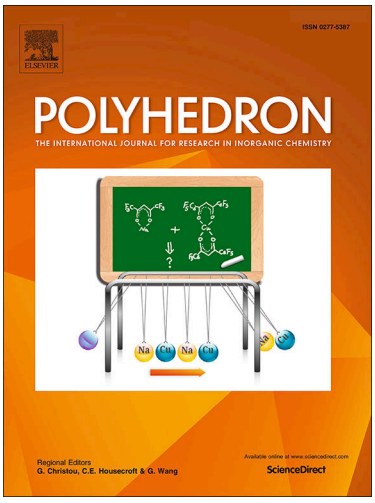

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Synthesis and Characterization of Pd(II) Complexes Bearing NS, CS, SNS and SCS Ligands. Evaluation of Their Microwave Assisted Catalytic Activity in C-C Coupling Reactions

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Abstract

A series of coordination (***Pd-NS***, ***Pd-SNS***, ***Pd-SNS-O***) and organometallic (***Pd-C*** and ***Pd-SCS***) Pd(II) complexes supported by bidentate and tridentate ligands featuring sulphur moieties have been prepared. All ligands and their palladium complexes were fully characterized by various analytical techniques, including the unequivocal determination of the solid-state structures of the ligand ***L-SNS-O*** and the ***Pd-CS*** and ***Pd-NS*** complexes by single crystal X-ray diffraction analysis. Complexes ***Pd-NS***, ***Pd-SNS***, ***Pd-CS***, ***Pd-SCS*** containing thioether groups were used as efficient catalysts in microwave-assisted Suzuki-Miyaura and Mizoroki-Heck C-C cross-coupling reactions, showing the organometallic catalysts (***Pd-CS, Pd-SCS***) to produce the better conversions, most likely due to enhanced thermal stability provided by the Pd-C bonds.

Keywords: C-C cross-coupling; Heck-Mizoroki reaction; Suzuki-Miyaura Reaction, Palladium complexes; Pincer Complexes, Catalysis.

1. Introduction

The applications of palladium complexes pervade in modern synthetic chemistry and have become ubiquitous in organometallic chemistry and catalysis. In part, because these complexes are among the most efficient catalysts for cross-coupling reactions leading to the formation of new C-C bonds allowing the design of new organic compounds with a wide range of different uses, such as new materials, optical devices, pharmaceuticals, and sensors. [1-4] The Suzuki-Miyaura and the Mizoroki-Heck reactions are among the best studied Pd-catalyzed coupling reactions. Currently, the Suzuki-Miyaura couplings between organic halides and boronic acids is one of the most versatile synthetic and successful methods for the construction of biaryls and substituted aromatic moieties. [5-7] Additionally, the Mizoroki-Heck reaction is also a very attractive process enabling the coupling of organic halides with alkenes to produce substituted alkenes with high stereoselectivity for *trans* coupling. [8-11]

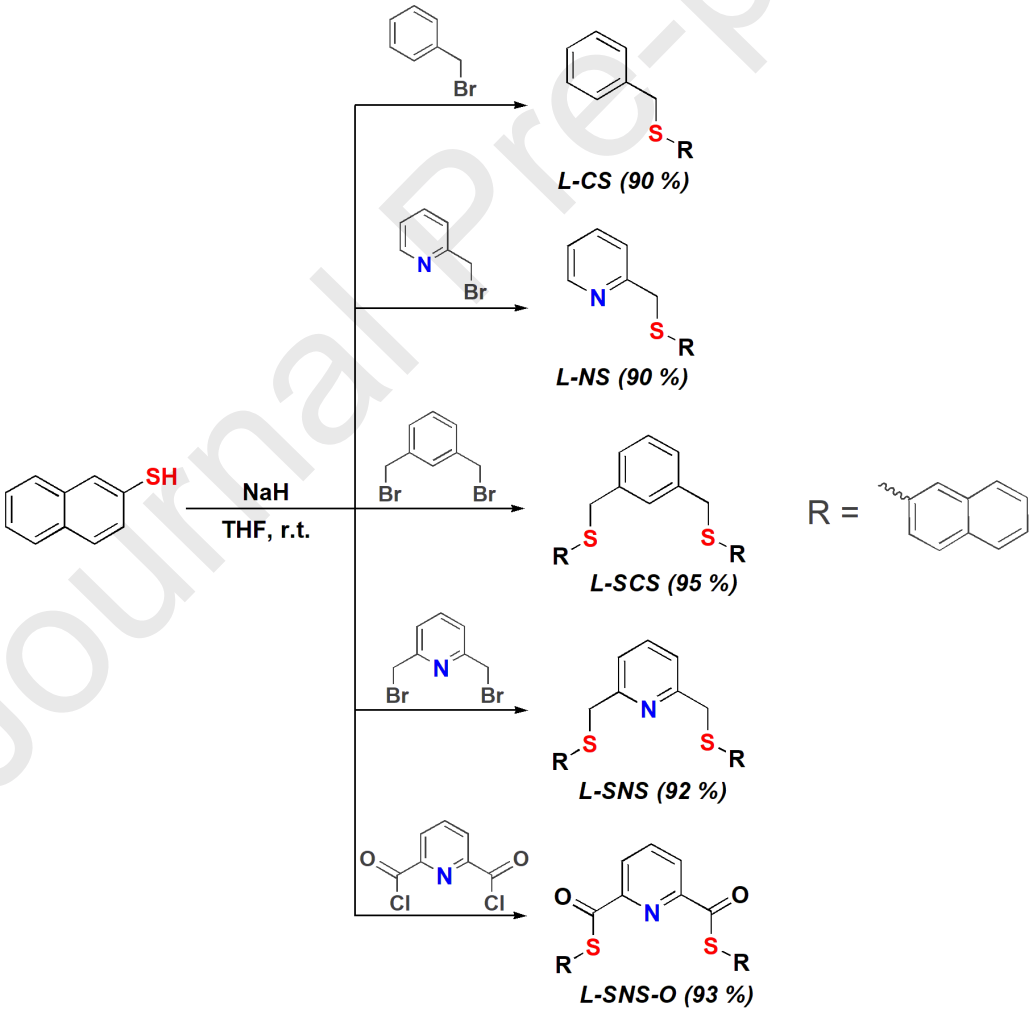
In this regard, palladium compounds bearing electron-rich phosphines have proved to be excellent catalysts precursors for these types of transformations. [12-14] However, the preparation of palladium complexes containing phosphines derivatives is often hampered by rigorous synthetic methods required to produce these ligands. Therefore, the research interest is now expanding to use novel phosphine-free, air- and water-stable and easy to synthesize catalysts. [15-20] The applications of these systems combined with the use of alternative energy sources such as microwave irradiation (MW), may lead to more eco-friendly, economical and sustainable protocols, themes of great relevance nowadays. The use of microwave irradiation has undeniable advantages compared with the conventional heating as superb reduction of reaction times, faster reaction kinetics and cleaner products. [21-23] Thus, following our continuous interest in the chemistry of sulphur donor ligands, [20,23] we report on this opportunity a series

of Pd(II) complexes bearing naphthalene substituted thioether ligands (Pd-NS, Pd-SNS, Pd-CS, Pd-SCS) and their use as catalysts in Suzuki-Miyaura and Mizoroki-Heck couplings under microwave irradiation.

2. Results and discussion

2.1 Synthesis and characterization of the ligands ***L-CS, L-NS, L-SCS, L-SNS***

The ligands were prepared in excellent yields *via* a nucleophilic attack of the naphthalene-2-thiolate over (bromomethyl)benzene, 2-(bromomethyl)pyridine, 1,3-bis(bromomethyl)benzene, 2,6-bis(bromomethyl)pyridine and pyridine-2,6-dicarbonyl dichloride in the presence of a base to give the corresponding compounds (Scheme 1).



Scheme 1. Synthesis of ligands ***L-CS, L-SN, L-SCS, L-SNS, L-SNS-O.***

The structure of the ligands, ***L-CS***, [24,25] ***L-SN***, [26] ***L-SCS***, [27] was confirmed by direct comparison of multinuclear NMR (^{1}H, $^{13}C\{^{1}H\}$), mass spectrometry and melting point data previously reported on the literature. The new ligands ***L-SNS*** and ***L-SNS-O*** were also fully characterized by the common analytical techniques quoted above. All the ligands display protonated molecular ion peaks in their electron impact mass spectra and signals for the thiomethylene protons (CH_2-S) in the range of δ 4.07-4.37 ppm in their ^{1}H NMR spectra, except for the ligand ***L-SNS-O***, which does not contain the thiomethyl group. The elemental analyses of the ligands ***L-SNS*** and ***L-SNS-O*** agree well with the proposed formulations. Further confirmation of the composition of ***L-SNS-O*** was achieved by single crystal X-ray determination.

2.1.1 Crystal structures of ***L-SNS-O***

The molecular structure of ***L-SNS-O*** with the atom labelling is shown in Figure 1, crystallographic data and details of structure determination are given in Table 1. The compound ***L-SNS-O*** crystallized in an orthorhombic system Cmc21. The asymmetric unit contains half of the molecule and the other half is generated by application of a mirror plane.

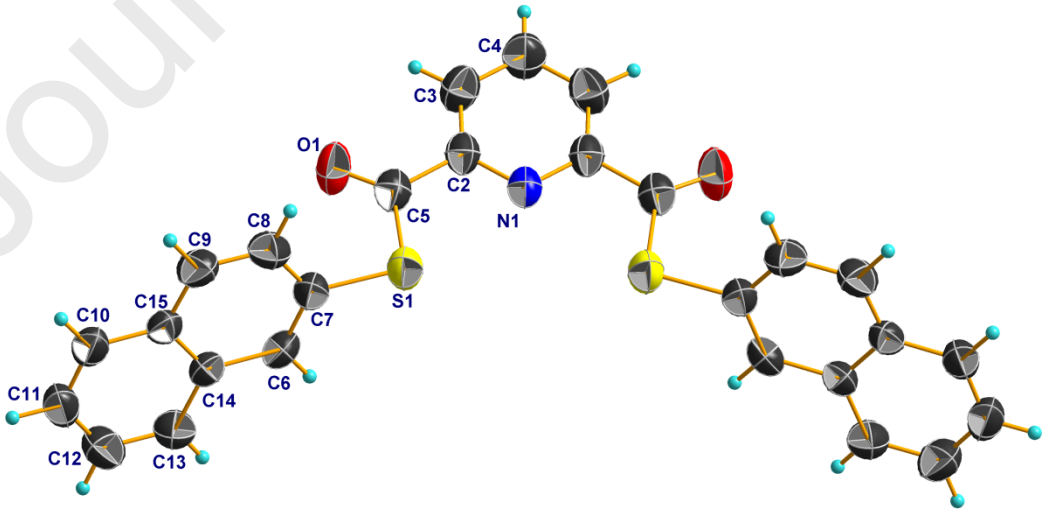


Figure 1. Molecular structure of ***L-SNS-O***. Thermal ellipsoids are drawn at 50% of probability level.

L-SCS-O presents a pyridine ring with two thioester groups in the 2 and 6 positions. The bond distances in C=O and C-S are 1.202(2) and 1.778(2) Å respectively, which are comparable with values reported for these types of bonds. Both pyridyl and thioester groups are found in the same plane. The planes of the pyridyl and naphthalene moieties are perpendicular with an angle of 69.92°. The crystal packing is dominated by the C-H--O=C hydrogen bonds and the C6C6--O1=C5 (d = 2.52 Å) and C12-H12--π ($d_{Cg\text{-}H}$= 2.98 Å) interactions generating a chain motif along the ***c*** axis (Figure 2). Those interactions that are extended along the **c** axis along with other C-H--- π interactions (Table 2) give place to the supramolecular array.

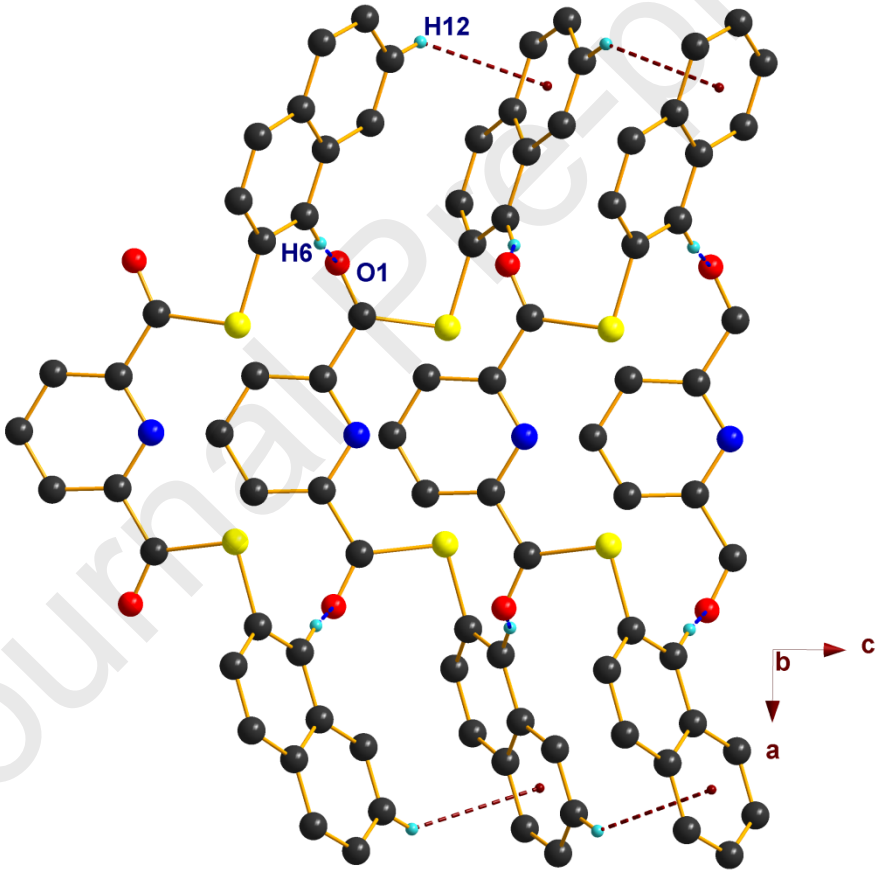


Figure 2. 1-D chain structure of ligand ***L-SNS-O*** formed by C-H---O=C, and C6-H---O=C interactions. Hydrogen atoms that do not participate in the interactions are omitted for clarity.

Table 1. Structural data and refinement for ligands ***L-SCS*** and ***L-SNS-O*** and palladium complexes ***Pd-CS*** and ***Pd-NS***.

	L-SNS-O	**Pd-CS**	**Pd-NS**
Formula	$C_{27}H_{17}NO_2S_2$	$C_{34}H_{26}Cl_2Pd_2S_2$ 2($CHCl_3$)	$C_{16}H_{13}Cl_2NPdS$
Formula weigh	451.54	1021.10	428.63
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	Cmc21	P21/c	C2/c
a (Å)	37.4321(15)	12.0476(5)	26.1557(10)
b (Å)	7.8319(3)	17.8986(7)	8.5932(3)
c (Å)	7.6128(3)	9.4460(4)	15.1931(6)
α (°)	90	90	90
β (°)	90	107.124(1)	98.493(1)
γ (°)	90	90	90
V ($Å^3$)	2231.80(15)	1946.59(14)	3377.4(2)
Z	4	2	8
δ calc (g/cm^3)	1.344	1.742	1.686
T (K)	298	298	298
R(%)		4.09	2.46

Table 2. Hydrogen bonding lengths in the crystal structures.

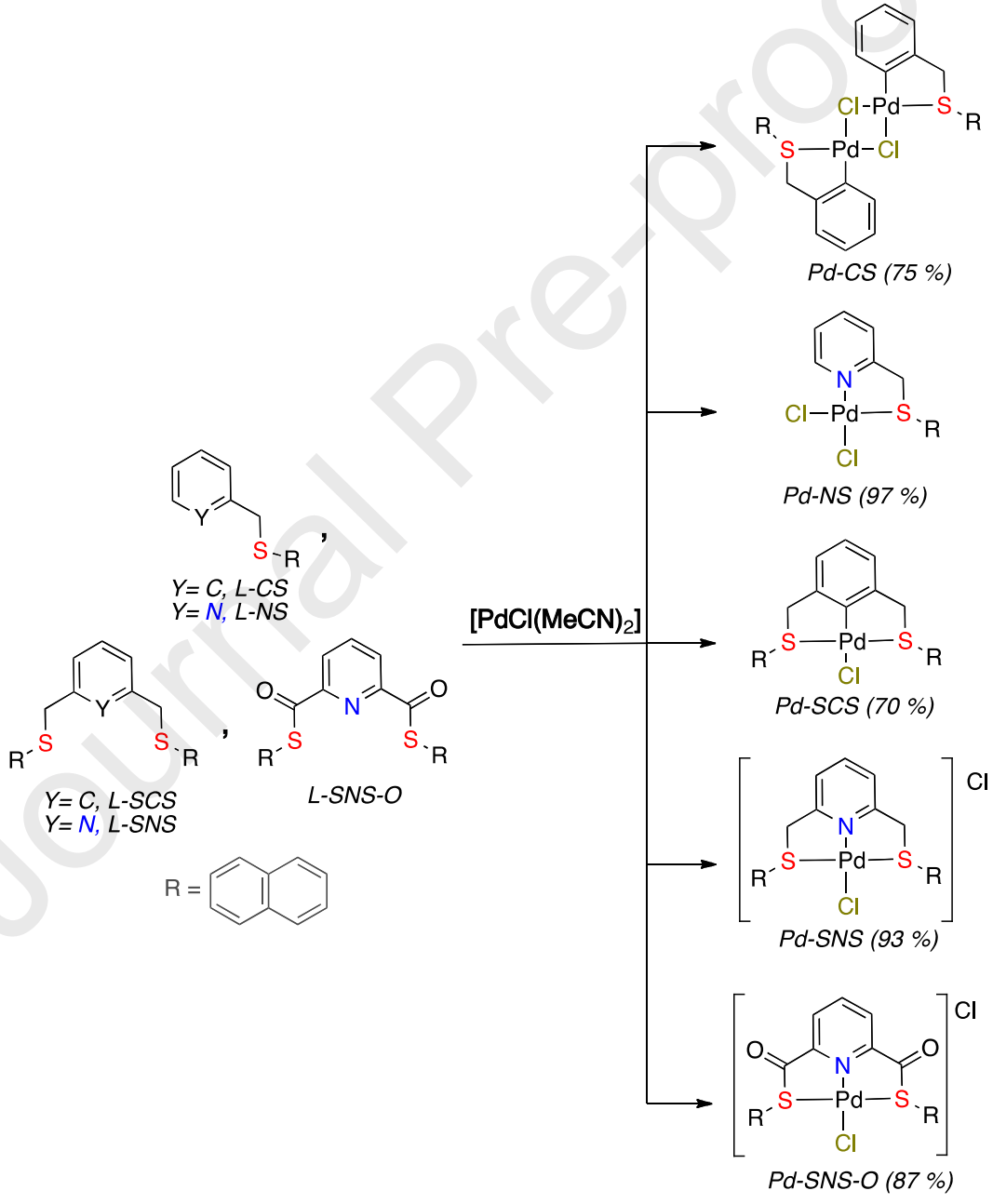
D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	∠DHA (°)	Symmetry code
L-SNS-O					
C6-H6···O1	0.93	2.52	3.352(2)	149	x, 1-y, ½+z
C8-H8···Cg1	0.93	2.87	3.538(2)	130	x, 2-y, -1/2+z
C12-H12···Cg2	0.93	2.98	3.705(2)	136	x, 1-y, ½+z
C9-H9···Cg2	0.93	2.83	3.652(2)	147	x, 2-y, -1/2+z
Pd-CS					
C7-H7A···Cg1	0.97	2.84	3.474(5)	124	x, ½-y, -1/2+z
Pd-NS					
C5-H5···Cl1	0.93	2.83	3.663(3)	150	x, 1+x, z
C7-H7A···Cl1	0.97	2.71	3.622(3)	156	x, -y, ½+z
C7-H7B···Cl2	0.97	2.78	3.590(3)	142	2-x, -y, -z

L-SNS-O**:** Cg1: C6,C7,C9,C15,C14; C10,C11,C12,C13,C14,C15. ***Pd-CS***: Cg1:C1-C6.

2.2 Synthesis and characterization of the Pd(II) complexes

Palladium complexes were synthesized *via* two different routes. First, the direct cyclopalladation of the ligands ***L-CS*** and ***L-SCS*** at the C2 position of the central phenyl

ring was achieved by refluxing equimolar amounts of ***L-CS*** or ***L-SCS*** and $[PdCl_2(MeCN)_2]$ in the presence of a base in acetonitrile for 24 h to afford the corresponding palladium complexes ***Pd-CS*** and ***Pd-SCS*** in good yields. Compound ***Pd-CS*** was obtained as a dimeric species. On the other hand, the coordination compounds ***Pd-NS***, ***Pd-SNS*** and ***Pd-SNS-O*** were synthesized in excellent yields by reacting the ligands, ***L-NS***, ***L-SNS*** and ***L-SNS-O***, with $[PdCl_2(MeCN)_2]$ in dichloromethane at room temperature for 2 h (Scheme 2).



Scheme 2. Synthesis of palladium complexes ***Pd-CS, Pd-SN, Pd-SCS, Pd-SNS, Pd-SNS-O.***

The formation of palladium complexes was fully confirmed using a combination of analytical techniques such as, NMR spectroscopy, mass spectrometry and elemental analysis. For instance, by comparing the ^{1}H NMR spectra of the ligands ***L-CS*** and ***L-SCS*** with those of the complexes ***Pd-CS*** and ***Pd-SCS***, it is possible to observe that one of the resonances of the aromatic protons (7.8-7.1 ppm) is absent in the latter, indicating the C-palladation of the phenyl ring has occurred. Additionally, the ^{1}H NMR spectra of all palladium complexes**,** except ***Pd-SCS-O***, show downfield shifted signals assigned to the thiomethylene (CH_2-S) protons due to the coordination of the ligand to the Pd center. Notably, the ^{1}H NMR spectrum of ***Pd-CS*** displays two broad singlets at 4.19 and 4.51 ppm attributed to the diastereotopic protons (-CH_2S), in contrast with the singlet observed in the free ligand (4.15 ppm), while the ^{1}H NMR spectra of the complexes ***Pd-NS***, ***Pd-SCS, Pd-SNS*** exhibit broad singlets assigned to -CH_2S at 4.73, 4.63 and 5.44 ppm respectively (δ in ppm for -CH_2S in the free ligands: ***L-NS****: 4.37,* ***L-SCS:*** 4.07 and ***L-SNS:*** 4.33). Additionally, the structure of ***Pd-CS*** and ***Pd-NS*** was fully authenticated by single-crystal X-ray diffraction analysis.

2.2.1 Crystal structures of ***Pd-SC*** *and* ***Pd-SN***

A perspective view of complex ***Pd-CS*** is given in Figure 3. Crystal and data collection details for the palladium complex ***Pd-CS*** are shown in Table 1. The crystal structure of ***Pd-CS*** belongs to the monoclinic system (P21/c). The asymmetric unit contains half of the molecule along with a chloroform molecule. The centrosymmetric structure of ***Pd-CS*** comprises two palladium centers in a distorted square planar geometry bridged through the chlorine atoms. Each palladium atom is coordinated to two bridging chlorides [$d_{Cl\text{-}Pd}$= 2.3625(13) and 2.4615(14) Å] as well as to the C [$d_{C\text{-}Pd}$= 1.985(5) Å] and S [$d_{S\text{-}Pd}$= 2.2404(13) Å] atoms of the ligand ***L-CS*** generating

palladacycles of five members. The supramolecular array is dominated by weak C-H--π interactions and van der Waals forces. The C7-H7A···π (d_{Cg-H}= 2.84 Å) interactions give place to a two-dimensional arrangement parallel to the ***bc*** plane illustrated in Figure 4. The solvent molecules are stabilized by free electron pair-π (C-Cl--π) interactions with distances of (3.639(3) Å for C16-Cl2···$Cg1_{(C1-C6)}$ and 3.591(3) Å for C16-Cl4···$Cg2_{(C11a,C12-C15,C15A)}$). These values are quite similar to other reported Cl--π interactions.

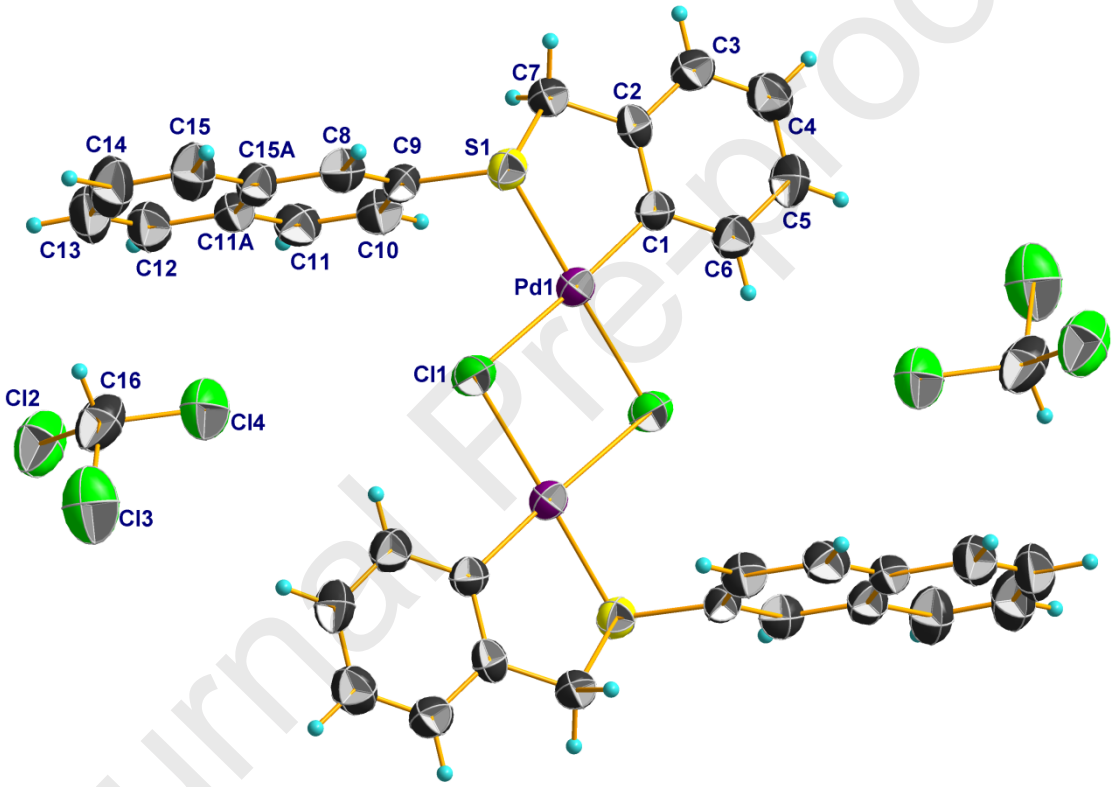


Figure 3. Molecular structure of complex ***Pd-CS***. Thermal ellipsoids are drawn at 50% probability level. *Selected bond lengths (Å):* Pd(1)-C(1) 1.985(5); Pd(1)-S(1) 2.2404(13); Pd(1)-Cl(1) 2.3624(13); Pd(1)-Cl(1)#1 2.4616(13); Cl(1)-Pd(1)#1 2.4616(13). *Selected bond angles (°):* C(1)-Pd(1)-S(1) 84.52(14); C(1)-Pd(1)-Cl(1) 96.51(14); S(1)-Pd(1)-Cl(1) 176.06(5); C(1)-Pd(1)-Cl(1)#1 177.21(14); S(1)-Pd(1)-Cl(1)#1 92.72(5); Cl(1)-Pd(1)-Cl(1)#1 86.23(5); Pd(1)-Cl(1)-Pd(1)#1 93.78(5)

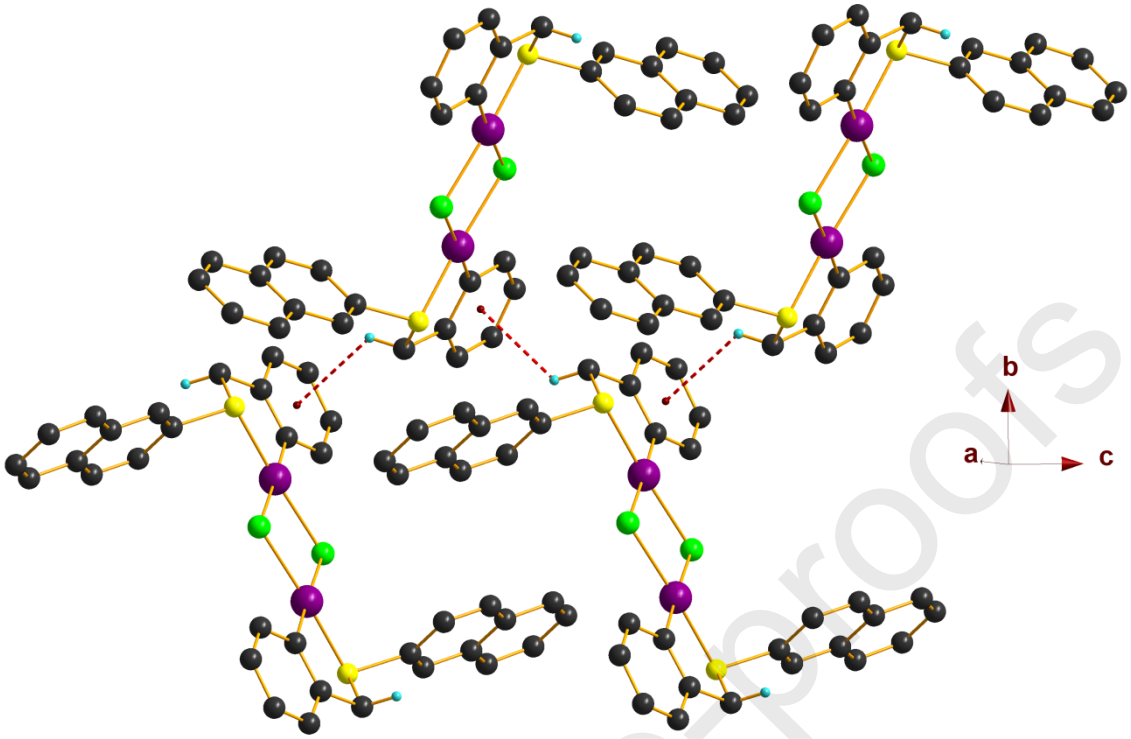


Figure 4. Fragment of the arrangement generated by C-H--π interactions in complex ***Pd-CS***. Hydrogen atoms not participating in the interactions are omitted for clarity.

The complex ***Pd-NS*** crystalized in a monoclinic system (C2/c) with one molecule of complex by asymmetric unit. Details of crystal data and refinements are shown in the table 1. Complex ***Pd-NS*** is a mononuclear species in which the Pd(II) atom is tetracoordinated to two chloride atoms ($d_{Cl\text{-}Pd}$= 2.2913(7) and 2.3134(8) Å) and to the bidentate ***L-NS*** ligand through the nitrogen ($d_{N\text{-}Pd}$= 2.0447(19) Å) and sulphur ($d_{S\text{-}Pd}$= 2.2621(8) Å) atoms forming a five-membered ring. The ***Pd-NS*** complex adopts a distorted square-planar geometry around the palladium center (Figure 5). Also, the structure is disordered in the naphthalene group generating two orientations in approximately 52:48 ratio. Only the major contributor is shown in Figure 5. The presence of highly polar bonds given by the chloride ions and the Pd allows the formation of intermolecular C-H--Cl-Pd hydrogen bonds, which are an important feature in the solid-state packing. Thus, the interactions C5-H5—Cl1 ($d_{H\text{-}Cl}$= 2.83 Å)

and C7-H7A—Cl1 ($d_{H\text{-}Cl}$= 2.71 Å) generate a two-dimensional arrangement parallel to the ***bc*** plane as shown in Figure 6. In addition, the Cl2 atom forms an interaction with the hydrogen of the methylene group (H7B) ($d_{Cl2\text{-}H\&B}$= 2.78 Å) giving a dimeric species (Figure 7).

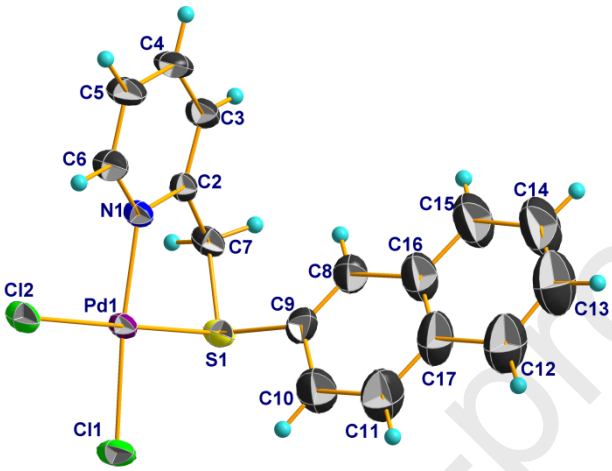


Figure 5. Molecular structure of complex P***d-NS***. Thermal ellipsoids are drawn at 40% probability level. The disorder in the naphthalene group is omitted for clarity. *Selected bond lengths (Å):* Pd(1)-N(1) 2.045(2); Pd(1)-S(1) 2.2621(7); Pd(1)-Cl(1) 2.2913(7); Pd(1)-Cl(2) 2.3134(7). *Selected bond angles (°):* N(1)-Pd(1)-S(1) 85.22(6); N(1)-Pd(1)-Cl(1) 174.39(6); S(1)-Pd(1)-Cl(1) 89.34(3); N(1)-Pd(1)-Cl(2) 94.20(6); S(1)-Pd(1)-Cl(2) 178.58(3); Cl(1)-Pd(1)-Cl(2) 91.27(3).

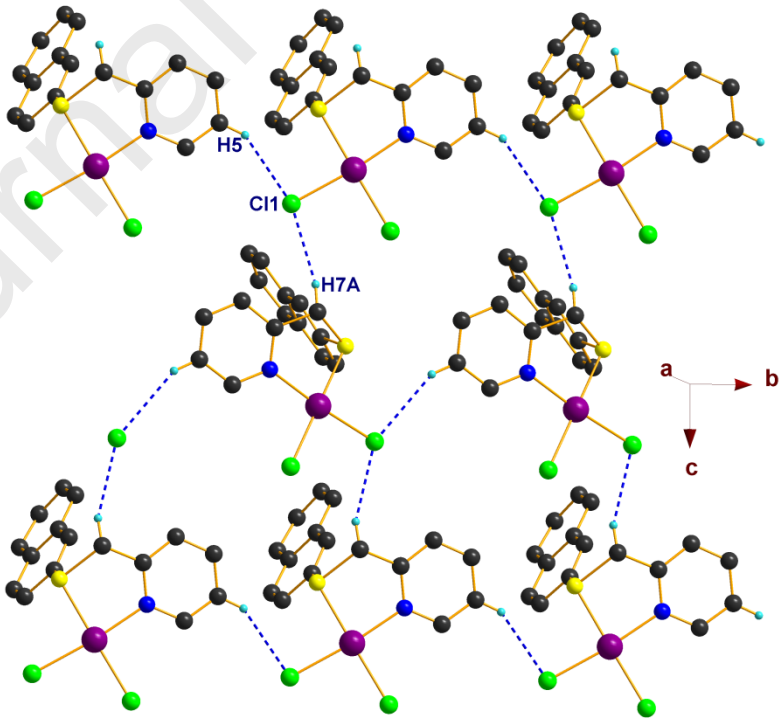


Figure 6. Fragment of the arrangement generated by C-H--Cl interactions in complex ***Pd-NS***. Hydrogen atoms not participating in the interactions are omitted for clarity.

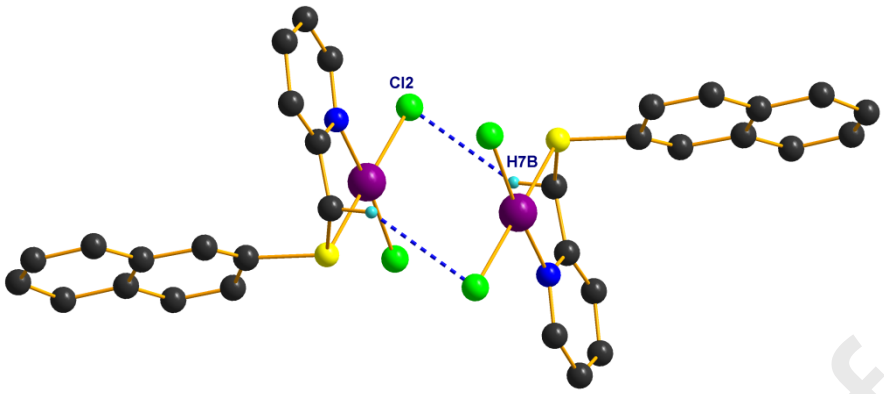


Figure 7. Dimeric arrangements of complex ***Pd-NS*** generated by the C-H7B--Cl2 interaction.

3. Catalytic activity

3.1 Suzuki-Miyaura cross-couplings

With the palladium complexes in hand, their activity was evaluated in Suzuki-Miyaura cross-couplings under the optimized reaction conditions previously established in our laboratory using analogous catalytic systems.[20] Initially, all palladium complexes were screened in the coupling reaction of bromobenzene with phenylboronic acid (selected as a model reaction), and the results are summarized in Table 3. Among all screened complexes, ***Pd-CS*** was by far the most efficient catalyst affording the coupled product 3 in 39 % (Table 3, entry 1). In general, palladacycle compounds ***Pd-CS*** and ***Pd-SCS*** showed better results than coordination compounds ***Pd-NS*** and ***Pd-SNS*** (Table 3, entries 1 and 3). While the ***Pd-SNS-O*** complex was not active in this coupling reaction under these conditions (Table 3, entry 5) probably due to decomposition, which was evidenced by the formation of palladium black. The ***Pd-SNS-O*** decomposition may be associated to a higher hemilabile character in the S-Pd coordination bond related to a decrease of the σ donor character of the S by the thiolate groups compared with the S-Pd coordination bond in the compounds bearing thioether groups.

Table 3. Suzuki-Miyaura couplings catalyzed by ***Pd-CS, Pd-SN, Pd-SCS, Pd-SNS, Pd-SNS-O***.

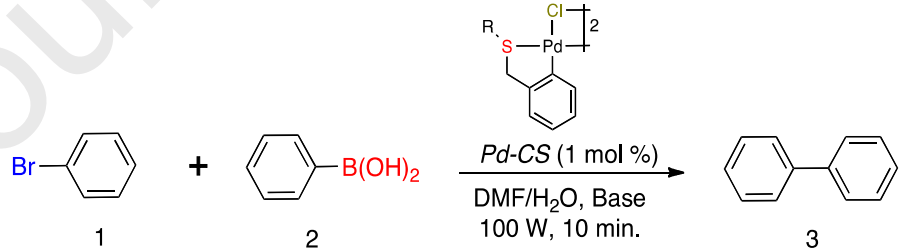
1 2 3

Entry	Pd-cat.	Pd (mol %)	Yield of 3 (%)
1	***Pd-CS***	1	39.2
2	***Pd-NS***	1	8.6
3	***Pd-SCS***	1	22.8
4	***Pd-SNS***	1	6.4
5	***Pd-SNS-O***	1	ND

Reaction conditions: [Pd] (0.01 mmol), bromobenzene (1 mmol), $PhB(OH)_2$ (1.2 mmol), Na_2CO_3 (2.4 mmol), DMF/H_20 4:1 (5 mL), 100 W, 10 min. Yields were determined by GC-MS analysis and are the average of two runs. ND: Not detected

As is well known, the Suzuki-Miyaura couplings are strongly dependent on the base used, thus, several bases were tested under the optimized reaction conditions using the best-found catalyst, ***Pd-CS*** (Table 4). The results obtained revealed that the inorganic bases are the most efficient and, as expected from our previous reports, the best yield was obtained when Na_2CO_3 was employed giving a conversion of 38.9 %. Organic bases such as Et_3N and DMAP were found not effective (Table 4, entries 7 and 8).

Table 4. Suzuki-Miyaura couplings catalyzed by ***Pd-CS*** using different bases.



1 2 3

Entry	Base	Yield of 3 (%)
1	K_2CO_3	16.1
2	Na_2CO_3	38.9
3	Na_3PO_4	10.3
4	Li_2CO_3	9.7

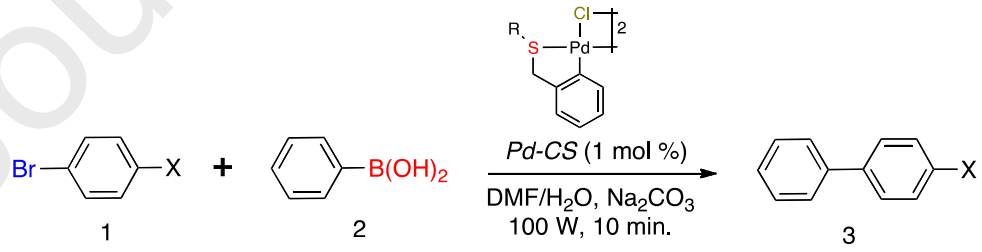
5	Cs_2CO_3	29.2
7	Et_3N	ND
8	DMAP	ND

Reaction conditions: [Pd] (0.01 mmol), bromobenzene (1 mmol), $PhB(OH)_2$ (1.2 mmol), base (2.4 mmol), DMF/H_20 4:1 (5 mL), 100 W, 10 min. Yields were determined by GC-MS analysis and are the average of two runs. ND: Not detected

*3.1.1 Scope of the **Pd-CS**-catalyzed Suzuki-Miyaura cross-coupling reactions.*

In order to examine the scope and limitations of the catalytic system, the optimized reaction conditions were applied to the coupling of phenylboronic acid with a series of substituted aryl bromides (Table 5). The results show a clear correlation between the yield of product and the nature of the aromatic substituent *para* to Br or its Hammett substituent constant. [28] Thus, excellent conversions were observed with electron-withdrawing (EWG) substituents with TONs up to 600 h^{-1} (Table 5, entries 5-8) and low conversions with electron-donating groups (EDG) (Table 5, entry 3). When 4-bromoaniline or 4-bromophenol were used no conversion was detected. This probably being due to coordination of this substrates to the metal center, hence hindering its function as catalyst.

Table 5. Suzuki-Miyaura couplings of $PhB(OH)_2$ and different *para* substituted bromobenzenes using ***Pd-CS*** as catalyst.



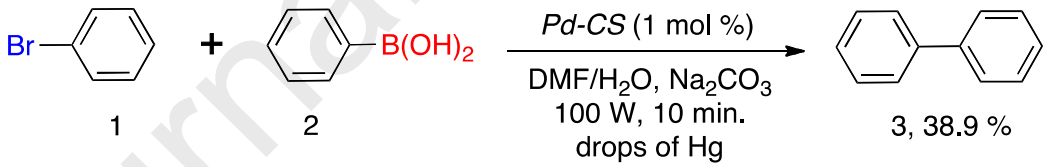
1 2 3

Entry	-X (1)	Yield of 3 (%)	TOF/h^{-1}
1	$-NH_2$	ND	---
2	-OH	ND	---
3	$-CH_3$	15.9	95
4	-H	39.2	227

5	-CHO	≥99	≥600
6	$-COCH_3$	≥99	≥600
7	-CN	≥99	≥600
8	$-NO_2$	≥99	≥600

Reaction conditions: [Pd] (0.01 mmol), *para* substituted aryl bromide (1 mmol), $PhB(OH)_2$ (1.2 mmol), Na_2CO_3 (2.4 mmol), DMF/H_20 4:1 (5 mL), 100 W, 10 min. Yields were determined by GC-MS analysis and are the average of two runs. ND: Not detected.

It is well known that some palladium complexes often decompose to Pd(0) nanoparticles during coupling reactions, and even a trace of such species can catalyze the reaction, thus palladium complexes merely serve as precatalyst. Hence, in order to investigate the probable involvement of Pd(0) nanoparticles during the Suzuki-Miyaura couplings catalyzed by ***Pd-CS***, the standard catalytic reaction was carried out adding drops of elemental mercury (Hg) wherein the yield of coupling product 3 obtained was unaltered (38.9 %) (Scheme 3). The presence of mercury did not suppress the C-C coupling suggesting that molecular palladium is responsible of the observed activity.



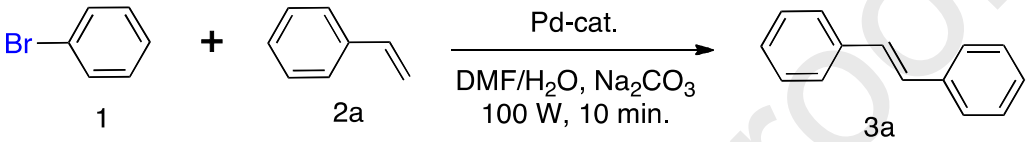
Scheme 3. Suzuki-Miyaura coupling between bromobenzene and phenylboronic acid ***Pd-CS***-catalyzed under the optimized reaction conditions in the presence of elemental mercury.

3.2 Mizoroki-Heck cross-couplings

The synthesized palladium complexes were also examined as catalysts in the Mizoroki-Heck cross-coupling reaction using microwave irradiation. Thus, the catalytic activity of palladacycles (***Pd-CS*** and ***Pd-SCS***) and coordination compounds (***Pd-NS*** and ***Pd-SNS***, ***Pd-SNS-O***) was examined in a model reaction between bromobenzene and

styrene (Table 6). As previously observed the palladacycles (entries 1 and 3) exhibited a better activity compared to the coordination compound ***Pd-NS*** (entry 2) with the usual, *trans*-selectivity of the Mizoroki-Heck couplings, observing only less of 1 % of the *cis* product. In this case, the complex ***Pd-SNS-O*** also decomposed before any coupled product could be formed and thus were not detected (Entry 5).

Table 6. *Mizoroki-Heck* couplings catalyzed by ***Pd-CS, Pd-SN, Pd-SCS, Pd-SNS, Pd-SNS-O***.

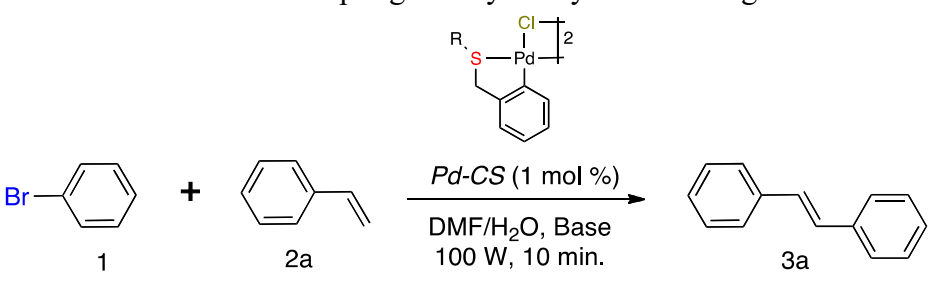


Entry	Pd-cat.	Pd (mol %)	Yield of 3A (%)
1	***Pd-CS***	1	28.5
2	***Pd-NS***	1	22.2
3	***Pd-SCS***	1	26.8
4	***Pd-SNS***	1	9.6
5	***Pd-SNS-O***	1	ND

Reaction conditions: [Pd] (0.01 mmol), bromobenzene (1 mmol), styrene (1.2 mmol), Na_2CO_3 (2.4 mmol), DMF/$H_2$0 4:1 (5 mL), 100 W, 10 min. Yields were determined by GC-MS analysis and are the average of two runs. ND: Not detected

The palladacycle ***Pd-CS*** proved again to be the best catalyst in the Mizoroki-Heck couplings. Thus, it was used to test the effect of the base in this reaction (Table 7). The use of Na_2CO_3 gave the highest conversion, and as it was the case for the Suzuki-Miyaura couplings, organic bases were not efficient in this process.

Table 7. Mizoroki-Heck couplings catalyzed by ***Pd-CS*** using different bases.



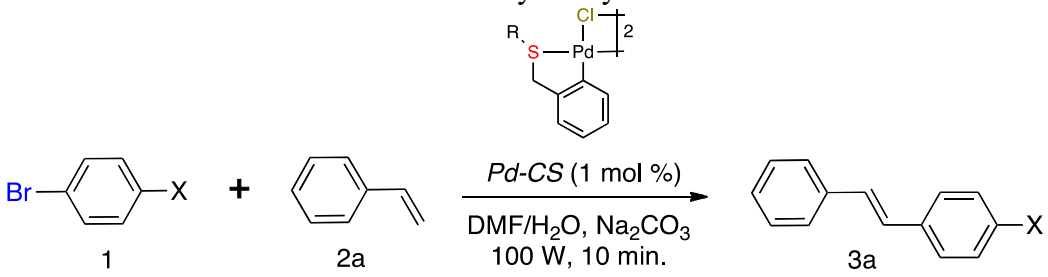
Entry	Base	Yield of 3a (%)
1	K_2CO_3	7.8
2	Na_2CO_3	28.5
3	Na_3PO_4	9.7
4	Li_2CO_3	2.6
5	Cs_2CO_3	7.2
7	Et_3N	ND
8	DMAP	ND

Reaction conditions: [Pd] (0.01 mmol), bromobenzene (1 mmol), styrene (1.2 mmol), base (2.4 mmol), DMF/$H_2$0 4:1 (5 mL), 100 W, 10 min. Yields were determined by GC-MS analysis and are the average of two runs. ND: Not detected

3.2.1 Scope of the Pd-CS-catalyzed Mizoroki-Heck couplings

Under the optimized conditions, the catalytic activity of ***Pd-CS*** was assessed in Mizoroki-Heck couplings using styrene and different *para* substituted aryl bromides. As noticed in the Suzuki-Miyaura couplings, the catalytic activity depends on the bromobenzene substituents. In this regard, the results presented in Table 8 exhibit a direct correlation between the yield to products and the nature of the aromatic substituent *para* to Br, or its Hammett substituent parameter.[28] The conversions in the Mizoroki-Heck couplings were moderate with electron-withdrawing groups (entries 5-8) and lower conversions were obtained with aryl bromides having electron-donating groups (entries 3 and 4) with a remarkable *trans*-selectivity (>1% of *cis*-product was observed in all the cases). On the other hand, the bromobenzenes including *para* -NH_2 or OH groups were inactive under these reaction conditions (entries 1 and 2) once again very likely due to coordination to the Pd center. These results suggest that the rate-determining step for both Suzuki-Miyaura and Mizoroki-Heck couplings is the oxidative addition of the aryl bromide to the metal center, which could be facilitated with electron-withdrawing groups on the aromatic ring.

Table 8. Mizoroki-Heck couplings of styrene and different *para* substituted aryl bromides catalyzed by ***Pd-CS***.



Entry	-X (1)	Yield of 3a (%)	TOF/h^{-1}
1	$-NH_2$	ND	---
2	-OH	ND	---
3	$-CH_3$	3.3	20
4	-H	28.5	155
5	-CHO	62.5	375
6	$COCH_3$	55.1	331
7	-CN	61.8	371
8	$-NO_2$	63.8	383

Reaction conditions: [Pd] (0.01 mmol), *para* substituted aryl bromide (1 mmol), styrene (1.2 mmol), Na_2CO_3 (2.4 mmol), DMF/$H_2$0 4:1 (5 mL), 100 W, 10 min. Yields were determined by GC-MS analysis and are the average of two runs. ND: Not detected

Finally, with exception of complex ***Pd-SNS-O***, in all systems investigated in the Mizoroki-Heck couplings, no decomposition of the complexes or formation of metallic palladium was observed. And, as it was the case in the Suzuki-Miyaura couplings the catalytic performance of ***Pd-CS*** was not affected by the presence of elemental mercury.

4. Conclusions

With the aim to provide air-, water-, and thermally stable catalytic systems a series of coordination (***Pd-NS***, ***Pd-SNS***, ***Pd-SNS-O***) and organometallic (***Pd-CS***, ***Pd-SCS***) Pd(II) complexes bearing thioether and thiolato groups were successfully synthesized in high yields and fully characterized. These reactions can be performed in air, rendering these systems highly attractive for synthetic purposes. With the

complexes on hand, their microwave assisted catalytic activity was examined in Suzuki-Miyaura and Mizoroki-Heck cross-coupling reactions. Apart from complex ***Pd-SNS-O*** that decomposed under these reaction conditions, all other complexes catalyze these reactions leading to moderate to excellent conversions with TONs up to 600 h^{-1} and 383 h^{-1} for Suzuki-Miyaura and Mizoroki-Heck couplings, respectively. Remarkably, in both cases the use of microwave irradiation notably reduced reaction times for the C-C couplings showing a clear advantage over the conventional heating.

5. Experimental section

Unless otherwise noted, all experiments were carried out in atmospheric conditions. Solvents were purchased from Aldrich and dried under standard procedures. THF was dried and distilled from dark-purple solutions of sodium/ benzophenone ketyl radical. CH_2Cl_2 was dried over CaH_2. All other chemicals and filter aids were reagent grade and were used as received. Compound $[PdCl_2(MeCN)_2]$ (**1)** were prepared according to the reported procedure. [29] Column chromatography was performed on silica gel (Merck, 230-700 mesh). Melting points were determined on a MEL-TEMP II in an open capillary tube. Elemental analyses were performed in a Thermo Scientific Flash 2000 elemental analyzer. The X-ray crystallographic analyses were made on a Bruker P4 diffractometer. The ^{1}H, and $^{13}C\{^{1}H\}$ Nuclear Magnetic Resonance (NMR) was performed on a JEOL 300 MHz equipment, using TMS or residual protio solvents as internal standard. The deuterated solvent used was $CDCl_3$; chemical shifts (d) are quoted in ppm and coupling constants in Hz.; to indicate the multiplicity of the signals of ^{1}H NMR spectra, the following abbreviations have been used: (s) singlet, (d) doublet, (t) triplet, (m) multiplet, (dd) double doublet. Catalysis experiments were performed in a CEM Discover reactor connected to a CEM Explorer robotic system. Catalysis products

were quantified with a GC-MS Agilent 6890N chromatograph equipped with a 30 m DB-1MS Agilent capillary column, coupled to an Agilent Technologies 5973 Mass Spectrometer equipped with an Inert Mass Selective Detector. Mass spectrometry of pure compounds were performed on a Thermo-Electron DFS (EI-MS), on a JEOL JMS AX505HA (FAB-MS) Mass measurements in FAB^+ were performed at a resolution of 3000 using magnetic field scans and the matrix ions as the reference material or, alternatively, by electric field scans with the sample peak bracketed by two (polyethylene glycol or cesium iodide) reference ions. MS-Electrospray determinations were recorded on a Bruker Daltonics-Esquire 3000 plus Electrospray Mass Spectrometer.

*5.1. Preparation of ligands (**L-CS, L-SN, L-SCS, L-SNS, L-SNS-O**)*

5.1.1. General procedure:

Ligands were prepared by slight modifications of procedures described in the literature. [20, 23, 30]. A solution of naphthalene-2-thiol (RSH) (ca. 1 mmol) and NaH (1.1 equivalents) in 15 mL of dry THF was stirred for 5 min at room temperature. Then, 1 equivalent of (bromomethyl)benzene (***L-CS***), 2-(bromomethyl)pyridine (***L-SN***) or 0.5 equivalent 1,3-bis(bromomethyl)benzene (***L-SCS***), 2,6-bis(bromomethyl)pyridine (***L-SNS***), pyridine-2,6-dicarbonyl dichloride (***L-SNS-O***) derivatives was added. The reaction mixture was stirred at room temperature for 24 h. After this time, 10 mL of water were added to the reaction mixture followed by extraction (2 X 30 mL) with dichloromethane. The resulting solution was evaporated to dryness and the residues were purified by column chromatography using hexane/ethyl acetate 90/10 as eluent.

*5.1.1.1. Synthesis of ligand **L-CS***

The ligand was prepared and purified using the general procedure described above; naphthalene-2-thiol (RSH) (160 mg, 1 mmol); NaH (28 mg, 1.1 mmol) and (bromomethyl)benzene (170 mg, 1 mmol). Yield 90% (225 mg). White solid, melting point: 70-72°C. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.62-7.73 (m, 4H, naph), 7.31-7.41 (m, 3H, bz, naph), 7.14-7.27 (m, 5H, bz, naph), 4.15 (s, 2H, CH_2). **^{13}C{^{1}H} NMR** ($CDCl_3$, 75 MHz): δ 137.3 (bz)., 134.2 (naph), 133.4 (naph), 132.5 (naph), 129.0 (naph), 128.8 (naph), 128.5 (bz), 127.8 (naph), 127.7 (Bz), 127.5 (naph), 126.7 (naph), 126.5 (naph), 126.2 (bz), 125.6 (naph), 38.9 (CH_2). **EI-MS** positive ion; Calc. 250.36 g/mol; Found. 250 m/z $[M]^+$.

*5.1.1.2. Synthesis of ligand **L-SN***

The ligand was prepared and purified using the general procedure described above. naphthalene-2-thiol (RSH) (160 mg, 1 mmol); NaH (28 mg, 1.1 mmol) and 2-(bromomethyl)pyridine (172 mg, 1 mmol). Yield 90% (155 mg). White solid, melting point: 53-55 °C. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 8.47 (d, $^{3}J_{HH}$= 4.2 Hz, 1H, py), 7.56-7.70 (m, 5H, py, naph), 7.32-7.40 (m, 4H, py, naph), 7.14 (t, $^{3}J_{HH}$= 6.9 Hz, 1H, naph), 4.37 (s, 2H, CH_2), **^{13}C{^{1}H} NMR** ($CDCl_3$, 75 MHz): δ 157.4 (py), 149.0 (py), 137.0 (py), 133.7 (naph), 133.2 (naph), 131.9 (naph), 128.4 (naph), 127.7 (naph), 127.6 (naph), 127.5 (naph), 127.2 (naph), 126.5 (naph), 125.8 (naph), 123.1 (py), 122.2 (py), 46.6 (CH_2), **EI-MS** positive ion; Calc. 251.35 g/mol; Found. 251 m/z $[M]^+$.

*5.1.1.3. Synthesis of ligand **L-SCS***

The ligand was prepared and purified using the general procedure described above. naphthalene-2-thiol (RSH) (160 mg, 1 mmol); NaH (28 mg, 1.1 mmol) and 1,3-bis(bromomethyl)benzene (132 mg, 0.5 mmol). Yield 95 % (400 mg). White solid,

melting point: 116-118°C. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.67-7.70 (m, 2H, naph), 7.58-7.62 (m, 6H, naph), 7.34-7.36 (m, 4H, naph), 7.26 (d, $^{3}J_{HH}$ = *6 Hz*, 2H, bz), 7.24 (s, 1H, bz) , 7.10 (s, 3H, bz, naph), 4.07 (s, 4H, CH_2). **^{13}C{^{1}H} NMR** ($CDCl_3$, 75 MHz): δ 137.7 (bz), 133.74 (naph), 133.71 (naph), 131.9 (naph), 129.4 (bz), 128.7 (naph), 128.35 (naph), 127.85 (naph), 127.81 (bz), 127.78 (naph), 127.71 (bz), 126.4 (naph), 125.7 (naph), 38.8 (CH_2). **EI-MS** positive ion: Calc. 422.6 g/mol; Found. 422 m/z $[M]^+$.

*5.1.1.4. Synthesis of ligand **L-SNS***

The ligand was prepared and purified using the general procedure described above. naphthalene-2-thiol (RSH) (160 mg, 1 mmol); NaH (28 mg, 1.1 mmol) and 2,6-bis(bromomethyl)pyridine (133 mg, 0.5 mmol). Yield 92 % (390 mg). White solid, melting point: 84-86°C. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.66-768 (m, 4H, naph), 7.56-7.61 (m, 4H, naph), 7.41 (t, $^{3}J_{HH}$= 7.8 Hz, 1H, py.), 7.30-7.36 (m, 6H, naph), 7.11 (d, $^{3}J_{HH}$ = 7.8 Hz, py.), 4.33 (s, 4H, CH_2). **^{13}C{^{1}H} NMR** ($CDCl_3$, 75 MHz): δ 156.7 (py), 138.5 (naph), 133.6 (py), 132.6 (naph), 131.9 (naph), 128.5 (naph.), 127.9 (naph.), 127.6 (naph.), 127.5 (naph), 127.3 (naph), 126.7 (naph), 125.9 (naph), 121.9 (py.), 39.1 (CH_2). **EI-MS** positive ion: Calc. 423.59 g/mol; Found. 423 m/z $[M]^+$. **Anal.** Calcd for $C_{27}H_{21}NS_2$ (423.59 g/mol): C, 76.56; H, 5.00; N, 3.31. Found: C, 76.49; H, 5.04; N, 3.29.

*5.1.1.5. Synthesis of ligand **L-SNS-O***

The ligand was prepared and purified using the general procedure described above. naphthalene-2-thiol (RSH) (160 mg, 1 mmol); NaH (28 mg, 1.1 mmol) and pyridine-2,6-dicarbonyl dichloride (102 mg, 0.5 mmol). Yield 93 % (420 mg). White solid, melting point: 168-170°C. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 8.12 (d, $^{3}J_{HH}$= 7.5 Hz,

2H, py), 8.05 (s, 2H, naph), 7.99 (t, $^{3}J_{HH}$= 7.8 Hz, 1H, py), 7.87 (d, $^{3}J_{HH}$= 8.7 Hz, 2H, naph), 7.79-7.84 (s, 4H, naph), 7.65 (d, $^{3}J_{HH}$= 8.7 Hz, 2H, naph), 7.44-7.51 (s, 4H, naph). **^{13}C{^{1}H} NMR** ($CDCl_3$, 75 MHz): 191.4 (C=O), 150.9 (py), 139.2 (py), 134.9 (naph), 133.7 (naph), 133.5 (naph), 131.2 (naph), 128.9 (naph), 128.0 (naph), 127.9 (naph), 127.2(naph), 126.6(naph), 125.2 (naph), 124.5 (py). **EI-MS** positive ion: Calc. 451.56 g/mol; Found. 451 m/z $[M]^+$. **Anal.** Calcd for $C_{27}H_{17}NO_2S_2$ (451.56 g/mol): C, 71.82; H, 3.79; N, 3.10. Found: C, 71.94; H, 3.75; N, 3.12.

*5.2. Synthesis of palladium complexes (**Pd-CS**, **Pd-NS**, **Pd-SCS**, **Pd-SNS**, **Pd-SNS-O**)*

*5.2.1 Organometallic compounds (**Pd-CS** and **Pd-SCS**). General procedure A.*

$[PdCl_2(MeCN)_2]$ (0.1 mmol) was added to a solution of the corresponding ligand (***L-CS*** or ***L-SCS***) (0.1 mmol) and sodium acetate (0.11 mmol) in acetonitrile (50 mL). The reaction mixture was stirred and refluxed for 48 h. After this time, the solution was filtered, and the resulting solution evaporated to dryness. The residues were purified by column chromatography using hexane/ethyl acetate 70:30 as eluent leading to the pure compounds.

*5.2.1.1 Synthesis of complex **Pd-CS***

The complex was prepared using the *general procedure A* for the organometallic palladium complexes (5.2.1). $[PdCl_2(MeCN)_2]$ (26 mg, 0.1 mmol), ligand ***L-CS*** (25 mg, 0.1 mmol) and sodium acetate (65 mg, 0.11 mmol) in acetonitrile (50 mL), refluxed for 48 h. Yield 75 % (58 mg). Red solid, melting point: 140-141°C. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 8.26 (s, 2H, naph), 7.66-7.88 (m, 8H, naph), 7.38-7.52 (m, 4H, Naf.), 7.23 (s, 2H, Ar.), 6.81-6.93 (m, 6H, Ar.), 4.51 (s, 2H, CH_2), 4.19 (s, 2H, CH_2). **^{13}C{^{1}H} NMR** ($CDCl_3$, 75 MHz)**:** 171.2 (bz)**,** 148.5 (bz), 147.1 (bz), 135.8 (naph), 133.6 (naph), 133.0

(naph), 132.2 (naph), 129.7 (naph), 128.6 (naph), 128.4 (bz), 128.3 (bz), 127.8 (naph), 127.2 (naph), 126.2 (naph), 125.3 (naph), 123.2 (naph), 50.9 (CH_2), **ESI-MS** positive ion: Calc. 782.45g/mol; Found. 784 m/z $[M+H]^+$. **Anal.** Calcd for $C_{34}H_{26}Cl_2Pd_2S_2$ (782.45g/mol): C, 52.19; H, 3.35. Found: C, 52.15; H, 3.31.

*5.2.1.2. Synthesis of complex **Pd-SCS***

The complex was prepared using the *general procedure A* for organometallic palladium complexes (5.2.1). $[PdCl_2(MeCN)_2]$ (26 mg, 0.1 mmol), ligand ***L-SCS*** (42 mg, 0.1 mmol) and sodium acetate (65 mg, 0.11 mmol) in acetonitrile (50 mL), refluxed for 48 h. Yield 70% (40 mg). Yellow solid, melting point: 188-190°C. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 8.24 (s, 2H, naph), 7.70-7.83 (m, 8H, naph), 7.40-7.47 (m, 4H, naph), 6.98 (s, 1H, bz), 6.95 (s, 2H, bz), 4.63 (s, 4H, CH_2). **^{13}C{^{1}H} NMR** ($CDCl_3$, 75 MHz)**:** δ 161.4 (bz), 149.5 (naph), 133.4 (naph), 133.2 (bz), 131.2 (naph), 129.8 (naph), 129.2 (naph)**,** 128.2 (naph), 127.6 (bz), 127.1 (naph), 125 (naph), 122.3 (naph), 51.7 (CH_2). **FAB-MS** positive ion: Calc. 563.47 g/mol; Found. 527 m/z $[M-Cl]^+$. **Anal.** Calcd for $C_{28}H_{21}ClPdS_2$ (563.47 g/mol): C, 59.68; H, 3.76. Found: C, 59.63; H, 3.70.

*5.2.2 Coordination compounds (**Pd-NS**, **Pd-SNS** and **Pd-SNS-**0). General procedure B:*

To a solution of the corresponding ligand (***L-SN***, ***L-SNS***, ***L-SNS-O***) (ca. 0.1 mmol) in dichloromethane (30 mL) was added 1 equivalent of $[PdCl_2(MeCN)_2]$ and the resulting solution was stirred for 2 h at room temperature. After this time, the solution was filtered and the resulting solid was washed with a mixture of hexane/ethyl acetate 7:3 (2 x 10 mL) (***Pd-SN***, ***Pd-SNS***) or dichloromethane (***Pd-SNS-O***) yielding the pure palladium complexes.

*5.2.2.1 Synthesis of complex **Pd-NS***

The complex was prepared using the *general procedure B* for coordination palladium complexes (5.2.2). $[PdCl_2(MeCN)_2]$ (26 mg, 0.1 mmol) and ligand ***L-NS*** (25 mg, 0.1 mmol) in CH_2Cl_2 (30 mL), room temperature for 48 h. Yield 97 % (41 mg). Yellow solid, decomposed at: 220°C. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 9.24 (d, $^3J_{HH}$= 6 Hz, 1H, py), 8.33 (s, 1H, naph), 7.88-7.94 (m, 1H, py), 7.75-7.85 (m, 4H, naph), 7.64 (d, *J* = 7.8 Hz, 1H, Py), 7.47-7.56 (m, 2H, naph), 7.39-7.43 (m, 1H, py.), 5.13 (d, $^2J_{HH}$ =18 Hz, 1H, CH_2), 4.73 (d, 1H, $^2J_{HH}$= 15 Hz, CH_2.). **^{13}C{^{1}H} NMR** ($CDCl_3$, 75 MHz)**:** δ 162.0 (py), 151.6 (py), 139.7 (naph), 132.9 (naph), 132.4 (naph), 130.4 (py), 129.5 (py), 127.7 (naph), 127.5 (naph), 127.4 (naph), 127.2 (Naf.), 125.9 (Py.), 125.6 (naph), 124 (naph), 123.5 (naph), 45.6 (CH_2). **ESI-MS** positive ion: Calc. 428.67 g/mol; Found. 468 m/z $[M+K]^+$. **Anal.** Calcd for $C_{16}H_{13}Cl_2NPdS_2$ (428.67 g/mol): C, 44.83; H, 3.26; N, 3.27. Found: C, 44.93; H, 3.36; N, 3.21.

*5.2.2.2. Synthesis of complex **Pd-SNS***

The complex was prepared using the *general procedure B* for coordination palladium complexes (5.2.2). $[PdCl_2(MeCN)_2]$ (26 mg, 0.1 mmol) and ligand ***L-SNS*** (42 mg, 0.1 mmol) in CH_2Cl_2 (30 mL), room temperature for 48 h. Yield 93 % (56 mg). Orange solid, melting point: 200°C. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 8.40 (s, 2H, naph), 8.09 (t, $^3J_{HH}$= 7.8 Hz, 1H, py.), 7.78-7.93 (m, 10H, py, naph), 7.52-7.62 (m, 4H, naph), 5.44 (s, 4H, CH_2). **^{13}C{^{1}H} NMR** ($CDCl_3$, 75 MHz)**:** δ 167.6 (py), 145.9 (py), 138.3 (naph), 137.9 (naph), 135.6 (naph), 135.2 (naph), 133.4 (naph), 133.1 (naph), 132.8 (naph), 132.7 (naph), 131.3 (naph), 130.8 (naph), 128.4 (py), 54.5 (CH_2). **ESI-MS** positive ion: Calc. 600.92 g/mol; Found. 565 m/z $[M-Cl]^+$. **Anal.** Calcd for

$C_{27}H_{21}Cl_2NPdS_2$ (600.92 g/mol): C, 54.37; H, 3.52; N, 2.33. Found: C, 54.35; H, 3.56; N, 2.37.

*5.2.2.3. Synthesis of complex **Pd-SNS-O***

The complex was prepared using the *general procedure B* for coordination palladium complexes (5.2.2). $[PdCl_2(MeCN)_2]$ (26 mg, 0.1 mmol) and ligand ***L-SNS-O*** (45 mg, 0.1 mmol) in CH_2Cl_2 (30 mL), room temperature for 48 h. Yield 87 % (55 mg). Red solid, decomposed at: 200 °C. **^{1}H NMR** (CD_3CO, 300 MHz): δ 8.47 (s, 2H, py), 8.46 (s, 2H, naph), 8.44 (s, 8H, py, naph), 8.39 (s, 1H, naph), 8.34 (m, 4H, naph). **^{13}C{^{1}H} NMR** ($CDCl_3$, 75 MHz)**:** δ 190.2 (C=O), 149.2 (py), 139.8 (py), 134.1 (naph), 133.6 (naph), 133.5 (naph), 130.9 (naph), 128.2 (naph), 127.1 (naph), 127.5 (naph), 126.9 (naph), 126.5 (naph), 125.0 (naph), 123.9 (py). **ESI-MS** positive ion: Calc. 628.89 g/mol; Found. 593 m/z $[M\text{-}Cl]^+$. **Anal.** Calcd for $C_{27}H_{17}Cl_2NO_2PdS_2$ (628.89 g/mol): C, 54.65; H, 3.75; N, 2.36. Found: C, 54.56; H, 3.74; N, 2.38.

5.3. Catalytic experiments

5.3.1 General procedure for Suzuki-Miyaura cross-coupling

Suzuki-Miyaura cross-couplings were carried out in 10 mL reaction tubes suitable for using in microwave apparatus equipped with an inner magnetic stirring bar. 5 mL of a DMF/H_2O 4:1 solution containing Pd-cat. (0.01 mmol), aryl bromide (1 mmol), $PhB(OH)_2$ (1.2 mmol) and a base (2.4 mmol) was stirred and heated in a microwave reactor at 100 ^oC and 100 W for 10 min. After the prescribed reaction time, the mixture was cooled to room temperature, extracted with CH_2Cl_2 (3 X 3 mL) and dried with anhydrous Na_2SO_4, filtered through celite and analyzed by GC-MS.

5.3.2 General procedure for Mizoroki-Heck cross-coupling

A 10 mL reaction tube designed for the monomode microwave equipped with an inner magnetic stirring bar was loaded with Pd-cat. (0.01 mmol), aryl halide (1 mmol), styrene (1.2 mmol), base (2.4 mmol) and 5 mL of a DMF/H_2O 4:1 mixture, and then, the reaction mixture was magnetically stirred and heated in a microwave reactor at 100 ^oC and 100 W for 10 min. After the prescribed reaction time, the mixture was cooled to room temperature. After the prescribed reaction time, the mixture was cooled to room temperature, extracted with CH_2Cl_2 (3 X 3 mL) and dried with anhydrous Na_2SO_4, filtered through celite and analyzed by GC-MS.

*5.4. Data collection and refinement for compounds **L-SNS-O**, **Pd-CS** and **Pd-NS**.*

Crystal suitable of ***L-SNS-O**, **Pd-CS** and **Pd-NS*** were mounted on glass fibers, then placed on a Bruker Smart Apex II diffractometer with Mo-target X-ray source (λ=0.71073 Å). The detector was placed at 5.0 cm from the crystal frames were collected with a scan width of 0.5 in ω and exposure time of 5 s/frame. 8365, 15414 and 9954 reflections for ***L-SNS-O**, **Pd-CS** and **Pd-NS*** respectively were collected and integrated with the Bruker SAINT software package[31] using a narrow-frame integration algorithm. Systematic absences and intensity statistics were used in monoclinic system and P2(1)/c space group for **Pd-CS**, Orthorhombic system and Cmc21 space group for ***L-SNS-O*** and monoclinic system C2/c for ***Pd-NS***. The structures were solved using Patterson methods using SHELXS-2018 program.[31] The remaining atoms were located via a few cycles of least squares refinements and difference Fourier maps. Hydrogen atoms were input at calculated positions and allowed to ride on the atoms to which they are attached. Thermal parameters were refined for all hydrogen atoms using a Ueq=1.2 Å. The final cycle of refinement was

carried out on all non-zero data using SHELXL-2014/7 [32]. Absorption correction was applied using SADABS program.[33]

Supplementary information

Supplementary data for compounds ***L-SNS-O***, ***Pd-CS*** *and* ***Pd-NS*** have been deposited at the Cambridge Crystallographic Data Centre. Copies of this information are available free of charge on request from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk) quoting the deposition numbers CCDC 1971695-1971697.

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Synthesis and Characterization of Pd(II) Complexes Bearing NS, CS, SNS and SCS Ligands. Evaluation of Their Microwave Assisted Catalytic Activity in C-C Coupling Reactions

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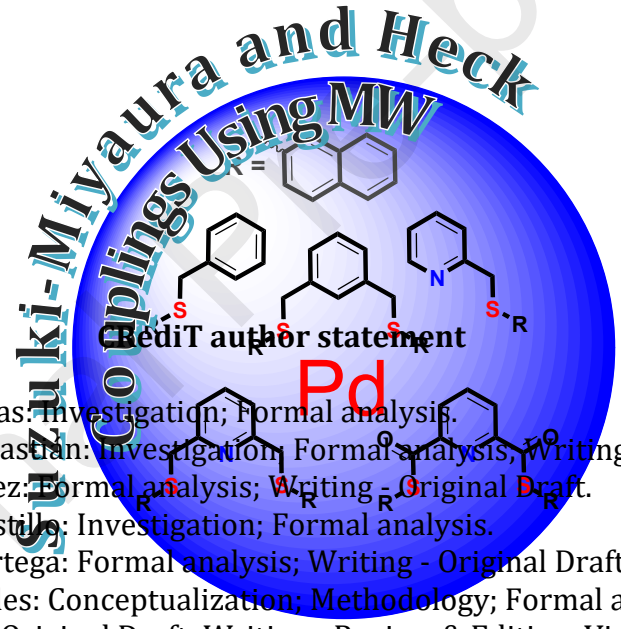

CRediT author statement

G. Gabriel Flores-Rojas: Investigation; Formal analysis.
Lucero González-Sebastián: Investigation; Formal analysis; Writing - Original Draft.
Reyna Reyes-Martínez: Formal analysis; Writing - Original Draft.
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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

N/A

Highlights

- A series of potentially chelate thioether based ligands were synthesized in a facile manner.
- Air stable coordination and organometallic complexes derived of these ligands were obtained in good yields.
- These complexes serve as efficient catalysts in the Suzuki-Miyaura and Heck couplings of a series of bromobenzenes.

Graphical Abstract-Pictogram

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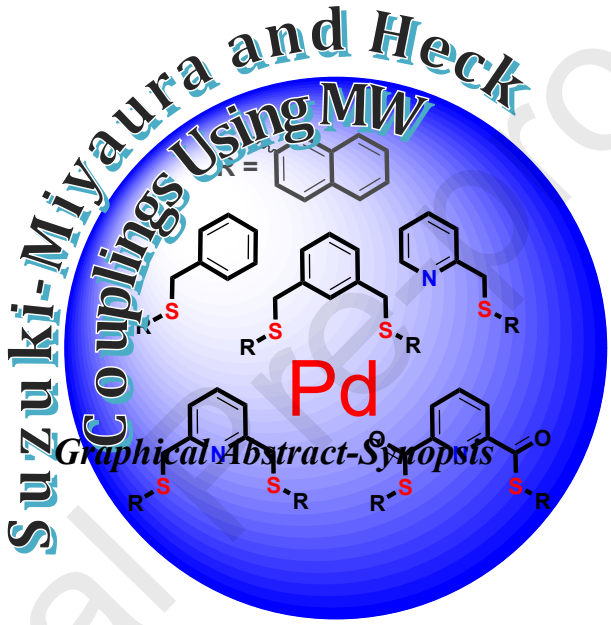

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Abstract

A series of coordination (***Pd-NS***, ***Pd-SNS***, ***Pd-SNS-O***) and organometallic (***Pd-C*** and ***Pd-SCS***) Pd(II) complexes supported by bidentate and tridentate ligands featuring sulphur moieties have been prepared. All ligands and their palladium complexes were fully characterized by various analytical techniques, including the unequivocal determination of the solid-state structures of the ligand ***L-SNS-O*** and the ***Pd-CS*** and ***Pd-NS*** complexes by single crystal X-ray diffraction analysis. Complexes ***Pd-NS***, ***Pd-SNS***, ***Pd-CS***, ***Pd-SCS*** containing thioether groups were used as efficient catalysts in microwave-assisted Suzuki-Miyaura and Mizoroki-Heck C-C cross-coupling reactions, showing the organometallic catalysts (***Pd-CS, Pd-SCS***) to produce the better conversions, most likely due to enhanced thermal stability provided by the Pd-C bonds.