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Di-palladium complex of terephthaldehyde bis(thiosemicarbazone) ligand: Synthesis, structure and catalytic application†

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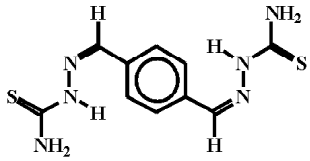
Reaction of terephthaldehyde bis(thiosemicarbazone), abbreviated as H_2tetsc (where H_2 depicts the two acidic hydrogens), with $[Pd(PPh_3)_2Cl_2]$ in refluxing ethanol in the presence of triethylamine affords a di-palladium complex of the type $[Pd_2(PPh_3)_2(tetsc)Cl_2]$. Structure of $[Pd_2(PPh_3)_2(tetsc)Cl_2]$ has been determined by X-ray crystallography. The thiosemicarbazone ligand binds to both the metal centers, via dissociation of the acidic protons, as a di-anionic bridging NS-donor forming two five-membered chelate rings. A triphenylphosphine and a chloride are also coordinated to each palladium. The $[Pd_2(PPh_3)_2(tetsc)Cl_2]$ complex displays intense absorptions spanning the visible and ultraviolet regions. The $[Pd_2(PPh_3)_2(tetsc)Cl_2]$ complex is found to serve as an efficient catalyst-precursor for three types of C-C cross coupling (viz. Suzuki, Heck and Sonogashira) reactions.

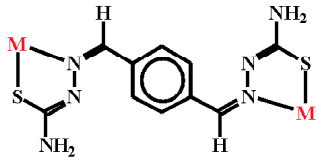
Keywords: Terephthaldehyde bis(thiosemicarbazone), di-palladium complex, crystal structure, catalytic C-C cross coupling reactions.

Introduction

There has been considerable interest in the chemistry of thiosemicarbazone complexes of the transition metal ions[1], which is largely due to their bioinorganic relevance and medicinal applications[2]. Systematic studies on the binding of thiosemicarbazone ligands to transition metal ions are of considerable importance in this respect. However, we have been exploring the chemistry of platinum metal complexes of the thiosemicarbazones[3], mainly because of the variable binding mode displayed by these ligands in their complexes. Besides, we also explored catalytic properties of selected thiosemicarbazone complexes[3a,c,d,e,f,j], particularly of the palladium thiosemicarbazone complexes[3a,c,e,f,j]. The palladium thiosemicarbazone complexes have been found to serve as efficient catalyst precursor for different types of cross coupling reactions[4,3a,c,e,f,j], because the thiosemicarbazones have the ability to stabilize the *in situ* generated Pd(0) in catalytic cycle. We have so far explored the catalytic efficiencies of different mononuclear palladium complexes[3a,c,e,f,j], and in the present study our plan has been to develop a molecular thiosemicarbazone complex with two palladium centers and assess its catalytic efficiency towards selected C-C coupling reactions. To achieve this target terephthaldehyde bis(thiosemicarbazone) has been chosen as the bridging ligand, which has two symmetric thiosemicarbazone wings. It is abbreviated as H_2tetsc, where H_2



H_2tetsc



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†Acharya P. C. Ray Memorial Lecture (2019).

stands for the two acidic hydrogens. This ligand is capable of binding to two metal centers forming five-membered chelate rings (**I**). As source of palladium the $[Pd(PPh_3)_2Cl_2]$ complex has been chosen, because of its demonstrated ability to undergo facile reaction with new ligands[3a,e,g,i,j]. Reaction of terephthaldehyde bis(thiosemicarbazone) with $[Pd(PPh_3)_2Cl_2]$ indeed afforded a di-palladium complex, and herein we report the formation and crystal structure of this complex, along with its catalytic application in three types of C-C cross coupling reactions.

Experimental section

Materials:

Palladium chloride was obtained from Arora Matthey, Kolkata, India. The $[Pd(PPh_3)_2Cl_2]$ complex was prepared by following a reported procedure[5]. Terephthaldehyde was obtained from Merck (India). The terephthaldehyde bis(thiosemicarbazone) ligand (H_2tetsc) was prepared by reacting terephthaldehyde and thiosemicarbazide in warm ethanol in 1:2 ratio. All other chemicals and solvents were reagent grade commercial materials and were used as received.

Synthesis of complex:

$[Pd_2(PPh_3)_2(tetsc)Cl_2]$: Terephthaldehyde bis(thiosemicarbazone) (20 mg, 0.07 mmol) was dissolved in warm ethanol (30 ml) and triethylamine (14 mg, 0.14 mmol) was added to it, followed by $[Pd(PPh_3)_2Cl_2]$ (100 mg, 0.14 mmol). The mixture was then refluxed for 5 h to yield a yellowish-brown solution. The solvent was evaporated and the solid mass, thus obtained, was subjected to purification by thin layer chromatography on a silica plate. With 1:10 acetonitrile-benzene as the eluant, an orangish-yellow band separated, which was extracted with acetonitrile. Evaporation of the acetonitrile extract gave the $[Pd_2(PPh_3)_2(tetsc)Cl_2]$ complex as an orangish-yellow crystalline solid. Yield: 65%. Anal. Calcd. for $C_{46}H_{40}N_6P_2S_2Cl_2Pd_2$: C, 50.84; H, 3.68; N, 7.74. Found: C, 50.92; H, 3.65; N, 7.76%; ^{1}H NMR[6] (300 MHz, $CDCl_3$): 5.71 (s, $2NH_2$, 4H), 7.34–7.72 ($2PPh_3$), 8.10 (4H, m), 8.56 (d, *J* 4.3 Hz, azomethine 2H); IR (cm^{-1}): 1612, 1565, 1481, 1435, 1314, 1190, 1098, 748, 722, 697 and 532 cm^{-1}; E. Spec. data in dichloromethane solution (λ, nm (ε, M^{-1} cm^{-1})): 352 (12900), 300 (18700).

Physical measurements:

Microanalyses (C, H and N) were performed using a Heraeus Carlo Erba 1108 elemental analyzer. ^{1}H NMR spectra were recorded in $CDCl_3$ solution on a Bruker Avance DPX 300 NMR spectrometer using TMS as the internal standard. IR spectra were obtained on a Perkin-Elmer Spectrum Two IR spectrometer with samples prepared as KBr pellets. Electronic spectra were recorded on a JASCO V-570 spectrophotometer. GC-MS analyses were performed using a Perkin-Elmer CLARUS 680 instrument.

X-Ray crystallography:

Single crystals of $[Pd_2(PPh_3)_2(tetsc)Cl_2]$ were obtained by slow evaporation of solvents from a solution of the complex in 1:1 dichloromethane-acetonitrile. Selected crystal data and data collection parameters are given in Table 1. Data were collected on a Bruker SMART CCD diffractometer using graphite monochromated MoKα radiation (λ = 0.71073 Å). Structure solution and refinement were done using SHELXS-97 and SHELXL-97 programs[7]. The structures were solved by the direct methods.

Table 1. Crystallographic data for $[Pd(PPh_3)_2(tetsc)Cl_2)]$

Empirical formula	$C_{46}H_{40}N_6P_2S_2Cl_2Pd_2$
Formula weight	1086.6
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	9.6621(1)
b (Å)	14.5145(2)
c (Å)	16.9874(3)
β (°)	106.291(1)
V (Å^3)	2286.67(6)
Z	2
$D_{calcd.}$ (g cm^{-3})	1.578
λ (Å)	0.71073
F (000)	1072
Crystal size (mm)	0.24×0.28×0.36
T (K)	298
μ (mm^{-1})	1.104
R_1[a]	0.0519
wR_2[b]	0.1776
GOF[c]	0.81

[a] $R_1 = \Sigma \,||F_o| - |F_c||/\Sigma|F_o|$

[b] $wR_2 = [\,\Sigma[\,w(F_o^2 - F_c^2)^2]/\Sigma\,[w(F_o^2)^2]\,]^{1/2}$

[c] $GOF = [\Sigma[w(F_o^2 - F_c^2)^2]/(M - N)]^{1/2}$, where M is the number of reflections and N is the number of parameters refined.

Application as catalysts:

Suzuki coupling reactions: In a typical run, an oven-dried 10 mL round bottom flask was charged with a known mole percent of catalyst, Na_2CO_3 (1.7 mmol), phenylboronic acid (1.2 mmol) and aryl halide (1 mmol) with the appropriate solvents (4 ml). The flask was placed in a preheated oil bath at required temp. After the specified time, the flask was removed from the oil bath and water (20 ml) added, followed by extraction with ether (4×10 ml). The combined organic layers were washed with water (3×10 ml), dried over anhydrous Na_2SO_4, and filtered. Solvent was removed under vacuum. The residue was dissolved in hexane and analyzed by GCMS.

Heck coupling reactions: In a typical run, an oven-dried 10 mL round bottom flask was charged with a known mole percent of catalyst, Cs_2CO_3 (1.7 mmol), *n*-butyl acrylate (1.2 mmol) and aryl halide (1 mmol) with polyethylene glycol (4 ml). The flask was placed in a preheated oil bath at required temperature. After the specified time the flask was removed from the oil bath and water (20 ml) added, followed by extraction with ether (4×10 ml). The combined organic layers were washed with water (3×10 ml), dried over anhydrous Na_2SO_4, and filtered. Solvent was removed under vacuum. The residue was dissolved in hexane and analyzed by GCMS.

Sonogashira coupling reactions: To a slurry of aryl halide (1 mmol), cuprous iodide (10 mol%) and palladium catalyst (a known mol%) in an appropriate solvent (4 ml), phenylacetylene (1.2 mmol) and NaOH (1.7 mmol) were added, and heated at the required temperature. After completion of the reaction (monitored by TLC), the flask was removed from the oil bath and water (20 ml) added, followed by extraction with ether (4×10 ml). The combined organic layers were washed with water (3×10 ml), dried over anhydrous Na_2SO_4, and filtered. Solvent was removed under vacuum. The residue was dissolved in hexane and analyzed by GCMS.

Results and discussion

Synthesis and characterizations:

As delineated in the introduction, the primary objective of the present study was to see how terephthaldehyde bis(thiosemicarbazone) interacts with the palladium center in $[Pd(PPh_3)_2Cl_2]$. The reaction between these two species proceeded smoothly in refluxing ethanol in the presence of triethylamine to afford an orangish-yellow complex in a decent yield. Preliminary characterization (microanalysis, IR and ^1H NMR) on this complex indicated the presence of a thiosemicarbazone and a triphenylphosphine in the coordination sphere. In order to unambiguously characterize this complex, and particularly to ascertain coordination mode of the thiosemicarbazone ligand in it, its structure was determined by X-ray crystallography. The structure is shown in Fig. 1 and selected bond parameters are given in Table 2. The crystal structure reveals that a single terephthaldehyde bis(thiosemicarbazone) ligand is coordinated to two palladium centers, via dissociation of the acidic protons, as a dianionic tetradentate NS-donor forming two identical five-membered chelate rings (**I**; M = Pd). A triphenylphosphine and a chloride are also coordinated to each metal center. Therefore this complex is represented henceforth as $[Pd_2(PPh_3)_2(tetsc)Cl_2]$. In this complex the triphenylphosphine is *trans* to the coordinated nitrogen and the chloride is *trans* to the sulfur. Each palladium is thus nested in an NSPCl core, which is slightly distorted from ideal square planar geometry, as manifested in the bond parameters around the metal center. The Pd-N, Pd-P, Pd-S and Pd-Cl distances are normal, as observed in structurally characterized complexes of palladium containing these bonds[3a,e].

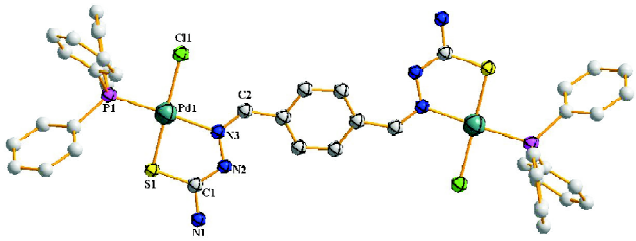


Fig. 1. View of the crystal structure of $[Pd_2(PPh_3)_2(tetsc)Cl_2]$.

Table 2. Selected bond distances and bond angels for $[Pd_2(PPh_3)_2(tetsc)Cl_2)]$

Bond distances (Å)			
Pd1-Cl1	2.3391(16)	S1-C1	1.725(6)
Pd1-P1	2.2500(14)	C1-N1	1.343(8)
Pd1-N3	2.102(4)	C1-N2	1.325(7)
Pd1-S1	2.2394(14)	N2-N3	1.367(6)
		N3-C2	1.287(6)
Bond angles (°)			
P1-Pd1-N3	175.66(11)	S1-Pd1-N3	83.52(10)
S1-Pd1-Cl1	177.95(6)		

Spectral studies:

^{1}H NMR spectrum of $[Pd_2(PPh_3)_2(tetsc)Cl_2]$, recorded in $CDCl_3$ solutions, showed all the expected signals. The phenyl protons of the PPh_3 ligands show broad signals within 7.34–7.72 ppm. From the coordinated thiosemicarbazone, the azomethine proton signal is observed as a doublet, due to coupling with the proton at the *ortho* position of the phenyl ring, at 8.56 ppm and the NH_2 proton signal is observed at 5.71 ppm. The expected signals from the phenyl ring of the coordinated thiosemicarbazone are clearly observed in the aromatic region. Infrared spectrum of $[Pd_2(PPh_3)_2(tetsc)Cl_2]$ shows many bands of different intensities in the 400–4000 cm^{-1} region. No attempt has been made to assign each individual band to a specific vibration. However, three strong bands at near 532, 697 and 748 cm^{-1} are observed due to the coordinated PPh_3 ligands. In comparison with the spectrum of *trans*-$[Pd(PPh_3)_2Cl_2]$, several new bands (at 1612, 1565, 1481, 1435, 1314, 1190, 1098 and 722 cm^{-1}) could be identified in the spectrum of $[Pd_2(PPh_3)_2(tetsc)Cl_2]$, which are attributable to the coordinated thiosemicarbazone ligand. Absence of ν(C=S) and ν(N-H) vibrational bands in the spectrum of the palladium complex (in comparison with the spectrum of the free H_2tetsc ligand) is consistent with the thiolate nature of the coordination of sulfur. The ^{1}H NMR and infrared spectral data of $[Pd_2(PPh_3)_2(tetsc)Cl_2]$ are therefore in well accordance with its composition and symmetric structure.

$[Pd_2(PPh_3)_2(tetsc)Cl_2]$ is found to be readily soluble in polar organic solvents like methanol, ethanol, acetonitrile, dichloromethane, chloroform, etc., producing bright yellow solutions. Electronic spectrum of the complex was recorded in dichloromethane solution. Spectral data are presented in the Experimental section. The complex showed two intense absorptions, one near the borderline of visible and ultraviolet region, and the other in the ultraviolet region, which are believed to be due to transitions within orbitals with dominant ligand character.

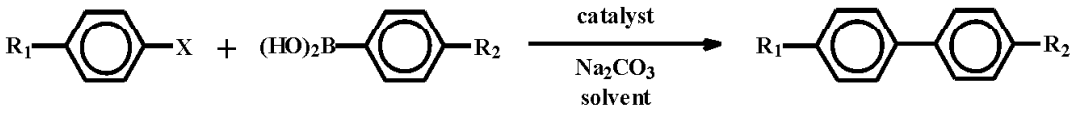
Catalytic C-C cross-coupling reactions:

The fact, that palladium complexes are well known to serve as efficient catalysts in bringing about C-C cross-coupling reactions of different types[8], led us to explore such catalytic properties in the $[Pd_2(PPh_3)_2(tetsc)Cl_2]$ complex. The catalytic activity of this complex was examined for C-C cross-coupling reactions of three types, viz. Suzuki, Heck and Sonogashira reactions.

Initially we tested $[Pd_2(PPh_3)_2(tetsc)Cl_2]$ as catalyst in the Suzuki coupling of phenylboronic acid and *p*-iodoacetophenone to yield the biphenyl product. After extensive optimization, it was found that 0.0001 mol% catalyst, 1.7 eqv. Na_2CO_3 as base, ethanol as solvent, 75°C reaction temperature, and 3 h reaction time, furnished an excellent yield of the desired C-C coupled product. The scope of the reaction is shown in Table 3, where several cross-coupling reactions performed by varying both the aryl halide and the arylboronic acid, are presented. Coupling of phenylboronic acid with three 4-R_1-phenyl iodides (R_1 = CH_3CO, CHO and CN) were tried, all of which afforded the expected C-C coupled products in excellent yields with high (~10^6) turnover numbers (entries 1–3). It may be mentioned here that such high turnover numbers are relatively less common[9]. Coupling of *para*-iodoacetophenone with two 4-R_2-phenylboronic acids (R_2 = CH_3 and Cl) also took place with similar efficiency (entries 4, 5). A similar trend was observed with the aryl bromides (entries 6–10), however, with a higher catalyst loading (0.001 mol%). The attempted C-C coupling involving aryl chlorides also proceeded smoothly, but with much higher catalyst loading (0.01 mol%) and slightly higher reaction temperature (entries 11–15). It is worth mentioning here that formation of new molecules through C-Cl bond activation is industrially very important due to easy availability of the relatively inexpensive aryl chlorides[10]. The impressive turnover numbers for the C-I, C-Br and C-Cl bond activation using $[Pd_2(PPh_3)_2(tetsc)Cl_2]$ as catalyst motivated us to try more tough C-F bond activation for C-C cross coupling reaction. It is interesting to note that though the turnover number was not so impressive, this di-palladium complex could successfully catalyse coupling between aryl fluoride and phenylboronic acid (entry 16), which is scarce in the literature[11].

Encouraged by the facile Suzuki coupling reactions catalyzed by $[Pd_2(PPh_3)_2(tetsc)Cl_2]$, we further investigated the catalytic activity of the same complex in Heck reaction of different aryl halides with *n*-butyl acrylate. Heck reactions of four *para*-substituted phenyl iodides and butyl acrylate were found to proceed well in 1:1 ethanol-toluene with 0.005 mol% catalyst to afford the coupled products in fairly good yields (entries 1–3, Table 4). Higher catalyst loading was needed

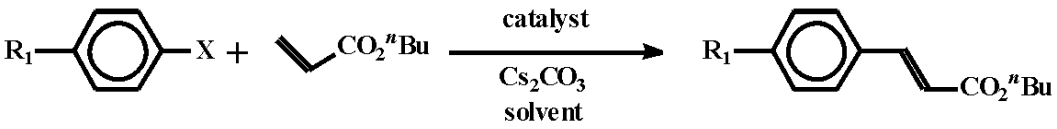
Table 3. Suzuki cross-coupling of aryl halides with phenylboronic acid[a]



Entry	R_1	R_2	X	Solvent	Temp. (°C)	Time (h)	Amt of cat. (mol%)	Yield[b] (%)	TON[c]
1	$COCH_3$	H	I	Ethanol	75	3	0.0001	100	1000 000
2	CHO	H	I	Ethanol	75	3	0.0001	100	1000 000
3	CN	H	I	Ethanol	75	4	0.0001	100	1000 000
4	$COCH_3$	CH_3	I	Ethanol	75	3	0.0001	100	1000 000
5	$COCH_3$	Cl	I	Ethanol	75	4	0.0001	100	1000 000
6	$COCH_3$	H	Br	Ethanol	75	4	0.001	100	100 000
7	CHO	H	Br	Ethanol	75	4	0.001	97	97 000
8	CN	H	Br	Ethanol	75	5	0.001	93	93 000
9	$COCH_3$	CH_3	Br	Ethanol	75	6	0.001	90	90 000
10	$COCH_3$	Cl	Br	Ethanol	75	6	0.001	86	86 000
11	$COCH_3$	H	Cl	Ethanol	85	8	0.01	87	8700
12	CHO	H	Cl	Ethanol	85	8	0.01	83	8300
13	CN	H	Cl	Ethanol	85	10	0.01	76	7600
14	$COCH_3$	CH_3	Cl	Ethanol	95	12	0.01	70	7000
15	$COCH_3$	Cl	Cl	Ethanol	95	12	0.01	67	6700
16	$COCH_3$	H	F	Polyethylene glycol	120	18	0.2	51	255

[a]Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), Na_2CO_3 (1.7 mmol), catalyst: $[Pd_2(PPh_3)_2(tetsc)Cl_2]$, solvent (4 mL).
[b]Product detected by GCMS and yield determined by GCMS on the basis of residual aryl halide.
[c]TON = turnover number ((mol of product)/(mol of catalyst)).

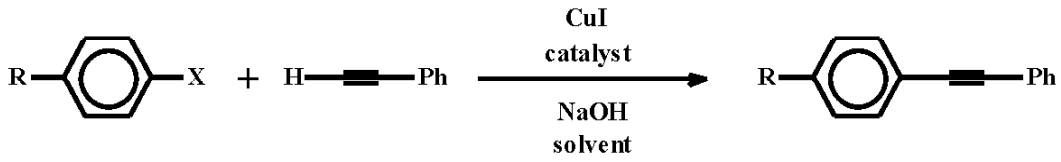
Table 4. Heck cross-coupling of aryl halides with *n*-butyl acrylate[a]



Entry	R_1	X	Solvent	Temp. (°C)	Time (h)	Amt of cat. (mol%)	Yield[b] (%)	TON[c]
1	$COCH_3$	I	Ethanol-toluene (1:1)	110	8	0.005	90	18000
2	CHO	I	Ethanol-toluene (1:1)	110	8	0.005	81	16200
3	CN	I	Ethanol-toluene (1:1)	110	9	0.005	70	14000
4	$COCH_3$	Br	Ethanol-toluene (1:1)	110	12	0.01	77	7700
5	CHO	Br	Ethanol-toluene (1:1)	110	12	0.01	71	7100
6	CN	Br	Ethanol-toluene (1:1)	110	14	0.01	62	6200
7	$COCH_3$	Cl	Polyethylene glycol	150	20	0.5	69	138
8	CHO	Cl	Polyethylene glycol	150	22	0.5	61	122
9	CN	Cl	Polyethylene glycol	150	24	0.5	53	106

[a]Reaction conditions: aryl halide (1.0 mmol), butyl acrylate (1.2 mmol), Cs_2CO_3 (1.7 mmol), catalyst: $[Pd_2(PPh_3)_2(tetsc)Cl_2]$, solvent (4 mL).
[b]Product detected by GCMS and yield determined by GCMS on the basis of residual aryl halide.
[c]TON = turnover number ((mol of product)/(mol of catalyst)).

Table 5. Sonogashira cross-coupling of aryl halides with phenylacetylene[a]



Entry	R	X	Solvent	Temp. (°C)	Time (h)	Amt of cat. (mol%)	Yield[b] (%)	TON[c]
1	$COCH_3$	I	Ethanol-toluene (1:1)	110	10	0.001	93	93000
2	CHO	I	Ethanol-toluene (1:1)	110	12	0.001	88	88000
3	CN	I	Ethanol-toluene (1:1)	110	14	0.001	81	81000
4	$COCH_3$	Br	Ethanol-toluene (1:1)	110	15	0.01	89	8900
5	CHO	Br	Ethanol-toluene (1:1)	110	15	0.01	75	7500
6	CN	Br	Ethanol-toluene (1:1)	110	18	0.01	69	6900
7	$COCH_3$	Cl	Polyethylene glycol	150	20	0.1	85	850
8	CHO	Cl	Polyethylene glycol	150	20	0.1	70	700
9	CN	Cl	Polyethylene glycol	150	20	0.1	63	630

[a]Reaction conditions: aryl halide (1.0 mmol), phenylacetylene (1.2 mmol), NaOH (1.7 mmol), catalyst: $[Pd_2(PPh_3)_2(tetsc)Cl_2]$, CuI (10 mol%), solvent (4 mL).

[b]Product detected by GCMS and yield determined by GCMS on the basis of residual aryl halide.

[c]TON = turnover number ((mol of product)/(mol of catalyst)).

for similar reactions with *para*-substituted phenyl bromides (entries 4–6). Whereas, for *para*-substituted aryl chlorides to obtain fairly good yield higher catalyst loading (0.5 mol%), higher temperature and a different solvent medium (polyethylene glycol) were required (entries 7–9).

Finally, we have scrutinized the catalytic efficiency of $[Pd_2(PPh_3)_2(tetsc)Cl_2]$ in Sonogashira coupling reaction between aryl halides and phenyl acetylene. The yields of Sonogashira coupling reactions were fairly good (Table 5). As before, the coupling involving aryl iodides was most facile with higher turnover numbers (entries 1–3). However, in case of aryl bromides to get fair yield ten times higher catalyst loading (0.01%) was required (entries 4–6). Reactions involving aryl chlorides were found to be more difficult (entries 7–9).

The present study thus demonstrates that $[Pd_2(PPh_3)_2(tetsc)Cl_2]$ is a highly efficient catalyst for all three types of C-C cross coupling reactions. A noticeable aspect of the observed catalysis is that no additional ligand was necessary to stabilize the palladium(0) species, generated *in situ*, and such ligand-free catalysis is relatively less common[12]. The catalytic efficiency of this present di-palladium complex is, in general, found to be better compared to our previously reported mono-palladium complexes[3a,c,e,f,j], and this is attributed to the presence of two catalytically active Pd-centers in the same complex molecule.

Conclusions

The present study shows that terephthaldehyde bis(thiosemicarbazone) can undergo facile reaction with $[Pd(PPh_3)_2Cl_2]$, and bind with two palladium centers symmetrically to afford the di-palladium complex, $[Pd_2(PPh_3)_2(tetsc)Cl_2]$. The di-palladium complex is found to serve as an efficient catalyst for C-C coupling (viz. Suzuki, Heck and Sonogashira) reactions. In particular, this complex shows remarkable catalytic efficiency towards Suzuki type C-C coupling reactions.

Supplementary data

CCDC 2047730 contains the supplementary crystallographic data for $[Pd_2(PPh_3)_2(tetsc)Cl_2]$.

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