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Journal Name New Journal of Chemistry
Dynamic Article Links►
View Article Online
DOI: 10.1039/C7NJ00067G

Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Oxine based unsymmetrical (O^-, N, S/Se) pincer ligands and their palladium(II) complexes: synthesis, structural aspects and applications as catalyst in amine and copper-free Sonogashira coupling

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Received (in XXX, XXX) XthXXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

The unsymmetrical pincer ligands having 8-hydroxyquinoline (oxine) core *viz*. 2-(phenylthio/ selenomethyl) quinolin-8-ol (**L1**/ **L2**), 2-(N,N-dimethylthiocarbamoyl) quinolin-8-ol **(L3)** and 2-(pyrrolidin-1-ylthiocarbamoyl) quinolin-8-ol (**L4**) were synthesized. 2-Methylquinolin-8-ol was converted to 2-bromomethylquninolin-8-ol, which reacted with PhENa (E= S or Se) to give **L1** and **L2**, Willgerodt-Kindler reaction on an appropriate aldehyde derivative of quinoline gave **L3** and **L4**. On reaction with Na_2PdCl_4/$[Pd(CH_3CN)_2Cl_2]$, **L1**−**L4** coordinated as a (O^-, N, E) donor (E = S/Se) resulting in complexes [Pd(**L**−H)Cl] (**1**–**4**; **L**= **L1**−**L4)**. Molecular structures of **L1**, **1** and **2** were established with single crystal X-ray diffraction. Palladium in **1** and **2** has nearly square planar geometry. The Pd−S bond distance in **1** is 2.2648(14) Å and in **2**, the Pd–Se bond distance is 2.3641(7) Å. Somewhat rare week interactions (*viz*. C−H···Pd and Se···Cl) were noticed in the crystals of **1** and **2** respectively. Complexes **1** and **2** were found efficient to catalyze Sonogashira coupling under amine and copper free conditions. The catalyst loading of 0.5−1.0 mol% was found promising for conversion of several aryl halides to their coupled products. Yields were lower for ArCl in comparison to ArBr/ArI. The catalytic activity of **1** was marginally lower than that of **2**. DFT calculations support the catalytic activity order and bond lengths and angles of **1** and **2**.

Introduction

Metal complexes of pincer ligands are of current interest[1-7] and acquire stability due to binding of the pincers with metal ions in a tridentate mode.[6] A wide range of donor groups (such as NR_2, PR_2, OR, SR, SeR , AsR_2, halogen, *etc.*)[8] are present in the two arms of these ligands, which generally form five or six-membered chelate rings with the metal ion on complexation.[4] The pincer ligands considered important for designing of transition metal based catalysts[6] are symmetrical as well as unsymmetrical.

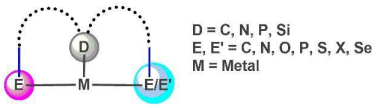

Fig. 1 Representation of metal-pincer complexes

The two arms of an unsymmetrical pincer ligand have different donor atom (Fig. 1) and/or length. Thus with unsymmetrical pincers the advantages of two electronically different donor atoms and / or chelate rings of different sizes can be afforded. Both these things enhance the possibility of hemilability favourable for catalytic activity. The number of catalysts based on unsymmetrical pincer ligands,[4,6] is less known than those of their symmetrical counterparts. This is because less convenient multi-step reactions are required to prepare unsymmetrical pincers and separation protocols often reduce their yield.[8d,9-11] The carbon is a common central atom in pincer frameworks, resulting M−C bond on complexation. Pd complexes of pincers having Pd-C bond are similar to palladacycles, popular as pre-catalysts for cross-coupling reactions. Its replacement with another donor atom *e.g.* N, P or Si may lead to substantial variation in the catalytic activity. It improves many fold in some cases.[6] The unsymmetrical backbone skeleton may reduce the strength of M–D bond (depending on the nature of D), which in conjunction with two E/E'–M bonds in side arms can release active Pd(0) species faster if the combination of E and E' results in a hemilabile ligand system (Fig. 1).[10,11] Thus unsymmetrical pincer ligands based on *N*-heterocycle framework (*e.g.* indole or quinoline) may result in efficient catalysts and are worth exploring.[12-19] The coordination chemistry of quinoline derivatives is well established.[15-19] However, quinoline as a core unit for designing pincer ligand has been scantly explored. The only examples in our knowledge is that of quinoline-based (P,N,F)/(O,N,P) pincer investigated by Vigalok and co-workers[15,19a] for designing Pd-complexes. The complexes of Pd(II) with pincer ligands (symmetrical and unsymmetrical) with chalcogen donor atoms (S/Se), have emerged as a family of efficient catalysts for various C-C coupling reactions[6,9,20-25] including Sonogashira coupling. They are more stable under ambient conditions in comparison to their organophosphorus analogues and often easy to synthesize.[23-25] Organochalcogen ligands generally contain combination of hard and soft donor

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atoms, which result in hemilabile character, considered important in catalytic activation and sensing.[5,7]

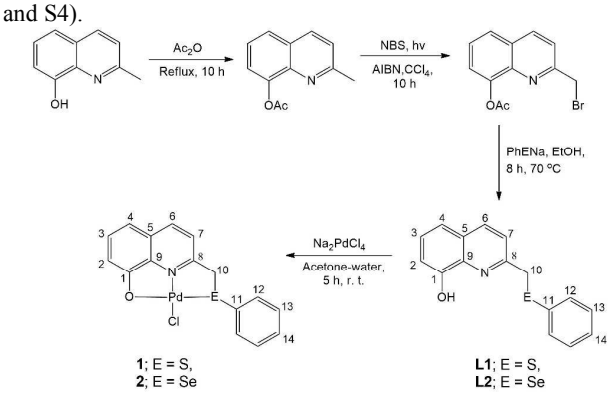
Palladium(II) complexes/palladacycles of several phosphorus, oxime, NHCs, imine, thiocarboxamide/semicarbazone, and 1,2,3-triazole based ligands are known to activate Sonogashira coupling.[26-35] The *in situ* formation of Pd(0) species (discrete or nano-sized) has also been reported in the catalytic process.[35b,36-38,39] Among metal complexes of pincer ligands known as a catalyst for Sonogashira coupling, the majority has symmetrical pincer *e.g.* (P,C$^-$,P),[40] (N,C$^-$,N),[41] (S,C$^-$,S),[42a] (C,N,C),[42b] (P, N, P)[42c] and (E,C$^-$,E) where E = Si^{II} or Ge^{II}.[39] The catalytic activation with them generally requires CuI as a co-catalyst.[39,41,42] The use of unsymmetrical pincer ligand based metal complex as a catalyst for this coupling reaction is rare. The examples in our knowledge are Pd(II)-complexes of (P,N,F) and (N,N,C) pincer.[15,43] They have shown good catalytic activity for Sonogashira coupling under Cu-free condition. The metal complexes of pincer ligands bearing combination of different donor groups[15,39-43] are, therefore, worth exploring as they may result in exciting applications in catalysis of C-C coupling including Sonogashira. Palladium complex of a (O, N, E) pincer having a combination of 'hard-soft' donor sites may have the advantages of hemilabile feature, which facilitates oxidative addition of substrate to the metal centre. When quinoline is central back bone of unsymmetrical pincer, (contributing N as a central donor atom) its metal complex can dynamically dissociate to generate coordinatively unsaturated active species.[39,43] Thus quinoline based unsymmetrical pincers are worth exploring to design catalyst of high stability and reactivity.

Thus current submission is focussed on (O$^-$, N, E) unsymmetrical pincer ligand (E = S/Se) (**L1**−**L4**) based on quinoline core and their Pd(II) complexes [Pd(**L**−H)Cl] (**1**−**4; L= L1**−**L4**). The **1** and **2** were found promising for catalysis of Sonogashira coupling of ArX (X = Cl, Br, I) under Cu and amine free conditions. Other substituent presents on Ar influence the yield of coupled product. The use of 0.5 to 1 mol% of **1** or **2**, gives up to 91% yield in a reaction time of the order 3 to 12 h.

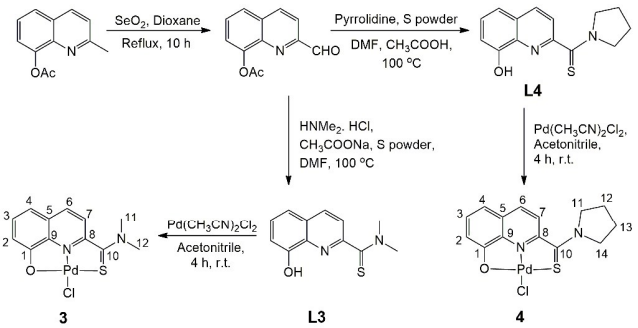
Results and discussion

In Schemes 1 and 2 syntheses of **L1**−**L4** along with their Pd(II) complexes **1**−**4** are shown. The ligands **L3** and **L4** were synthesized by Willgerodt-Kindler reaction on their aldehyde precursors.[44a] This reaction, a one-pot and three-component process, is among important methods known for the synthesis of thioamides (Scheme 2).[44b] The complexes **1**−**4** can be stored under ambient conditions for several months. Palladium(II) complexes of organochalcogen ligands are known for their longer stability than their organophosphorus counterparts.[23,24] The **L1**−**L4** were found soluble in common organic solvents. The **1**−**2** showed moderate solubility in common organic solvents except for DMSO and DMF in which it was very good. The solubility of **3** and **4** in DMSO/DMF was only moderate. The structures of ligands (**L1**−**L4**) and their palladium complexes (**1**−**4**) were authenticated with C, H and N analyses, ^{1}H, ^{13}C{^{1}H} and ^{77}Se{^{1}H} NMR, FT-IR, high-resolution mass spectrometry (HR-MS) and X-ray diffraction on single crystals in the case of **L1**, **1** and **2**.

NMR and mass spectra. ^{1}H, ^{13}C{^{1}H} and ^{77}Se{^{1}H}(for **2** and **L2**) NMR spectra (See in ESI Figs. S2-S21) of **L1**−**L4** and **1**−**4** were found consistent with their molecular structures shown in Schemes 1 and 2. The signal in ^{77}Se{^{1}H} NMR spectrum of **2** was found deshielded by ~33.9 ppm, with respect to that of free **L2**, which appears at 372.1 ppm, supporting coordination of **L2** with Pd *via* Se donor site. In ^{1}H NMR of **1** and **2**, a broad singlet of H_{10} (−SCH_2/−$SeCH_2$) appears at 5.33 and 5.14 ppm respectively, shielded by ~0.94 and 0.86 ppm with respect to those of free ligands **L1** and **L2** respectively (See ESI; Figs. S2 and S4).



Scheme 1 Synthesis of **L1** and **L2** and their Pd(II) complexes



Scheme 2 Synthesis of **L3** and **L4** and their Pd(II) complexes

Probably pyramidal inversion at S/Se causes this broadening. It results in two interconverting degenerate isomers due to the exchange of *syn* and *anti* configuration of the phenyl group attached to S/Se relative to methylene protons (−SCH_2/−$SeCH_2$). The signal of (−SCH_2/−$SeCH_2$) in ^{13}C{^{1}H} NMR spectra of **L1** and **L2** appears at 40.9 and 33.8 ppm respectively. On complexation, the signals shift to 53.3 and 45.5 ppm respectively, deshielded by ~12.4 and 11.7 ppm (See ESI; Figs. S14 and S16). The signal of –OH in ^{1}H NMR spectra (recorded in DMSO-d_6) of free **L3** and **L4** appears at 9.76 and 9.74 ppm respectively. The disappearance of –OH signal in **3** and **4** supports the coordination of **L3** and **L4** with palladium via O$^-$. The signal of >C=S group in ^{13}C{^{1}H} NMR spectra of **L3** and **L4** appearing at 197.3 and 193.1 ppm respectively, on complexation gets shielded (~4.6 and 4.8 ppm) and appears at 192.7 and 188.3 ppm for complexes **3** and **4** respectively (See ESI; Figs. S19 and S21). This may be attributed due to reduction in C=S bond order on coordination of **L3/L4** with palladium through the S donor site.[44c]

The high-resolution mass spectra (HR-MS) of all ligands and complexes are consistent with their simulated HR-MS (See ESI; Figs. S22-S29). In HR-MS of **L1**−**L4** peak of [M+H]$^+$ was

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observed. In the case of complexes **1** and **2,** the peaks appearing at *m/z* = 429.9250 and 477.8680 are due to $[M+Na]^+$. In case of complexes **3** and **4**, peaks appear at *m/z* = 354.9731 and 380.9937, respectively. They may be assigned to $[(M-Cl).(H_2O)]^+$ fragment.

Crystal structures. The single crystal structures of **L1, 1** and **2** were solved. Their single crystals of **L1**, complex **1** and **2** suitable for X-ray diffraction were grown by slow evaporation of their solutions made in the chloroform-hexane mixture (1:6). However attempts made to grow single crystals of Pd(II) complexes **3** and **4** suitable for X-yay diffraction in several solvents (pure as well as mixtures) were unsuccessful. Therefore, their structures could not be determined. The ORTEP diagrams of **L1** and **1** and **2** are shown in Figs. 2-4. The Tables S1-S4 in ESI contain crystal data, refinement details and selected bond distances and angles of **L1** and complexes **1** and **2**. Each ligand from **L1**−**L4** forms two five-membered chelate rings with palladium, resulting in complexes **1**−**4**. The geometry of palladium in both **1** and **2** is distorted square-planar. The S/Se is in a position *trans* to O^- whereas chloride and N are *trans* to each other. The Pd−S bond lengths of **1**, 2.2648(14) Å is close to that of palladacycle of 2,3-bis[(phenylthio)methyl]quinoxaline [2.259(2) Å],[45a] and Pd(II) complex of a sulfated Schiff base of 1-hydroxy-2-acetophenone [2.2704(16) Å].[45b] In **2**, the Pd–Se bond distance [2.3641(7) Å] is very close to the value, 2.3654(10) Å, reported for palladacycle of an indole-based unsymmetrical (N, C^-, Se) pincer[9] and consistent with the values reported for Pd(II) complexes of selenoether ligands (2.385(5) Å).[25b,c] The Pd−N bond distances in both **1** and **2** are almost same [1.958(4) and 1.962(4) Å] and consistent with the value [2.053(2) Å] reported for Pd(II) complex of a quinoline-based (P, N, F) pincer.[15] The Pd−O bond lengths in **1** and **2** are 2.042(3) and 2.049(3) Å respectively. They are somewhat shorter than the Pd−O bond length, 2.159(8) Å, reported earlier[15] but close to that of Pd(II) complex of (*E*)-8-hydroxyquinoline-2-carbaldehyde O-benzyl oxime [1.986(3)].[16] The Pd−Cl bond lengths in **1** and **2** are 2.3001(14) and 2.3001(14) Å respectively and normal.[25]

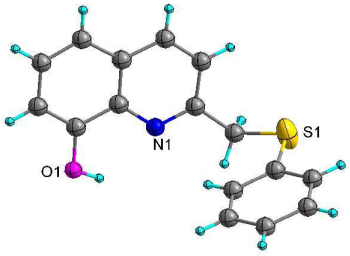

Fig. 2 Molecular structure of **L1** Bond lengths (Å): S(1)—C(11) 1.757(3); S(1)—C(10) 1.795(3); O(1)—C(1) 1.357(3); N(1)—C(9) 1.315(3); N(1)—C(6) 1.363(3); Bond angles(°): C(11) —S(1) —C(10) 104.78(13); C(9)—N(1)—C(6) 118.5(2); O(1)—C(1)—C(6) 119.2(2); C(12)—C(11)—S(1) 116.0(2).

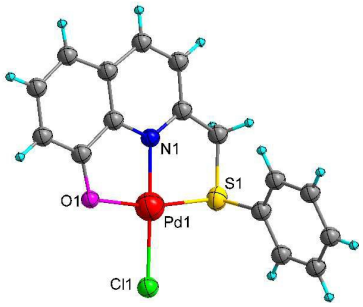

Fig. 3 Molecular structure of **1**. Bond lengths (Å): Pd(1)─N(1) 1.958(4); Pd(1)─Cl(1) 2.3001(14); Pd(1)─O(1) 2.042(3); Pd(1)─S(1) 2.2648(14). Bond angles (°): N(1)─Pd(1)─S(1) 85.23(12); N(1)─Pd(1)─O(1) 83.13(15); O(1)─Pd(1)─Cl(1) 95.10(10); S(1)─Pd(1)─Cl(1) 96.52(5).

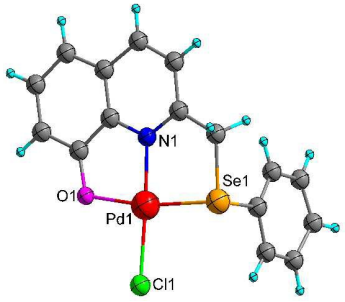

Fig. 4 Molecular structure of **2**. Bond lengths (Å): Pd(1)─N(1) 1.962(4); Pd(1)─Cl(1) 2.3001(14); Pd(1)─O(1) 2.049(3) Pd(1)─Se(1) 2.3641(7). Bond angles (°): N(1)─Pd(1)─O(1) 83.03(15); O(1)─Pd(1)─Cl(1) 95.30(11); Se(1)─Pd(1)─Cl(1) 95.38(4); Se(1)─Pd(1)─N(1) 86.41(11).

The packing and non-covalent interactions in the crystals of **L1, 1** and **2** are interesting. Only weak and rare intermolecular interactions hold the molecules together and stabilize the crystal structure. One molecule of **L1** is connected to six other molecules of **L1** through weak C–H···π, O–H···π and C–H···S intermolecular interactions (See ESI; Fig. S1-a). The π···π interactions between the two molecules (See ESI; Fig. S1-b) further contribute to the stabilization of crystal structure.

One molecule of the complex **1** is surrounded by six other similar molecules connected through non-covalent and weak intermolecular C–H···O and C–H···Cl interactions (Fig. 5a). In contrast to the crystal of **L1**, no C–H···π interaction is present in the crystal structure of **1** but the molecules of **1** stacked together have π···π interactions (Fig. 5b). A rare weak C–H···Pd intermolecular interaction is also noticed in this crystal structure (Fig. 5c). It is worth to note here that the anagostic C–H···Pd intermolecular interaction is important in the constructions of the supramolecular network present in the crystal.[46a] However, the C–H···Pd interaction has also been considered important to understand the catalytic reactions.[46b]

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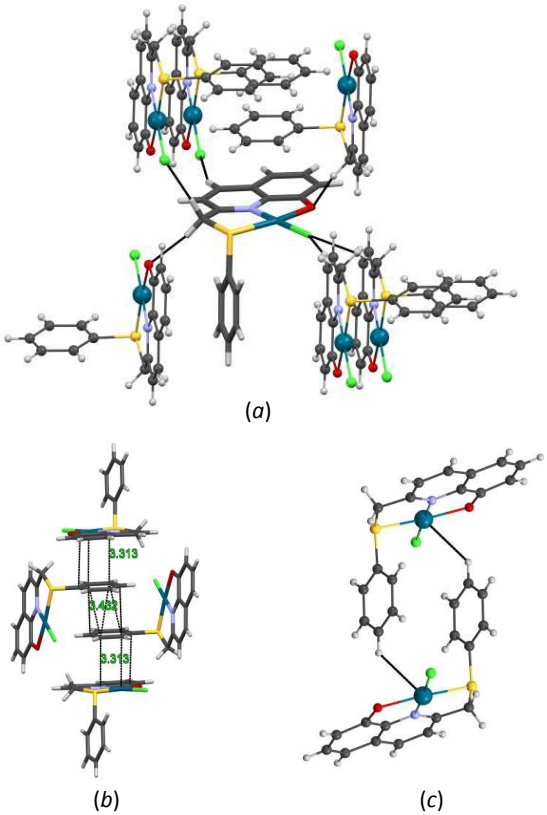
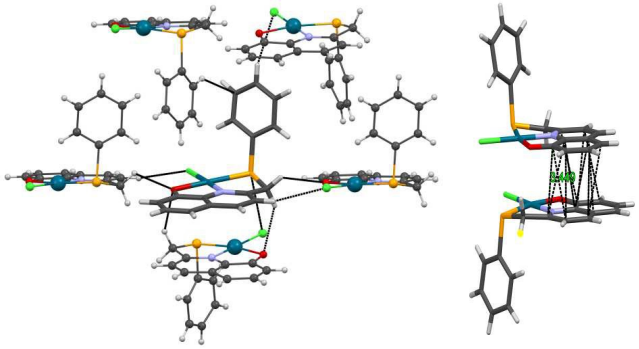


(*a*) (*b*) (*c*)

Fig. 5 Secondary interactions in the crystal of complex **1**

One molecule of complex **2** is connected to five other similar molecules through weak C–H···O, C–H···π and C–H···Cl intermolecular interactions (Fig. 6a). Interestingly, a weak non-covalent Se···Cl interaction is present between two molecules of **2**. Such interactions are considered important in the synthesis of various organic compounds.[46c] The selenium···halogen interactions are useful in the designing of several types of crystalline organoselenium compounds and also for seeing other types of non-covalent interactions, in which a halogen atom is taken as an electron donating group. Similar to **L1** and complex **1**, the molecules of complex **2** in the crystal are engaged in π ···π interactions (Fig. 6b).



(*a*) (*b*)

Fig. 6 Interactions in the crystal of complex **2**.

Catalysis of Sonogashira coupling

The catalysis of Sonogashira coupling (C_{sp^2}–C_{sp}) having many applications in the synthesis of optical/electronic materials, liquid crystals, drugs (antibiotics, antimycotics *etc.*) and polymers,[33a,42b] was explored with complexes **1-4.** The **3** and **4** have poor solubility in organic solvent and this turned out a limitation for their applications to Sonogashira coupling. In attempts to catalyze this coupling in several solvents / bases with them, the reaction mixture turned black immediately or within 15 - 30 min and no coupled product was observed. The situation did not change even in the presence of copper/amine. However performance of **1** and **2** as catalysts for Sonogashira coupling was found promising. Therefore, coupling of aryl bromide with phenylacetylene catalyzed with **2** was first optimized. For this purpose, 4-bromobenzaldehyde was used as a substrate and in its coupling with phenylacetylene, complex **2** was employed as a catalyst, under amine and Cu-free conditions. The conversion into coupled product was monitored with ^{1}H NMR. The results for various organic solvents and bases are given in Table 1. The N_2 atmosphere was used in the catalysis as in the presence of air, conversion reduced significantly (Table 1; entry 3). For best results, the reaction mixture was degassed with N_2 and thereafter solution of catalyst made in DMF was added slowly. In the presence of Cu(I) as a co-catalyst *in situ* formation of Cu(I) acetylide, and its oxidative dimerization to diphenyldiacetylene (Glaser coupling)[32b,34c,d] may occur to some extent and its removal from the coupled product may require good separation strategy. Therefore the reaction in the absence of Cu as a co-catalyst is desirable.

Table 1 Optimization of reaction condition for Sonogashira coupling reaction catalyzed with **2**[a]

4-Br–C_6H_4–CHO + PhCCH → 4-CHO–C_6H_4–CCPh

Entry No.	Solvent	Base	Yield[c] (%)
1	DMA	K_2CO_3	86
2	DMF	K_2CO_3	89
3[b]	DMF	K_2CO_3	52
4	DMSO	KOH	--
5	DMF	K^{t}OBu	60
6	DMF	KOH	<10
7	Toluene	K_2CO_3	38
8	THF	K_2CO_3	--
9	THF	K^{t}OBu	--
10	Toluene	K^{t}OBu	47

[a]Reaction conditions: 0.5 mmol of 4-bromobenzaldehyde, 0.6 mmol of phenylacetylene, 1.0 mmol of base, 0.5 mol % complex **2**, 3 mL of dry solvent, N_2 atmosphere, temperature of bath 90 °C, reaction time 6 h, [b]reaction was performed in air for 12 h, [c]Isolated yield in %.

The best results were obtained with K_2CO_3 and DMF (Table 1; entry 2). In the coupling of electron-deficient aryl bromides, impurity with coupled product was found insignificant. In the case of deactivated (electron-rich) aryl halides, small impurities were noticed and removed from the coupled product with column chromatography. The crossed coupled product was not obtained in the absence of **1** or **2**, and reactant ArBr recovered, ruling out the possibility of palladium-free coupling. The present Sonogashira coupling protocol being amine free, may be labelled as somewhat environmentally friendly.[34c] The isolated yields of the cross-coupled products for various substrates are given in Table 2. For 4-bromobenzaldehyde the yield of the coupled product was ~90% when loading of **1** or **2** was 1 mol% (Table 2; entry 1). The yield reduced slightly on reducing the catalyst

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loading to half but increasing the reaction time (Table 2; entry 2). The yield of coupled product for 4-bromoacetophenone was 58 and 66% with 1.0-0.5 mol% loading of **2** and **1** respectively (Table 2, entry 4). The loading of 1.0-0.5 mol% of **1/2** as a

Table 2 Sonogashira coupling reaction catalyzed with complexes **1** and **2**[a]

4-R−C_6H_4−X + PhCCH → 4-R−C_6H_4−CCPh (X= Cl, Br, I)

Entry No.	Aryl halide	1			2		
		Mol%	t (h)	Yield[b]	Mol%	t (h)	Yield[b]
1	4-Bromobenzaldehyde	1	6	86	1	6	91
2	4-Bromobenzaldehyde	0.5	8	84	0.5	10	89
3	4-Bromobenzonitrile	1	8	91	1	8	95
4	4-Bromoacetophenone	0.5	12	66	1	12	58
5	4-Bromonitrobenzene	0.5	6	98	0.5	6	94
6	Bromobenzene	0.5	6	72	0.5	6	79
7	4-Bromotoluene	1	12	61	1	12	63
8	4-Iodoanisole	0.5	8	56	1	6	72
9	4-Bromoanisole	1	12	35	1	12	56
10	4-Chlorobenzaldehyde	2	12	28	2	12	31
11	4-Chloronitrobenzene	2	15	36	2	15	28

[a]Reaction conditions: 1.0 mmol of aryl halide, 1.1 mmol of phenylacetylene, 2.0 mmol of base (K_2CO_3), 3 mL dry DMF, temperature of bath 90 °C, N_2 atmosphere, [b]Isolated yield in %.

catalyst resulted in good conversion of 4-bromobenzonitrile and 4-bromonitrobenzene into coupled product (Table 2, entries 3 and 5). In the case of deactivated and neutral aryl halides (*viz.* 4-bromotoluene, bromobenzene and 4-bromoanisole and 4-iodoanisole), yield of the cross-coupled product was good with 1.0-0.5 mol% loading of **1** or **2** (Table 2, entries 6-9). The coupling of 4-bromoanisole and 4-bromotoluene, with alkyne was negligible when catalyst was 0.5 mol%. The increase in the amount of catalyst **1/2** up to 1 mol% results in significant coupling (Table 2; entries 7 and 9). 4-Iodoanisole and 4-bromobenzene gave good yield of the coupled product in 6-8 h with 0.5 mol% of **1** or **2** (Table 2; entries 6 and 8). For some substrates (Table 2, entries 1, 3 and 6-9), the activity of **1** was marginally lower than that of **2**. The activated 4-chlorobenzaldehyde and 4-chloronitrobenzene under optimum conditions for coupling with alkyne gave ~28-36 % yield with 2 mol% loading of **1**/**2** in 12-15 h (Table 2; entries 10 and 11).

The scope of **1** and **2** for catalysis of Sonogashira coupling was explored for other alkynes and results are summarized in Table 3. For this purpose ArBr/ArI were reacted with 1-ethynyl-4-(trifluoromethyl)benzene, 3-ethynyl- thiophene and ethynyltri-isopropylsilane under the optimized reaction conditions at 1 mol% of catalyst loading. The **2** having Se ligand was found somewhat more effective with these alkynes than **1,** as the conversions were good (Table 3; entries 1-6). Complex **1** gave good results with 1-ethynyl-4-(trifluoromethyl)benzene and 3-ethynyl-thiophene when they were reacted with iodobenzene (Table 3; entries 1 and 5). Both **1** and **2** were found ineffective with ethynyltri-isopropylsilane (Table 3; entries 7 and 8) as the reactivity of aliphatic alkynes is significantly lower than aromatic ones.

Table 3 Sonogashira coupling of various alkynes catalyzed with **1** and **2**[a]

R-4-C_6H_4-X + R'CCH → 4-R−C_6H_4−CCR' (X= Br, I)

Entry No.	Aryl halide	Alkyne	1	2
			Yield[b]	Yield[c]
1	Iodobenzene	1-Ethynyl-4-(trifluoromethyl)benzene	55	56
2	Bromobenzene		<10	41
3	4-Iodoacetophenone	3-Ethynyl-thiophene	43	51
4	4-Bromoacetophenone		27	47
5	Iodobenzene		61	70
6	Bromobenzene		50	65
7	4-Iodoacetophenone	Ethynyltri-isopropylsilane	--	15
8	4-Iodoanisole		--	14

[a]Reaction conditions: 1.0 mmol of aryl halide, 1.1 mmol of alkyne, 2.0 mmol of base (K_2CO_3), 2 mol% of catalysts **1** or **2**, 3 mL dry DMF, temperature of bath 90 °C, N_2 atmosphere, [b]Isolated yield in %.

The comparison of catalytic efficiency of **1**/**2** for Sonoagashira coupling with those of other Pd(II) complexes of symmentrical/ unsymmetrical pincers (in presence/absence of co-catalyst) is important. On using Pd(II) complex[40a] of a (P,C,P)-pincer as a catalyst good conversion can be achieved with its 5 mol% loading in presence of $ZnCl_2$ (10 mol%) as a co-catalyst) at 160 °C. Aminophosphine-based (P,C,P) pincer complex catalyzes Sonogashira Coupling under Cu and amine free conditions with 1-2 ppm loading of catalyst which much lower than our catalysts. Though the catalysis is carried out in environmentally more benign solvents but at higher temp (140 °C)[40b]. The protocols with **1**/ **2** are much milder than those of (P, C, P) pincer and free from the requirement of co-catalyst. In efficiency **1/2** is better than Pd(II) complexes of diimino (N,C,N)[41a] pincer and pyrazole based (N,C,N) pincer catalyzes Sonogashira coupling of ArI using amine as a solvent/base at moderate temperature but the catalyst loading is found to be only 0.1 mol% of Pd.[41b] (S,C,S) pincers[42a] as for good yield their 1-2 mol% loading is required and the reaction has to be run for 12-18 h. The Pd(II) complexes designed with unsymmetrical (P,N,F)[15] and (N,N,C) pincers[43] give good results at their 1-2 mol% loading (Cu-free) and moderate reaction temperature (55 and 80 °C respectively). Bis-NHCs based (C,N,C) pincers form Pd(II)[34b,42b,] complexes efficient for Sonoagashira coupling. The optimum loading is 0.1-1.7 mol% and comparable with that of the present catalysts. The catalytic activity of bis(Py-tzNHC)-Pd(II)[35a] complex is also comparable with those of **1** and **2**.

The homogeneous nature of catalyst **1/2** in Sonoagashira coupling was supported by mercury poisoning and two phase tests.[15,34b,35,47] In the representative Hg poisoning experiment, reaction of 4-bromobenzaldehyde with alkyne was catalyzed with **2** under optimum conditions (Table 2, entry 1), in the presence of a large excess of elemental Hg (Pd: Hg:: 1: 400) added at different time to the catalytic reaction as given in Table 4. The reaction was continued in each case with vigorous stirring after addition of Hg up to 8 h. The conversion into coupled product (monitored with ^{1}H NMR), did not reduce significantly on the addition of Hg at different stages and almost reached to maximum after 8 h of reaction. The results of the poisoning test reveal that catalytic process is not quenched in the presence by Hg.

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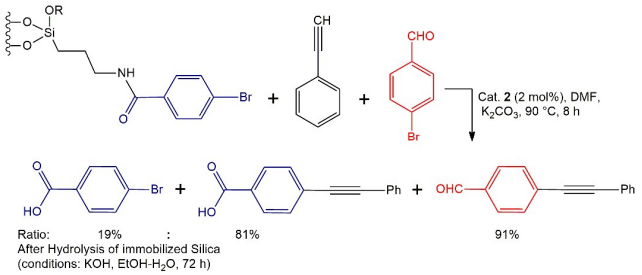
Table 4 Mercury poisoning experiment for Sonogashira coupling with **2**[a]

Entry No.	time	% Conversion at the time of Hg addition	% Conversion[b] after 8 h of Hg addition
1	0 h	Nil	83
1	0.5	15	77
2	2 h	47	78
3	3 h	81	85

[a]Reaction conditions: 4-bromobenzaldehyde (1.0 mmol), 1.1 mmol of phenylacetylene, 2.0 mmol of K_2CO_3, 3 mL DMF, temperature of bath 90 °C, N_2 atmosphere, 1 mol % complex **2**, [b]After standard workup of the whole reaction mixture).

The blackening of catalytic reaction mixture due to the formation of colloidal Pd was also not noticed. Therefore the formation of Pd cluster or NPs is unlikely in significant amount as indicated by Hg poisoning test.[15,34b] The two-phase test[47a,b] (also called three-phase test when catalyst is in solid form) as shown in Scheme 3 was also applied (See experimental details in ESI). 4-Bromobenzaldehyde and 4-bromobenzoic acid (as amide) immobilized on silica were treated with phenyl acetylene under optimum reaction conditions (given



Scheme 3 Two-phase test

in Table 2; entry 1) loading 2 mol% of complex **2** as catalyst. In case of heterogeneous catalysis, the substrate immobilized on solid-phase is not expected to be converted into a coupled product. In the present case anchored substrate is converted ~81% to the coupled product. This implies that the required Pd(0)[15,34b,23,24] is released from **1/2** and drives the catalysis homogeneously.

In solid state, complexes have good thermal stability as revealed by their m.p.'s. ^{1}H NMR spectrum of solution of **1/2** made in DMSO-d_6, on heating at 120 °C for 0.5 h, does not show any change. This indicates that on using **1/2** as a catalyst in Sonogashira coupling carried out at 90 °C their just thermal decomposition to new catalytic species is unlikely. The stability of complexes is also supported by thermogravimetric analysis (TGA) plots of complexes **1**−**4** (See Figs. S30–S33 in ESI), which do not have any sign of decomposition below 200 °C. Due to skeleton of the ligand present in the complex the weight loss in the temperature range 200−400 °C occurs. Thus overall good thermal stability of complexes **1** /**2** in conjunction with the results of poisoning and two-phase experiment suggests that the catalysis with **1/2** occurs homogeneously *via in situ* generated Pd(0)[15,34b,35a] which appears to be real catalytic species for this coupling. However, it may be protected with ligands **L1**/**L2** or their fragments in the present case.[23,24]

DFT calculations

The density functional theory (DFT) calculations made for **1** and **2** gave a qualitative idea of the lowest energy configuration and frontier orbitals of the complexes. For both the complexes **1** and **2,** the HOMO−1 (highest occupied molecular orbital) is contributed by Pd *d*-orbital, *p*-orbitals of S or Se, chlorine and oxygen as shown in Fig. 7. The complex **2** having lower value HOMO−LUMO energy gap[48] is expected to be a better catalyst than **1** (Fig. 7), as found experimentally in case of present Sonogashira coupling reactions, of course marginally only.

The experimentally observed and calculated (by DFT) distances for Pd−Cl, Pd−N, and Pd−O bonds are consistent. Some variations exist between calculated and observed Pd−E (E = S/Se) bond distances but it is not exceptional.[35b] The DFT-calculated and experimentally found bond angles are also close to each other (See Tables S5 and Table S1-S4 in ESI).

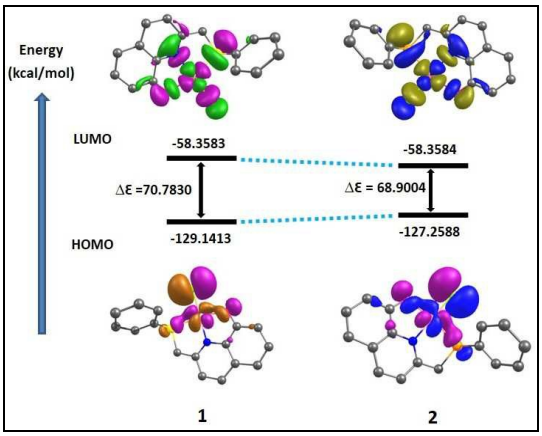


Fig. 7 Frontier molecular orbital diagrams of complexes **1**−**2**

Conclusions

Unsymmetrical pincer ligands (O^-, N, E-type) where E=S/Se, having quinoline as a core unit and their palladium complexes of the type [Pd(**L**−H)Cl] (**1**−**4**) (where **L** = **L1**−**L4**) have been synthesized and characterized by multinuclear NMR, IR and mass spectrometry. Single-crystal structures of **L1**, complexes **1** and **2** were solved. The geometry around Pd in **1** and **2** is distorted square planar. Some interesting intermolecular rare week interactions (such as C–H···Pd and Se···Cl) were found in **1** and **2** which stabilizes their crystal structures. The **1** and **2** act as a catalyst for amine and Cu-free Sonogashira coupling. The catalyst loading 0.5−1.0 mol% is optimum for the coupling of aryl halides with terminal alkynes viz phenyl acetylene, 1-ethynyl-4-(trifluoromethyl)benzene, 3-ethynyl- thiophene and ethynyltri-isopropylsilane. The results of DFT calculations support the experimental observation that Pd(II) complex **2** (Se ligated) is marginally better for Sonogashira coupling than the complex **1** (sulfur analogue). The experimentally observed and theoretically calculated (by DFT) bond lengths and angles are consistent.

Experimental

Diphenyl diselenide, sodium borohydride, 2-(hydroxymethyl)-

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DOI: 10.1039/C7NJ00067G

quinolin-8-ol, phenyl acetylene, 1-Ethynyl-4-(trifluoromethyl)benzene, 3-Ethynyl-thiophene and Ethynyltri-isopropylsilane were used as received from Sigma-Aldrich (USA). For thiophenol, sulfur powder, N,N-dimethylamine hydrochloride, pyrrolidine and aryl halides local resources were used. Bis(acetonitrile)dichloropalladium(II) was prepared by a known procedure.[49] The ligands, their precursors and coupled products were purified by column chromatography on silica gel (60−120 mesh). *n*-Hexane and its mixtures with chloroform/ethyl acetate in varying proportions were used as eluent. Glassware dried under ambient condition was used for all reactions. Melting points were determined by taking the sample in a glass capillary sealed at one end, with an apparatus equipped with electric heating and reported as such. The commercially available nitrogen gas was purified by passing it successively through traps containing solutions of alkaline anthraquinone sodium dithionite, alkaline pyrogallol, conc. H_2SO_4 and KOH pellets. A nitrogen atmosphere was created using Schlenk techniques.

Physical measurements

Bruker Spectrospin DPX 300 NMR spectrometer was used to record ^{1}H, ^{13}C{^{1}H} and ^{77}Se{^{1}H} NMR spectra at 300.13, 75.47 and 57.24 MHz respectively. The chemical shifts are reported relative to internal standards. ^{13}C DEPT NMR was used routinely to determine the number of hydrogen atoms linked to a carbon atom. IR spectra (4000−400 cm^{-1}) in KBr were recorded on a Nicolet Protége 460 FT-IR spectrometer. Elemental analyses were carried out with a Perkin–Elmer 2400 Series II C, H, N analyzer. Thermogravimetric analyses (TGA) (up to 700 ºC) were carried out on a Perkin-Elmer Pyris Diamond thermogravimetric analyzer (N 535-0010).

Bruker AXS SMART Apex CCD diffractometer with Mo-Kα (0.71073 Å) source was used to collect single-crystal data. The software SADABS[50] was used for absorption correction and SHELXTL for space group, structure determination, and refinement.[51] For hydrogen atoms included in idealized positions isotropic thermal parameters were set at 1.2 times those of the carbon atoms to which they were bonded The least-squares refinement cycles on F^2 were performed until the model converged. Bruker Micro TOF-Q II machine using electron spray ionization (10 eV, 180 °C source temperature and sodium formate as a calibrant) was used for high-resolution mass spectral (HR-MS) measurements on solutions made in CH_3CN. HR-MS was simulated using program developed by Scientific Instrument Services.[52] All DFT calculations were carried out at the Supercomputing Facility for Bioinformatics and Computational Biology, IIT Delhi, with the GAUSSIAN-03[53] programs. The geometries of complexes **1**−**2** were optimized at the B3LYP[54] level using an SDD basis set for metal atoms and chalcogen and 6-31G* basis sets for C, N, and H. Geometry optimization was carried out without any symmetry restriction with X-ray coordinates of the molecule. Harmonic force constants have been computed at the optimized geometries to characterize the stationary points as minima. The molecular orbital plots are created using the Chemcraft program package (http://www.chemcraftprog.com).

Syntheses of L1 and L2: 2-(Bromomethyl)quinolin-8-yl acetate (0.560 g, 2.0 mmol) prepared from 2-(hydroxymethyl)-quinolin-8-ol by reported method[55] was dissolved in ethanol. A solution of PhSNa/PhSeNa (2.0 mmol) generated *in situ* by the reaction of NaOH with thiophenol/$NaBH_4$ reduction of diphenyldiselenide at 70 °C under nitrogen atmosphere was added dropwise. The reaction mixture was heated at 70 °C for 8 h and cooled to room temperature. Its solvent was reduced to 4-5 mL on a rotary evaporator and mixed with 50 mL of water. The mixture was neutralized with 10% HCl and extracted with chloroform (3 × 20 mL). The organic extracts were combined, washed with water (3 × 30 mL) and dried over anhydrous sodium sulfate. Its solvent was evaporated off on a rotary evaporator resulting **L1/L2** as yellow solid. Further purification was done by column chromatography on silica gel using hexane-chloroform mixture (95:5) as an eluent.

L1: 2-(phenylthiomethyl)quinolin-8-ol, Light yellow crystalline solid, Yield: (0.485 g, 91%); m.p. 78 °C; Anal. Found: C, 71.85; H, 4.80; N, 5.75 %. Calcd. for [$C_{16}H_{13}NOS$]: C, 71.88; H, 4.90; N, 5.64 %. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS); δ (ppm): 4.39 (s, 2H, H_{10}), 7.12−7.17 (m, 1H), 7.19−7.28 (m, 4H), 7.34−7.42 (m, 3H), 7.49 (d, 1H, H_6, J= 8.4), 8.04 (d, 1H, H_7, J= 8.7). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 40.9 (C10), 110.1, 117.5, 121.6, 126.6, 127.2 (C5), 127.4, 128.9 (C13), 130.1 (C12), 135.3 (C8), 136.8, 137.3, 151.9 (C9), 156.0 (C_q1). IR (KBr; cm^{-1}): 478 (w), 570 (w), 746 [m; ν_{C-H} (*bending*)], 1134 (m; ν_{C-O}), 1238 (m), 1361 [m; ν_{C-H} (*rocking*)],1437 [m; ν_{C-C} (*aromatic*)], 1505 [m; ν_{C-H} (*aromatic*)], 1632 [w; *overtones*], 2914 [s; ν_{C-H} (*aliphatic*)], 3051 [m; ν_{C-H} (*aromatic*)], 3401 [b; ν_{O-H}]. HR-MS [M + H] (m/z) = 268.0790; calcd. value for $C_{16}H_{14}NOS$ = 268.0791 (error δ : 0.4 ppm).

L2: 2-(phenylselenomethyl)quinolin-8-ol, Yellow solid, Yield: (0.554 g, 88%); m.p. 73 °C; Anal. Found: C, 56.15; H, 4.17; N, 6.16 %. Calcd for [$C_{16}H_{13}NOSe$]: C, 56.22; H, 3.97; N, 6.04 %. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS); δ (ppm): 4.28 (s, 2H, H_{10}), 7.03−7.06 (m, 1H), 7.15−7.20 (m, 3H), 7.26−7.34 (m, 3H), 7.40−7.43 (m, 2H), 7.96 (d, 1H, H_7, J = 8.7). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 33.8 (C10), 110.1, 117.5, 122.0, 127.0 (C5), 127.3, 127.8 (C13), 128.9, 131.6 (C11), 133.9 (C12), 136.7, 134.4 (C8), 151.9 (C9), 157.2 (C1). ^{77}Se{^{1}H} NMR (57 MHz, $CDCl_3$, 25 °C, Me_2Se): δ (ppm) 372.1. IR (KBr; cm^{-1}): 476 (w), 529 (w), 774 [m; ν_{C-H} (*bending*)], 1071 (m; ν_{C-O}), 1134 (w), 1333 [m; ν_{C-H} (*rocking*)], 1421 [m; ν_{C-C} (*aromatic*)], 1517 [m; ν_{C-H} (*aromatic*)], 1607 [w; *overtones*], 2923 [s; ν_{C-H} (*aliphatic*)], 3043 [m; ν_{C-H} (*aromatic*)], 3436 [br; ν_{O-H}]. HR-MS [M + H] (m/z) = 316.025047; calcd. value for $C_{16}H_{14}NOSe$ = 316.023571 (error δ: -4.7 ppm).

Syntheses of L3: 2-Formylquinolin-8-yl acetate (4.30 g, 2.0 mmol) prepared from 2-(hydroxymethyl)quinolin-8-ol as reported earlier,[56] was taken in round bottom flask with sulfur powder (0.086 g, 3.0 mmol), CH_3COONa (0.246 g, 3.0 mmol), and N,N-dimethylamine hydrochloride (0.243 g, 3.0 mmol). The mixture was heated at 100 °C in presence of 5 mL of DMF. It turned dark brown after sometime under ambient conditions. The heating was continued further for 6 h. Thereafter this mixture was cooled to

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DOI: 10.1039/C7NJ00067G

room temperature and poured into cold water (~5 ºC) with stirring. The stirring was continued until a yellow precipitate appeared. It was separated by filtering through G4 crucible. The solid residue left in the crucible was dissolved in $CHCl_3$ (30 mL) and washed with 20 mL of water (only once). The organic phase, so obtained, was dried over anhydrous sodium sulfate and its solvent was evaporated off on a rotary evaporator resulting **L3** as a yellow solid. Its further purification was done by column chromatography on silica gel using hexane-ethyl acetate mixture (95:5) as an eluent.

L3: 2-(N,N-dimethylthiocarbamoyl) quinolin-8-ol, Light yellow solid, Yield: (0.431 g, 93%); m.p. 122 °C; Anal. Found: C, 61.88; H, 5.01; N, 11.98 %. Calcd. for [$C_{12}H_{12}N_2OS$]: C, 62.04; H, 5.21; N, 12.06 %. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS); δ (ppm): 3.22 (s, 3H, H_{12}), 3.65 (s, 3H, H_{11}) 7.16−7.19 (m, 1H), 7.30−7.33 (m, 1H), 7.43−7.48 (m, 1H), 7.69 (d, 1H, H_6, *J*= 8.4 *Hz*), 7.80−8.08 (br s, 1H, OH), 8.17 (d, 1H, H_7, *J*= 8.7). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 42.9 (C12), 43.7 (C11), 110.9, 107.7, 121.4, 127.5 (C5), 128.3, 135.9 (C8), 136.9, 152.1 (C9), 156.0 (C1), 197.3 (C10).
^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS); δ (ppm): 3.21 (s, 3H, H_{12}), 3.58 (s, 3H, H_{11}), 7.12 (d, 1H, *J*= 6.9 *Hz*), 7.39−7.47 (m, 2H), 7.61 (d, 1H, H_6, J= 9 *Hz*), 8.35 (d, 1H, H_7, *J*= 8.4 *Hz*), 9.76 (s, 1H, OH). IR (KBr; cm^{-1}): 508 (w), 549 (w), 749 [m; ν_{C-H} (*bending*)], 1146 (m; ν_{C-O}), 1239 (m), 1318 [m; ν_{C-H} (*rocking*)], 1453 [m; ν_{C-C} (*aromatic*)], 1535 [m; ν_{C-H} (*aromatic*)], 1628 [w; *overtones*], 2928 [s; ν_{C-H} (*aliphatic*)], 3053 [m; ν_{C-H} (*aromatic*)], 3438 [br; ν_{O-H}]. HR-MS [M + H] (m/z) = 233.074558; calcd. value for $C_{12}H_{13}N_2OS$ = 233.074310 (error δ : 1.1 ppm).

Syntheses of L4: In a round bottom flask 2-formylquinolin-8-yl acetate (4.30 g, 2.0 mmol), sulfur powder (0.086 g, 3.0 mmol), pyrrolidine (0.221 g, 3.0 mmol) and 5 mL DMF were taken. The mixture was heated for 30 min at 100 °C with protection from moisture. The temperature was maintained for 6 h by heating it further. On completion of the reaction, the resulting dark brown solution was cooled to room temperature. Cold water (40 mL) was poured into the reaction mixture with stirring resulting in a dark yellow precipitate. After a work up similar to the one used for **L3,** dark yellow solid **(L4)** was obtained.

L4: 2-(pyrrolidin-1-ylthiocarbamoyl) quinolin-8-ol Dark yellow solid, Yield: (0.474 g, 92%); m.p. 114 °C; Anal. Found: C, 64.85; H, 5.32; N, 10.66 %. Calcd for [$C_{14}H_{14}N_2OS$]: C, 65.09; H, 5.46; N, 10.84 %. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS); δ (ppm): 2.01−2.14 (m, 4H, H_{12-13}), 4.04 (t, 2H, H_{11}, J= 6.3 *Hz*), 3.68 (t, 2H, H_{14}, J= 6.0 *Hz*), 7.17−7.19 (d, 1H, H_4, J= 6.9 *Hz*), 7.33 (d, 1H, H_2, J= 8.1 *Hz*), 7.44−7.49 (m, 1H, H_3), 7.82 (d, 1H, H_6, *J*= 8.4 *Hz*), 8.17 (d, 1H, H_7, *J*= 8.4). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 24.2 (C13), 26.4 (C12), 53.4 (C14), 53.5 (C11), 110.8, 117.8, 121.8, 127.8 (C5), 128.5, 135.8, 136.8 (C8), 152.2 (C9), 156.2 (C1), 193.1(C10).
^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS); δ (ppm): 1.94−2.02 (m, 4H, H_{12-13}), 3.70−3.72 (m, 2H, H_{14}), 3.84−3.86 (m, 2H, H_{11}), 7.10-7.12 (m, 1H), 7.40−7.49 (m, 2H), 7.71−7.73 (m, 1H), 8.31−8.35 (m, 2H), 9.74 (s, 1H, -OH). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm): 24.3 (C13), 26.5 (C12), 53.4 (C11), 53.8 (C14), 112.7, 118.0, 122.0, 128.6 (C5), 128.7, 136.5 (C8), 137.0, 154.0 (C9), 156.6 (C1), 192.4 (C10). IR (KBr; cm^{-1}): 465 (w), 507 (w), 754 [m; ν_{C-H} (*bending*)], 1109 (m; ν_{C-O}), 1240 (m), 1320 [m; ν_{C-H} (*rocking*)], 1395 [m; ν_{C-C} (*aromatic*)], 1489 [m; ν_{C-H} (*aromatic*)], 1561 [m; ν_{C-H} (*aromatic*)], 1631 [w; ν_{C-H} *overtones*], 2968 [s; ν_{C-H} (*aliphatic*)], 3042 [m; ν_{C-H} (*aromatic*)], 3375 [br; ν_{O-H}]. HR-MS [M + H] (m/z) = 259.089806; calcd. value for $C_{14}H_{15}N_2OS$ = 259.089961 (error δ : -0.6 ppm).

Synthesis of Pd-complexes 1 and 2: To a solution of **L1** (0.106 g, 0.4 mmol)/**L2** (0.126 g, 0.4 mmol) in acetone (5 mL) was added a solution of [Na_2PdCl_4] (0.120 g, 0.41 mmol) in water (2 mL). The appearance of pale yellow colour indicated the formation of the complex. The reaction mixture was stirred for 6 h at room temperature. After completion of the reaction, the solvent was removed under reduced pressure on a rotary evaporator and the residue left in the flask was mixed with water (20 mL). The mixture was extracted with $CHCl_3$ (3 × 10 mL). The organic layers were combined together, washed with water (20 mL) and dried over anhydrous sodium sulfate. Its volume was reduced (~1 mL) with a rotary evaporator and hexane was added till precipitation of the complex as a yellow solid was complete. The precipitate was filtered and dried in *vacuo*.

Complex 1; Yellow solid, Yield: (0.138 g, 85%); m.p. 178 °C (d); Anal. Found: C, 29.91; H, 1.96; N, 2.02 %. Calcd for [$C_{16}H_{12}ClNOPdS$]: C, 30.07; H, 2.17; N, 2.30 %. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS); δ (ppm): 5.04−5.63 (br m, 2H, H_{10}), 6.80 (d, 1H, *J*= 8.1 *Hz*), 7.10 (d, 1H, *J*= 7.8 *Hz*), 7.40−7.45 (m, 1H), 7.49−7.58 (m, 3H), 7.61 (d, 1H, H_6, J= 8.7 *Hz*), 7.91−7.94 (m, 2H), 8.49 (d, 1H, H_7, *J*= 8.7 *Hz*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 53.3 (C10), 111.7, 114.5, 119.3, 128.8 (C5), 129.1 (C11), 130.0 (C6), 130.5, 130.7, 130.9 138.5, 142.3 (C8), 157.2 (C9), 170.8 (C1). IR (KBr; cm^{-1}): 457 (w), 508 (w), 756 [m; ν_{C-H} (*bending*)], 1018 (m; ν_{C-O}), 1197 (m; ν_{C-C}), 1373 [m; ν_{C-H} (*rocking*)],1439 [m; ν_{C-C} (*aromatic*)], 1587 [m; ν_{C-H} (*aromatic*)], 1650 [w; ν_{C-H}; *overtones*], 2922 [s; ν_{C-H} (*aliphatic*)], 3056 [m; ν_{C-H} (*aromatic*)], 3432 [br; ν_{O-H}]. HR-MS [M + Na] (m/z) = 429.9250; calcd. value for $C_{16}H_{12}ClNNaOPdS$ = 429.9258 (error δ : 1.8 ppm).

Complex 2: Yellow solid, Yield: (0.148 g, 82%); m.p. 172 °C (d); Anal. Found: C, 38.81; H, 2.61; N, 2.58 %. Calcd for [$C_{16}H_{12}ClNOPdSe$]: C, 38.91; H, 2.66; N, 2.60 %. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS); δ (ppm): 4.84−5.44 (br m, 2H, H_{10}), 6.79 (d, 1H, *J*= 8.1 *Hz*), 7.03 (d, 1H, *J*= 7.8 *Hz*), 7.39−7.42 (m, 1H), 7.48−7.56 (m, 4H), 8.01−8.03 (m, 2H), 8.41 (d, 1H, H_7, *J*= 8.7 *Hz*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 45.5 (C10), 112.1, 114.9, 120.8, 128.6 (C5), 129.6 (C11), 130.6 (C13), 130.7, 131.0, 132.6 (C12), 138.6, 143.5 (C8), 158.9 (C9), 171.1 (C1). $^{77}Se\{^1H\}$ NMR (57 MHz, $CDCl_3$, 25 °C, Me_2Se): δ (ppm) 406.0. IR (KBr; cm^{-1}): 440 (w), 521 (w), 741 [m; ν_{C-H} (*bending*)], 1020 (m; ν_{C-O}), 1154 (m; ν_{C-C}), 1276 (w), 1361 [m; ν_{C-H} (*rocking*)], 1444 [m; ν_{C-C} (*aromatic*)], 1564 [m; ν_{C-H} (*aromatic*)], 1632 [w; ν_{C-H}; *overtones*], 2919 [s; ν_{C-H} (*aliphatic*)], 3053 [m; ν_{C-H} (*aromatic*)], 3436 [br; ν_{O-H}]. HR-MS [M + Na] (m/z) = 477.8680; calcd. value for $C_{16}H_{12}ClNNaOPdS$ =

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DOI: 10.1039/C7NJ00067G

477.8706 (error δ : 5.4 ppm).

Syntheses of palladium complexes 3 and 4: To a solution of **L3** (0.092 g, 0.4 mmol)/**L4** (0.103 g, 0.4 mmol) in acetonitrile (5 mL) was added a solution of bis(acetonitrile) dichloropalladium(II) (0.103 g, 0.4 mmol). The appearance of dark yellow-green colour indicated the formation of the complex. The reaction mixture was stirred for 4 h at room temperature. After completion of the reaction, the solvent was removed under reduced pressure and the residue left in the flask was mixed with water (20 mL). The complex was extracted with $CHCl_3$ (3 × 10 mL) and extracts combined together. The combined extract was washed with water (2 × 20 mL) and dried over anhydrous sodium sulfate. Its volume was reduced to ~1 mL with a rotary evaporator and mixed with *n*-hexane to complete precipitation of the complex. The Pd(II) complex precipitated as yellow solid was filtered and dried *vacuo*.

Complex 3: Yellow solid, Yield: (0.128 g, 79%); m.p. 187 °C (d); Anal. Found: C, 43.32; H, 2.58; N, 5.31 %. calcd for $[C_{12}H_{11}ClN_2OPdS]$: C, 43.45; H, 2.60; N, 5.40 %. ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS); δ (ppm): 3.71 (s, 3H, H_{12}), 3.97 (s, 3H, H_{11}), 6.67 (d, 1H, H_4, *J*= 7.8 *Hz*), 6.98 (d, 1H, H_2, *J*= 6.9 *Hz*), 7.50-7.52- (m, 1H, H_3), 7.98 (d, 1H, H_6, *J*= 9.6 *Hz*), 8.49 (d, 1H, H_7, *J*= 9.0 *Hz*). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm): 47.7 (C12), 48.9 (C11), 111.3, 115.6, 122.7, 132.7, 136.2 (C5), 138.5, 145.5 (C8), 147.2 (C9), 173.4 (C1), 192.7 (C10). IR (KBr; cm^{-1}): 515 (w), 548 (w), 762 [m; ν_{C-H} (*bending*)], 1098 (m; ν_{C-O}), 1339 (w), 1378 [m; ν_{C-H} (*rocking*)], 1499 [m; ν_{C-C} (*aromatic*)], 1541 [m; ν_{C-H} (*aromatic*)], 1621 [w; ν_{C-H} *overtones*], 2960 [s; ν_{C-H} (*aliphatic*)], 3048 [m; ν_{C-H} (*aromatic*)]. HR-MS [(M – Cl) .H_2O] (m/z) = 354.9744; calcd. value for $C_{12}H_{13}N_2O_2PdS$ = 354.9731 (error δ : -3.7 ppm).

Complex 4: Yellow solid, Yield: (0.134 g, 75%); m.p. 181 °C (d); Anal. Found: C, 41.88; H, 3.25; N, 6.98 %. Calcd for $[C_{14}H_{13}ClN_2OPdS]$: C, 42.12; H, 3.28; N, 7.02 %. ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS); δ (ppm): 2.09−2.16 (m, 4H, H_{12-13}), 4.02−4.07 (m, 2H, H_{14}), 4.42−4.47 (m, 2H, H_{11}), 6.65 (d, 1H, H_4, *J* = 7.8 *Hz*), 6.95 (d, 1H, H_2, *J* = 7.5 *Hz*), 7.51 (m, 1H, H_3, *J* = 7.8 *Hz*), 8.01 (d, 1H, H_6, *J* = 9 *Hz*), 8.45 (d, 1H, H_7, *J* = 9.3 *Hz*). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm): 23.7 (C13), 26.7 (C12), 57.5 (C14), 57.6 (C11), 111.4, 115.5, 121.6, 132.6 (C5), 136.0, 138.4, 145.2 (C8), 146.8 (C9), 173.1 (C1), 188.3 (C10). IR (KBr; cm^{-1}): 536 (w), 589 (w), 762 [m; ν_{C-H} (*bending*)], 1011 (m; ν_{C-O}), 1228 (m), 1339 [m; ν_{C-H} (*rocking*)], 1441 [m; ν_{C-C} (*aromatic*)], 1548 [m; ν_{C-H} (*aromatic*)], 1657 [w; ν_{C-H} *overtones*], 2863 [s; ν_{C-H} (*aliphatic*)], 3023 [m; ν_{C-H} (*aromatic*)], 3416 [br; ν_{O-H}]. HR-MS [(M – Cl) .H_2O] (m/z) = 380.9937; calcd. value for $C_{14}H_{15}N_2O_2PdS$ = 380.9889 (error δ : -12.7 ppm).

General procedure for Sonogashira coupling reaction catalyzed with 1 and 2

A three neck round bottom flask was charged with aryl halide (1.0 mmol), alkyne (1.1 mmol) and K_2CO_3 (0.276 g, 2.0 mmol) and 3 mL of dry DMF. The mixture was degassed with N_2 to protect it from moisture. Thereafter solution of palladium complex **1** or **2** (0.5–1 mol%) (0.5-1 mol%) made in DMF was added and the mixture heated at 90° C for an optimum time under nitrogen atmosphere. The progress of reaction was monitored by ^{1}H NMR. When maximum conversion of ArX into coupled product occurred, the reaction mixture was cooled to room temperature and extracted with ethylacetate (2×10 mL) and washed with water (2×15 mL). After drying over anhydrous Na_2SO_4, the solvent of organic phase was evaporated off with rotary evaporator. The resulting residue was purified by column chromatography on silica gel (60−120 mesh) using *n*-hexane and its mixtures with chloroform/ethyl acetate in varying proportions as eluent. The yields are reported in Table 2. The authentication by matching ^{1}H and ^{13}C{^{1}H} NMR with literature data[15,35] was carried out for each coupled product. The spectra are given in ESI.

Acknowledgements

Council of Scientific and Industrial Research, Department of Atomic Energy (BRNS), and Nanomission, Department of Science and Technology, India supported the work through the award of projects. SK, and FS thank UGC (India).

Notes and References

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† Electronic Supplementary Information (ESI) available: Spectral data of **L1**–**L4** and **1**–**4**; single crystal data of **L1** and complexes **1** and **2** (CCDC 1523404–1523406), See DOI: 10.1039/b000000x/

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Oxine based unsymmetrical (O^-, N, S/Se) pincer ligands and their palladium(II) complexes: synthesis, structural aspects and applications as catalyst in amine and copper-free Sonogashira coupling

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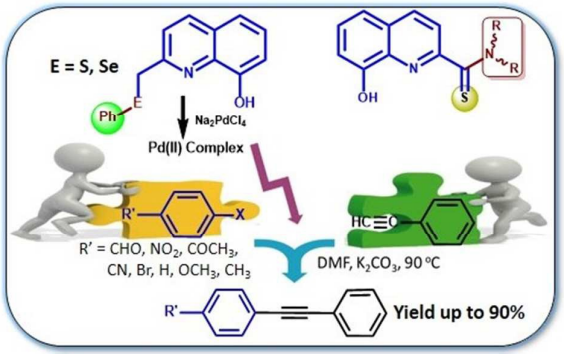

Newly synthesized and characterized (single crystal structure),[Pd(O^-, N, S/Se)Cl], efficiently catalyse Sonogashira coupling of ArX at 0.5-1 mol%.