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C–S bond formation catalyzed by *N*-heterocylic carbene palladium phosphine complexes

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ABSTRACT

N-Heterocyclic carbenes (NHCs) are known to be useful ligands for palladium-complex catalysis. It was found that [(NHC)Pd(PPh_3)Cl_2] is an effective pre-catalyst in Pd-catalyzed C–S cross coupling reactions to produce the functionalized sulfides in excellent yields. The turn over frequency (TOF) for the coupling of *p*-$CH_3C_6H_4Br$ with *p*-$CH_3C_6H_4SH$ reaches to 6.25 (mol of product) (mole of catalyst)$^{-1}$ h^{-1}.

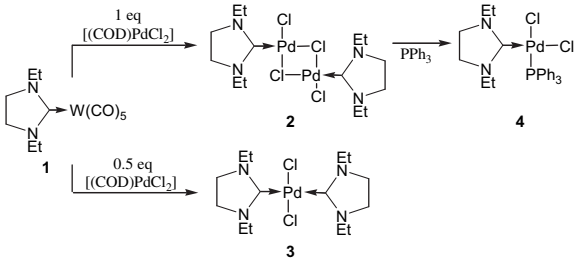
1. Introduction

Organosulfur molecules stand at an important class of compounds in pharmaceutical uses and synthetic intermediates. Thus, the formation of the C–S bond becomes a crucial indispensable process in synthetic organic chemistry. However, methodology leading to C–S bond formation has been a challenge until the recent development of transition metal (TM)-catalyzed coupling of thiols with organic halides particularly via the use of palladium-phosphine catalysts.[1,2]

N-Heterocyclic carbenes (NHCs) have appeared as an useful class of ligands for palladium-complex catalysis.[3] It is known that TM–NHC complexes often show better stability and reactivity compared to their TM–phosphine counterparts.[4] Recently, Ni–NHC complexes have demonstrated that they can serve as the catalysts for the coupling of thiols with aryl halides.[5] In this context, the use of Pd–NHC complexes as catalysts for C–S coupling has not been explored. Here, we would like to report the investigation of catalytic activity of Pd–NHC complexes on this coupling reaction.

2. Results and discussion

Palladium–NHC complexes **2** and **3** were prepared according to the previously reported procedure via a carbene transfer reaction of the tungsten carbene complex **1** with Pd(II) ions (Scheme 1).[6] Substitution of **1** with triphenylphosphine readily provided the mono-nuclear palladium species **4** quantitatively. The spectral data of complexes **2** and **3** are consistent with the reported data.



Scheme 1. Preparation of NHC palladium complexes.

In the ^{31}P NMR spectrum of **4**, a single shift appears at 27.3 ppm (coordination shift δ_P=34 ppm), consistent with the coordination of triphenylphosphine to the metal center. The ^1H NMR spectrum of **4** in $CDCl_3$ is illustrative and shows the presence of two signals for the methylene units of ethyl groups in a 1:1 ratio as well-separated doublet of quartet (^3J=7 Hz, J_{gem}=14 Hz) at 4.14 and 3.17 ppm, respectively. These diastereotopic hydrogens of methylene units indicate the asymmetry of the complex, i.e. carbene and phosphine ligands are in cis arrangement. A crystal structure analysis of **4** provides unambiguous evidence for the anticipated arrangement (Fig. 1).

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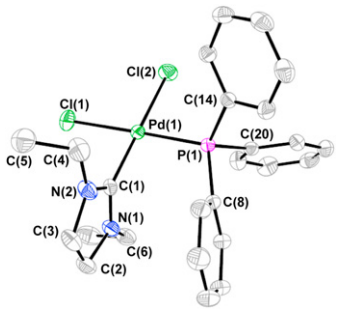

Figure 1. ORTEP plot of **4**. Pd(1)–C(1) 1.995(2)Å, Pd(1)–P(1) 2.2606(5)Å, Pd(1)–Cl(1) 2.3489(6)Å, Pd(1)–Cl(2) 2.3713(6)Å, C(1)–Pd(1)–P(1) 91.56(6)°.

The slightly distorted square-planar geometry around palladium is completed by one carbene moiety, phosphine and two chlorides. The Pd(1)–Cl(2) bond *trans* to carbene [Pd(1)–Cl(2)], is slightly longer (ca. 0.03 Å) than the Pd(1)–Cl(1) bond *trans* to the phosphine, thus reflecting the high trans influence of the NHC ligand. The azole ring adopts an almost perpendicular orientation with respect to the coordination plane of the [$PdCl_2$] metal fragment, as indicated by the torsion angles Cl(1)–Pd(1)–C(1)–N(1) and P(1)-Pd(1)–C(1)–N(2) of 88.9° and 89.2°, respectively.

In the first stage of the investigation for C–S coupling, we tried to seek the optimal catalytically conditions for the reaction of the model substrate *p*-methylbenzenethiol **6** with *p*-bromoacetophenone **5** to produce the coupling product **7** in the presence of **2**–**4** as the catalysts (Eq. 1). Table 1 shows the catalytic results of the model reaction over palladium catalysts with NHC ligands. It was found that the activities of the catalysts were quite sensitive to the base and solvent used for the reactions. A screening suggested that *t*-BuOK is the most suitable base, whereas toluene and ethanol are the best solvents, but carrying out the reaction in an ethanol solution requires a longer reaction time to achieve a better yield. Reactions of thiophenol with weaker bases (e.g., carbonate or phosphate) gave low conversions. The activity of complex **2** with PPh_3 additive is essentially similar to that of **4** (entry 17). Since the substitution of **2** with phosphine gives **4**, the best catalyst for C–S coupling reaction appears to be the phosphine-substituted complex **4**.

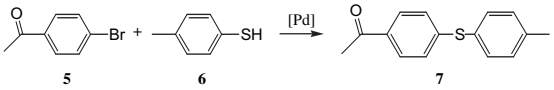

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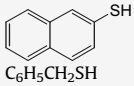
Table 1
Optimal conditions for the C–S coupling[a]

Entry	Complex	Base	Solvent	Additive	Time (h)	Yield[b]
1	**3**	*t*-BuOK	Toluene	*t*-Bu_3P	24	70%
2	**3**	*t*-BuOK	Toluene	Ph_3P	24	75%
3	**3**	*t*-BuOK	Toluene	—	24	23%
4	**2**	*t*-BuOK	Toluene	*t*-Bu_3P	24	54%
5	**2**	*t*-BuOK	Toluene	Ph_3P	8	99%
6	**2**	*t*-BuOK	Toluene	Ph_3P	4	55%
7	**2**	*t*-BuOK	Toluene	—	24	0
8	**2**	EtONa	toluene	—	24	0
9	**2**	K_3PO_4	Toluene	*t*-Bu_3P	24	4%
10	**2**	K_2CO_3	Toluene	Ph_3P	24	9%
11	**2**	Et_3N	Toluene	Ph_3P	24	31%
12	**2**	*t*-BuOK	CH_3CN	Ph_3P	24	2
13	**2**	*t*-BuOK	EtOH	Ph_3P	24	99%
14	**2**	*t*-BuOK	EtOH	Ph_3P	8	38%
15	**2**	*t*-BuOK	$Cl(CH_2)_2Cl$	Ph_3P	24	0
16	**2**	*t*-BuOK	THF	Ph_3P	24	10%
17	**4**	*t*-BuOK	Toluene	—	8	99%
18	**4**	*t*-BuOK	Toluene	Ph_3P	8	55%

[a] *p*-$CH_3COC_6H_4Br$ (0.4 mmol), $CH_3C_6H_4SH$ (0.25 mmol), Pd complex (0.005 mmol), base (0.4 mmol), additive (0.005 mmol) in toluene (0.5 mL), reflux 24 h under N_2 atmosphere.
[b] Determined by the integration of ^1H NMR with internal standard.

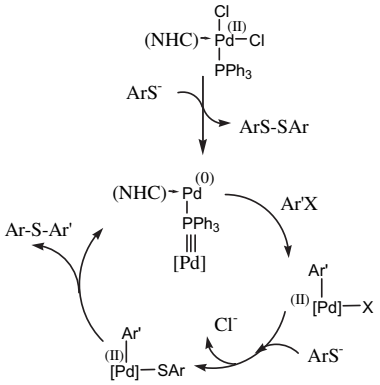
Catalyst **4** was used for screening different substrates. It showed excellent activities for deactivated both aryl iodides and bromides, but not chlorides. Quantitative yields were achieved by using 2 mol % of Pd-catalysts in toluene at refluxing temperature (Table 2, entries 1–2). For aryl bromides with electron-donating substituents, complex **4** also demonstrates high activities (Table 2, entry 11). Other aryl bromides give moderate to good yields, indicating the potential application of this catalytic system. However, poor yield was attained with alkyl thiols (Table 2, entry 16 and 17) and the catalytic system is inert toward aryl chloride. Thus, reaction of *p*-ClC_6H_4Br with *p*-toluenethiol yielded *p*-$ClC_6H_4SC_6H_4CH_3$ exclusively. The lower conversion for the alkyl thiols is probably due to the decomposition of the palladium complex in the presence of these thiols as evidenced by the formation of precipitates.

Table 2
Results of C–S coupling of various substrates[a]

Entry	Ar-X	R′SH	t (h)	Yield[b](%)
1	*p*-$CH_3COC_6H_4I$	*p*-$CH_3C_6H_4SH$	8	98
2	*p*-$CH_3COC_6H_4Br$	*p*-$CH_3C_6H_4SH$	8	99 [94]
3	*p*-$CH_3COC_6H_4Cl$	*p*-$CH_3C_6H_4SH$	8	0
4	*p*-$CH_3COC_6H_4I$	*p*-$CH_3C_6H_4SH$	4	82
5	*p*-$CH_3COC_6H_4Br$	*p*-$CH_3C_6H_4SH$	4	89
6	C_6H_5Br	C_6H_5SH	8	92
7	*p*-$CH_3C_6H_4Br$	*p*-ClC_6H_4SH	8	45
8	*p*-ClC_6H_4Br	*p*-$CH_3C_6H_4SH$	8	98 [97]
9	*p*-$NO_2C_6H_4Br$	*p*-$CH_3C_6H_4SH$	8	99 [88]
10	*p*-$CH_3OC_6H_4Br$	*p*-$CH_3C_6H_4SH$	8	54
11	*p*-$CH_3C_6H_4Br$	*p*-$CH_3OC_6H_4SH$	8	91 [75]
12	*m*-$CH_3COC_6H_4Br$	C_6H_5SH	8	48
13	*o*-$CH_3C_6H_4Br$	C_6H_5SH	8	70
14	*p*-$CH_3C_6H_4Br$	*p*-$CH_3C_6H_4SH$	8	99 [86]
15	C_6H_5Br		8	85 [77]
16	C_6H_5Br	$C_6H_5CH_2SH$	8	<5
17	C_6H_5Br	$C_{12}H_{25}SH$	8	27

[a] ArX (0.4 mmol),R′SH (0.25 mmol), Pd complex (0.005 mmol), ^tKOBu (0.4 mmol) in toluene (0.5 mL) at refluxing temperature under N_2 atmosphere.
[b] Determined by the integration of ^1H NMR. Isolated yield given in square brackets.

The reaction mechanism of Pd-phosphine catalysts in coupling of C–S bonds has been well studied.[7] Here, the palladium carbene complex **4** is believed to be undergoing the similar pathway (Scheme 2). It is known that the donating ability of coordinating ligands could affect the activity of catalysts dramatically. Under the same reaction conditions, complexes **2**–**4** show various catalytic activities on the C–S coupling reaction. In the absence of phosphine, the mono-carbene complex **2** displays no catalytic activity at all (Table 1, entry 7). Also, the bis-carbene complex **3** exhibits poor activity (Table 1, entry 3). On the contrary, complex **4** reveals its excellent activity, suggesting that the combination of phosphine



Scheme 2. Catalytic cycle for C–S coupling reaction.

and HNC ligands on the palladium ions could create the most active catalyst for the coupling reaction. The turn over frequency (TOF) for the coupling of *p*-$CH_3C_6H_4Br$ with *p*-$CH_3C_6H_4SH$ reaches to 6.25 [(mol of product) (mole of catalyst)$^{-1}$ h^{-1}], which is better than that of $Pd(PPh_3)_4$ (TOF~2).[1c] It is noted that the use of tri(*t*-Bu)phosphine as the auxiliary ligand (Table 1, entry 1) decreases the yields on the coupling reactions. Thus, fine-tuning the steric hindrance and electron-donating properties of ligands is important for catalyst development and this study illustrates a good example.

In summary, we have described an efficient palladium catalyst for C–S cross coupling of aryl bromides and thiols. The new catalyst is easy to synthesize and could be an excellent candidate for large scale reactions. In this study, it is also found that ligands around the metal center affect the catalytic activities dramatically. Fine-tuning of ligand effect to improve the catalytically performance is currently under investigation.

3. Experimental

3.1. General

All reactions, manipulations and purifications steps were performed under a dry nitrogen atmosphere. Tungsten carbene complexes **2** and **3** were prepared accordingly to the method reported previously.[6a] Nuclear magnetic resonance spectra were recorded in $CDCl_3$ or acetone-d_6 on either a Bruker AVANCE 400 spectrometer. Chemical shifts are given in parts per million relative to Me_4Si for ^1H and ^{13}C NMR. Chemicals and solvents were of analytical grade and used as received unless otherwise stated.

3.2. Preparation of complex 4

Triphenylphosphine (13.2 mg, 5.0×10^{-2} mmol) was added to a solution of **2** (15 mg, 2.5×10^{-2} mmol) in acetonitrile (2 mL). The resulting mixture was stirred at room temperature for 48 h. Upon concentration, the residue was *re*-crystallized from CH_2Cl_2/hexane to give **4** as white crystalline solids (22 mg, 80%). Mp: 250–255 °C (dec); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.69–7.74 (m, 6H, Ar-*H*), 7.38–7.47 (m, 9H, Ar-*H*), 4.09–4.16 (dq, *J*=14, 7 Hz, 2H, –CH*H*–), 3.41 (t, 2H, imi-*H*, *J*=9 Hz), 4.10–4.24 (dq, *J*=14, 7 Hz, 2H, –C*H*H–), 2.83 (t, 2H, imi-*H*, $^3J_{HH}$=9 Hz), 1.07 (t, 6H, –C*H*$_3$, $^3J_{HH}$=7.2 Hz); ^{31}P {^1H} NMR ($CDCl_3$, 162 MHz): δ 27.3; ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 191.4 (M=*C*), 134.4 (d, J_{P-C}=11.2 Hz), 131.2 (d, J_{P-C}=2.3 Hz), 130.2 (d, J_{P-C}=53.3 Hz), 128.4 (d, J_{P-C}=11.1 Hz), 47.0, 45.1, 12.5. ESIMS calcd for $C_{25}H_{29}N_2ClPPd$ [M−Cl]: *m*/*z*: 529.13; found: (529.08). Anal. Calcd for $C_{25}H_{29}Cl_2N_2PPd$: C, 53.07; H, 5.17; N, 4.95. Found: C, 52.87; H, 5.32; N, 5.05.

3.3. Catalysis-general procedure

A mixture of palladium complex (2.5×10^{-3} mmol), aryl halide (0.4 mmol), thiol (0.25 mmol), and potassium *tert*-butoxide (0.4 mmol) in solvent (0.5 mL) was placed in flask under nitrogen atmosphere. The mixture was stirred at room temperature for 10 min, and then heated to reflux for a period of time. The reaction was then monitored by ^1H NMR. After the completion of the reaction, brine (3 mL) and CH_2Cl_2(5 mL) were added. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (5 mL×2). The combined organic extracts were dried over magnesium sulfate and concentrated. The residue was chromatographed on the silica gel with the elution of a mixture of hexane and ethyl acetate. Products obtained in this work were characterized by spectral methods particularly with ^1H and ^{13}C NMR, and the data were consistent with those reported.

3.3.1. p-Acetylphenyl p-tolyl sulfide[8]. Light yellow solids, mp: 89–92 °C, ^1H NMR(400 MHz, $CDCl_3$): δ 7.78 (d, *J*=8.6 Hz, 2H, Ar-*H*), 7.39 (d, *J*=8.1 Hz, 2H, Ar-*H*), 7.21 (d, *J*=8.1 Hz, 2H, Ar-*H*), 7.14 (d, *J*=8.6 Hz, 2H, Ar-*H*), 2.52 (s, 3H, –COC*H*$_3$), 2.38 (s, 3H, –C*H*$_3$).These data are similar to those reported.

3.3.2. Diphenyl sulfide[9]. Liquids, ^1H NMR ($CDCl_3$, 400 MHz): δ 7.24–7.33 (m, 10H, *Ph*).

3.3.3. p-Chlorophenyl p-tolyl sulfide[10]. White solids, mp: 71–73 °C, ^1H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, *J*=8.1 Hz, 2H, Ar-*H*), 7.16–7.24 (m, 4H, Ar-*H*), 7.13 (d, *J*=8.1 Hz, 2H, Ar-*H*), 2.40 (s, 3H, C*H*$_3$).

3.3.4. 4-Nitrophenyl p-tolyl sulfide[11]. Light yellow solids., mp: 86–87 °C, ^1H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J*=8.9 Hz, 2H, Ar-*H*), 7.42 (d, *J*=8.1 Hz, 2H, Ar-*H*), 7.25 (d, *J*=8.1 Hz, 2H, Ar-*H*), 7.12 (d, *J*=8.9 Hz, 2H, Ar-*H*), 2.40 (s, 3H, C*H*$_3$).

3.3.5. 4-Methoxyphenyl p-tolyl sulfide[10]. Viscous liquids, ^1H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J*=8.9 Hz, 2H, Ar-*H*), 7.11 (d, *J*=8.1 Hz, 2H, Ar-*H*), 7.05 (d, *J*=8.1 Hz, 2H, Ar-*H*), 6.85 (d, *J*=8.9 Hz, 2H, Ar-*H*), 3.79 (s, 3H, OC*H*$_3$), 2.28 (s, 3H, C*H*$_3$).

3.3.6. m-Acetylphenyl phenyl sulfide[12]. Viscous liquids, ^1H NMR (400 MHz, $CDCl_3$): δ 7.87–7.88 (m, 1H, Ar-*H*), 7.76–7.79 (m, 1H, Ar-*H*), 7.43–7.50 (m, 1H, Ar-*H*), 7.29–7.36 (m, 6H, Ar-*H*), 2.53 (s, 3H, C*H*$_3$).

3.3.7. Phenyl o-tolyl sulfide[13]. Viscous liquids, ^1H NMR (400 MHz, $CDCl_3$): δ 7.17–7.27 (m, 9H, –*Ar*), 2.35 (s, 3H, –C*H*$_3$).

3.3.8. Di(p-tolyl) sulfide[10]. Light brown solid, mp: 54–56 °C, ^1H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, *J*=8.1 Hz, 4H, Ar-*H*), 7.08 (d, *J*=8.1 Hz, 4H, Ar-*H*), 2.30 (s, 6H, –C*H*$_3$).

3.3.9. 2-Naphthyl phenyl sulfide[13]. Light brown solid, mp: 51–52 °C, ^1H NMR (400 MHz, $CDCl_3$): δ 7.70–8.03 (m, 4H, Ar-*H*), 7.25–7.48 (m, 8H, Ar-*H*).

3.3.10. Benzyl phenyl sulfide[13]. Viscous liquids, ^1H NMR (400 MHz, $CDCl_3$): δ 7.13–7.35 (m, 10H, *Ar*), 4.06 (s, 2H, –C*H*$_2$–).

3.3.11. n-Dodecylthiobenzene[14]. Viscous liquids, ^1H NMR (400 MHz, $CDCl_3$): δ 7.13–7.33 (m, 5H, Ar-*H*), 2.94 (t, *J*=7.4 Hz, 2H, S–C*H*$_2$–), 1.55–1.68 (m, 4H, –C*H*$_2$–), 1.24–1.40 (m, 16H, –C*H*$_2$–), 0.84–0.88 (m, 3H, –C*H*$_3$).

3.4. Crystallography

Crystals suitable for X-ray determination were obtained for **4** by recrystallization at room temperature. Cell parameters were determined either by a Siemens SMART CCD diffractometer. The structure was solved using the SHELXS-97 program and refined using the SHELXL-97 program by full-matrix least-squares on F^2 values. Crystal data of the complex **4**: $C_{25}H_{29}Cl_2N_2PPd$, M_w=565.77, Orthorhombic, P2(1)2(1)2(1), *a*=9.7720(1) Å, *b*=13.1533(1) Å, *c*=18.8063(2) Å, *V*=2417.25(4) Å^3, *Z*=4, D_{calcd}=1.555 Mg/m^3, *F*(*000*)=1152, 0.25×0.20×0.15 mm^3, 2θ=2.60–27.49°, 23927 reflns collected, 5547 independent reflns [*R*(int)=0.0219], Full-matrix least-squares on F^2, *R*1=0.0199, w*R*2=0.0508 [$I>2\sigma(I)$]. CCDC reference number for **4**: 755885.

Acknowledgements

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