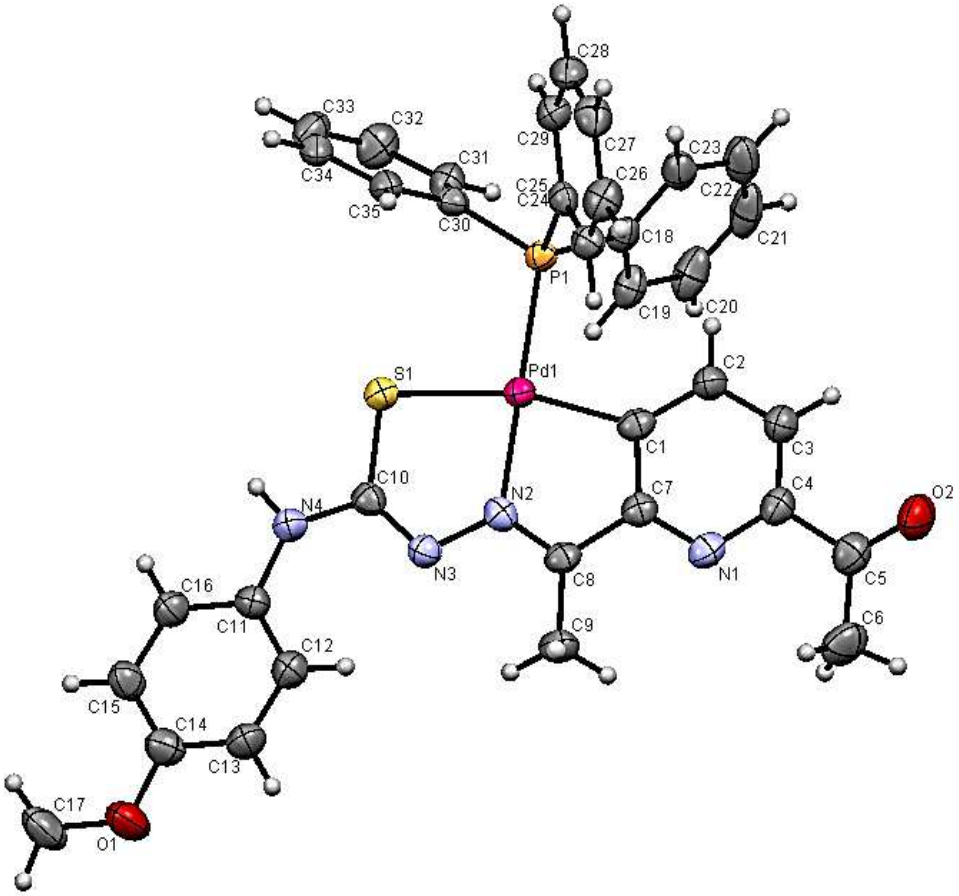

Figure S1. Molecular structure of **II**.

Figure S2

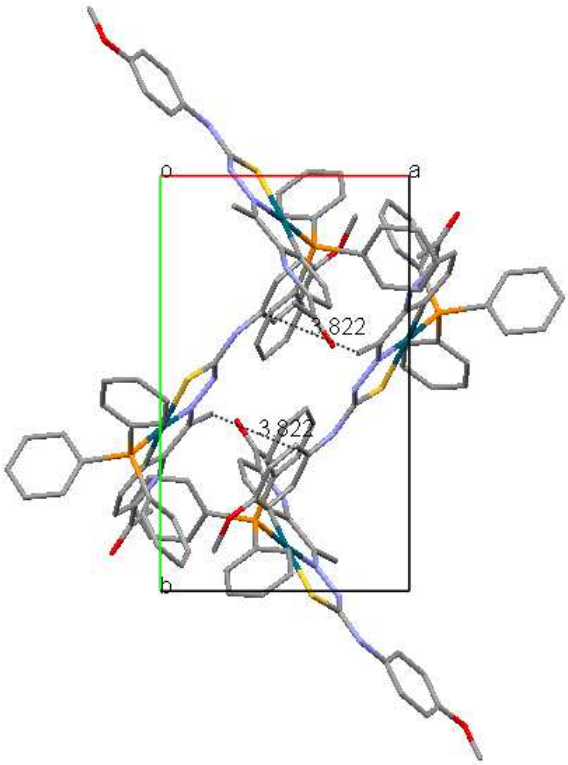

Figure S2. Crystal packing view of II along c axis.