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ARTICLE TYPE

"Click" generated 1,2,3-triazole based organosulfur/selenium ligands and their Pd(II) and Ru(II) complexes: their synthesis, structure and catalytic applications

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1-(2,6-Diisopropylphenyl)-4-(phenylthio/selenomethyl)-1*H*-1,2,3-triazole (**L1**/**L2**) synthesized by 'Click' reaction, on treatment for 5 h with $[Pd(CH_3CN)_2Cl_2]$ and 8 h with $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)]_2$ (followed by reaction with NH_4PF_6), at room temperature results in complexes $[Pd(\mathbf{L})Cl_2]$ (**1** and **2)** and $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{L})Cl]PF_6$ (**3** and **4**) (**L** = **L1** or **L2**) respectively. The four complexes (**1**−**4)** and ligands (**L1** and **L2)** were authenticated with ^1H, $^{13}C\{^1H\}$ and $^{77}Se\{^1H\}$ NMR and high resolution mass spectrometry. Single crystal structures of **1**−**4** were solved. The geometry of Pd in **1** and **2** is distorted square planar. The Pd–S and Pd–Se bond distances in **1** and **2** are 2.277(3) and 2.384(6) Å respectively. In **3** and **4** there is a pseudo octahedral "piano-stool" type disposition of donor atoms around Ru. The Ru−S and Ru−Se bond lengths in **3** and **4** are 2.3728(12) and 2.4741(6) Å respectively. Catalytic activity of the complexes **1** and **2** was explored for Suzuki−Miyaura coupling (SMC) in water and Sonogashira coupling reactions. For various aryl bromides including deactivated ones the complexes **1** and **2** were found efficient for both the couplings. The optimum loading of **1** and **2** required as a catalyst for both the coupling reactions is of the order of 0.001−2 mol% of Pd. For SMC no additive or phase transfer catalyst was added. For catalysis of transfer hydrogenation (TH) of aldehydes and ketones both half sandwich Ru(II) complexes **3** and **4** were explored. Their optimum loading as catalyst was found to be 0.1−0.4 mol % of Ru. In TH both water used as a solvent, and glycerol as a hydrogen source are environmentally friendly. The catalytic efficiency of both **3** and **4** is comparable with those of other catalysts reported for TH carried out with 2-propanol or glycerol as a H-source. The **1** having sulfur ligand is more efficient than **2** (Se analog) for both SMC and Sonogashira coupling. The activity of **3** and **4** for TH is in the order Se > S.

Introduction

Copper(I) catalyzed 1,3-dipolar cycloaddition reaction of terminal alkyne with organic azide to form 1,4-disubstituted 1,2,3-triazole called 'Click' reaction has facilitated synthesis of various triazole compounds needed in modern chemistry and biology,[1-5] including ligands with triazole core.[6-8] The advantages *viz*. mild reaction conditions, excellent functional group tolerance, selectivity and simple work up procedure which results in quantitative yield, give 'Click' reaction an edge over other protocols.[1a-b,7b-c] 1,2,3-Triazole functionalized with donor atom containing groups coordinates in conjunction with two nitrogen atoms and one carbon atom of the heterocyclic ring. Thus functionalized 1,2,3-triazoles constitute a class of versatile ligands for a variety of metal ions.[8a,b,c,e,i,k] Their several metal complexes including those of palladium(II) and ruthenium(II) are known for promising activity as a catalyst for organic transformations.[5,9-12] The ligand architecture is considered important to design an efficient catalyst. Consequently replacement of benzene framework with 1,2,3-triazole backbone in ligands found rewarding is also envisaged as worth exploring further.[6,9,12] Thus 1,2,3-triazole based organochalcogen ligands were designed and their metal complexes found to show promising catalytic efficiency for various organic reactions.[11a,b,12] However, it may also be partially attributed to strong electron donating ability of S/Se.[11a,b,12] The incorporation of the bulky 2,6-diisopropylphenyl (dipp) group as a substituent in 1,2,3-triazole based ligand may provide kinetic stability to the free ligand[13] and more electron density to metal center[14a] in its complex. The presence of electron rich donor site in the ligand strengthens its coordination with metal and increases electron density on it. High electron density on metal may reduce activation energy for oxidative addition and in turn, gives high efficiency to complex catalyst functioning through this step.[14b] It is known that introduction of a dipp group in N-heterocyclic carbenes (NHC's) leads to a catalyst of high activity for Suzuki coupling of aryl/heteroaryl chlorides in water.[15] Thus introduction of 2,6-diisopropyl phenyl group in a triazole based ligand is worth exploring and sulfated/selenated 1,2,3-triazole based ligands (**L1** and **L2**) and their Pd(II) and Ru(II) complexes **1**−**4** have been synthesized and explored for Suzuki−Miyaura and Sonogashira coupling and transfer hydrogenation(TH).

The known catalysts for the two coupling reactions include palladium(II) complexes of several phosphorus, carbene, imine, thiocarboxamide/semicarbazone, palladacyles and pincer

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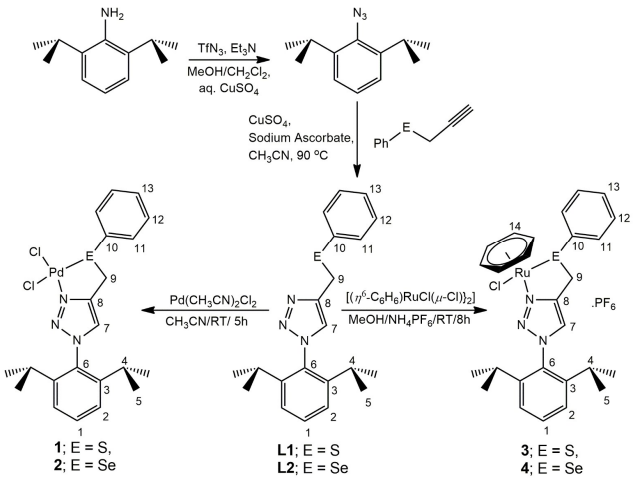
ligands.[16-22] They are also reported to function *via in situ* formation of Pd(0) species (discrete or nano-sized).[23-25] On 1,2,3-triazole-based organosulfur/selenium ligands and applications of their metal complexes as catalysts there are limited reports.[11a,b,d,12] Lone report on SMC[12] using such a complex is from our group but for Sonogashira coupling none is in our knowledge. Palladium(II) complexes (**1** and **2**) of sterically encumbered 1,2,3-triazole-based organosulfur/selenium ligands reported herein catalyze SMC in water with good yield in short time.

Ruthenium(II) complex catalyzed transfer hydrogenation (TH)[26] using organic solvents as a H-source, avoids use of hazardous H_2 as a reducing agent.[27] The organic solvents generally used as a H-source cum solvent are, 2-propanol, formic acid, glycerol and cyclopentanol. The BINAP, 1,2-diamines and PR_3, pyridyl/bipyridyl ligands, benzimidazoles, thioamide and NHCs are among the ligands forming complexes with Ru(II), suitable to catalyze TH.[28-32] Few Ru(II) complexes of organochalcogen ligands promising for catalytic TH have been reported by our research group.[33] 2-Propanol and in some cases glycerol were used as a H-source and solvent in them.[33] The Ru(II) complexes of 1,2,3-triazole based organosulfur/selenium ligands for TH[11a,b] are reported scantly and the present ones (**3**/**4**) are probably the first examples of such complexes explored to catalyze TH in water. The biodegradable glycerol is attractive due its low cost, ready availability, renewability[34,35] and its ability to dissolve bases, transition-metal complexes and organic compounds even when they are sparingly soluble in water.[35] The protocol based on **3**/**4** and a nontoxic H-source glycerol in aqueous medium for TH is also partially green.

Results and discussion

Syntheses of **L1** and **L2,** and their complexes with Pd(II) and Ru(II) (**1**−**4**) are summarized in Scheme 1. The possibility of thermal cycloaddition reaction to give **L1**/**L2** is ruled out as we do not get 1,5-disubstited-1,2,3-triazole as an additional product. Thus ligand formation is *via* 'Click' reaction carried out at 90 ºC, as at room temperature yield was 25% only. The presence of sterically demanding isopropyl groups probably make the reaction temperature high. The complexes **3** and **4** are formed by chloro bridge cleavage of $[(\eta^6\text{-benzene})RuCl(\mu\text{-}Cl)]_2$ followed by reaction with 1-(2,6-diisopropylphenyl)-4-(phenylthio/selenomethyl)-1*H*-1,2,3-triazole (**L1**/**L2**) at room temperature, facilitated by anion exchange with NH_4PF_6. The complexes **1** and **2** moderately soluble in $CHCl_3$, CH_3OH and CH_3CN show good solubility in DMSO and DMF. Half sandwich Ru(II) complexes, **3** and **4** are soluble in CH_3CN. Elemental analyses, multinuclear NMR, IR and high-resolution mass spectrometry (HR-MS) consistent with simulated HR-MS (see Figs. S1-S20 in ESI) have authenticated each compound. Single crystal structures of **1**−**4** have been established with X-ray crystallography. In TGA plots of all complexes (see Figs. S22-S25 in ESI) there is no decomposition before 200 ºC, indicating their suitability for high temperature catalytic reactions.



Scheme 1 Syntheses of ligands and their complexes

NMR spectra. NMR spectra of **L1**−**L2** and **1**−**4** are consistent with their molecular structures depicted in Scheme 1 and given in ESI (Figs. S1−S15). The signal in the $^{77}Se\{^1H\}$ NMR spectrum of **L2** (366.3 ppm) is at lower frequency with respect to that of selenated alkyne (375.8 ppm). The signals in $^{77}Se\{^1H\}$ NMR spectra of **2** and **4** appear at higher frequency (100.2 and 85.2 ppm respectively) relative to corresponding signal of free **L2** (ESI; Figs. S5, S10 and S15). These shifts probably imply coordination of **L2** with Pd or Ru center *via* Se. In ^1H NMR of free **L1** and **L2** signals of $H_2C(9)$ (*i.e.* ECH_2, E=S/Se) appear as a singlet. On complexation these signals in the spectra of complexes **1** and **2** appear at a higher frequency (up to ~0.47 ppm) relative to those of corresponding free ligands, supporting the coordination of ligands with metal centres through S or Se. Signals of $H_2C(9)$ in ^1H NMR spectra of **3** and **4** appear at a lower frequency (up to ~0.25 ppm) relative to those of free **L1** and **L2**. Such observation has been made in case of half sandwich complexes of Ru(II) with organochalcogen ligands earlier.[11a,b] It may be due the effect of electron rich arene ligand. The signals of C(9) in $^{13}C\{^1H\}$ NMR spectra of **3** and **4** observed at a higher frequency (up to ~8.5 ppm) with respect to those of free ligands, support their coordination with Ru *via* S/Se.

Crystal structures. Single crystals of **1**−**4** suitable for X-ray diffraction were grown by slow evaporation of their solutions made in methanol-acetonitrile mixture (1:6). The crystallographic data and refinement parameters are given in ESI (Table S1). The

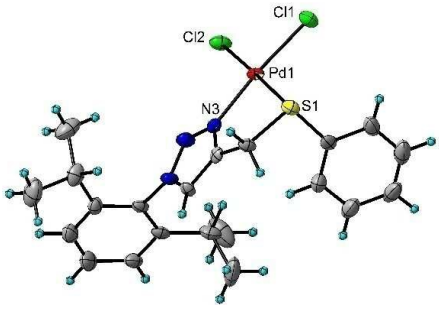


Fig. 1 ORTEP diagram of **1**. Bond lengths (Å): Pd(1)─N(3) 2.002(8); Pd(1)─Cl(2) 2.297(3); Pd(1)─Cl(1) 2.295(3); Pd(1)─S(1) 2.277(3). Bond angles (°): N(3)─Pd(1)─S(1) 84.7(2); S(1)─Pd(1)─Cl(1) 89.52(11); N(3)─Pd(1)─Cl(2) 93.6(2); Cl(1)─Pd(1)─Cl(2) 92.07(11).

ORTEP diagrams of **1**−**4** with 30% probability ellipsoids are shown in Figs. 1−2 and 5−6 with selected bond distances and angles. Ligands **L1** and **L2** exhibit identical bonding mode in the

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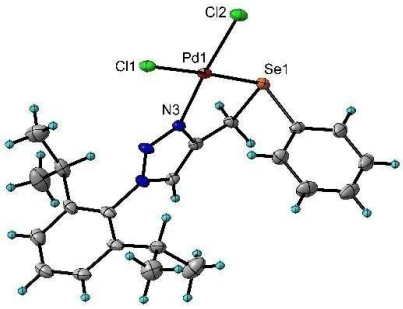

Fig. 2 ORTEP diagram of **2**. Bond lengths (Å): Pd(1)─N(3) 2.011(3); Pd(1)─Cl(2) 2.2815(12); Pd(1)─Cl(1) 2.3188(12); Pd(1)─Se(1) 2.3840(6). Bond angles (°): N(3)─Pd(1)─Cl(1) 93.13(11); Cl(2)─Pd(1)─Cl(1) 91.57(4); N(3)─Pd(1)─Se(1) 85.05(10); Cl(2)─Pd(1)─Se(1) 90.23(4).

complexes **1**−**4**, *i.e.* a five-membered chelate ring is formed by their coordination with each metal centre. The palladium in complexes **1** and **2** has a distorted square-planar geometry with sulfur or selenium *cis* to N (two Cl *cis* to each other). The Pd−S bond distance in **1**, 2.277(3) Å is consistent with that of palladacycle formed with 2,3-bis[(phenylthio)methyl] quinoxaline (2.259(2)Å)[36] and Pd(II) complex of sulfated Schiff base of 1-hydroxy-2-acetophenone (2.2704(16) Å).[37]

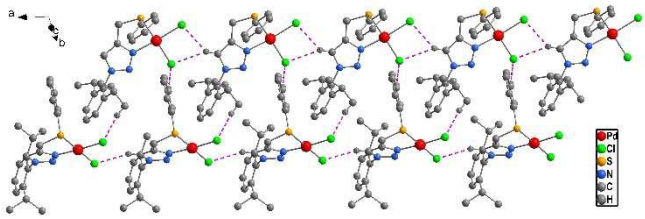

Fig. 3 Non-covalent interactions in **1**

In **2**, Pd–Se bond distance (2.3840(6) Å) is close to the values reported for Pd(II) complex of bis[(phenylseleno)methyl] quinoxaline [2.3924(15) and 2.3991(15)Å],[36] and somewhat shorter than that of Pd(II) complex of (Se, N, Se) pincer ligand (2.4104(5)/2.4222(6) Å).[23c] The Pd−N bond distances in both **1**

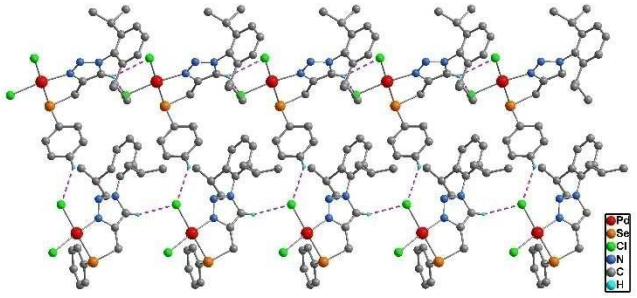

Fig. 4 Non-covalent interactions in **2**

and **2** are almost same [2.002(8) and 2.011(3) Å] and comparable to the value reported for Pd(II) complex of a (P, N) ligand (2.015(19) Å).[38] The Pd(1)−Cl(1) and Pd(1)−Cl(2) bond lengths in **1** [2.295(3) and 2.297(3) Å] and **2** [2.3188(12) and 2.2815(12) Å] are normal.[23c] Non-covalent secondary interactions (C−H···Cl) in **1** and **2** result in the formation of a sheet like structure (Figs. 3 and 4).

In single crystal structures of complexes **3** and **4** ruthenium has pseudo-octahedral half-sandwich "piano-stool" geometry. η^6-Benzene ring, nitrogen of 1,2,3-triazole, S or Se and Cl complete coordination sphere of Ru. The Ru–S bond length in cation of **3** (2.3728(12) Å) is consistent with the values reported for half-

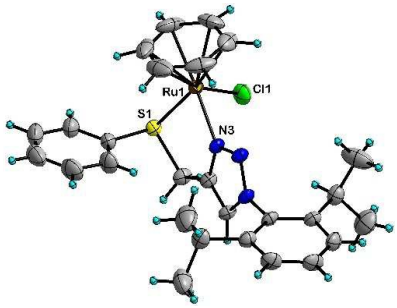

Fig. 5 ORTEP diagram of **3**. PF_6^- anion has been omitted for clarity. Bond lengths (Å): Ru(1)─N(3) 2.082(3); Ru(1)─S(1) 2.3728(12); Ru(1)─Cl(1) 2.3993(14); Ru(1)─C 1.675(1); Bond angles (°): N(3)─Ru(1)─S(1) 80.42(9); N(3)─Ru(1)─Cl(1) 84.93(10); S(1)─Ru(1)─Cl(1) 80.89(5).

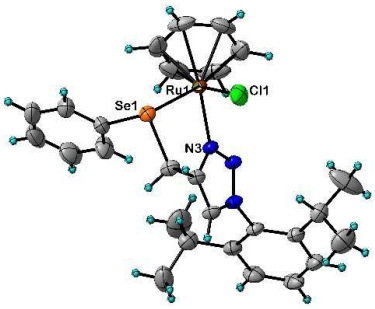

Fig. 6 ORTEP diagram of 4. PF_6^- anion has been omitted for clarity. Bond lengths (Å): Ru(1)─N(3) 2.081(3); Ru(1)─Cl(1) 2.3973(14); Ru(1)─Se(1) 2.4741(6); Ru(1)─C 1.438(0). Bond angles (°): Cl(1)─Ru(1)─Se(1) 80.15(4); N(3)─Ru(1)─Cl(1) 84.53(10); N(3)─Ru(1)─Se(1) 81.36(9).

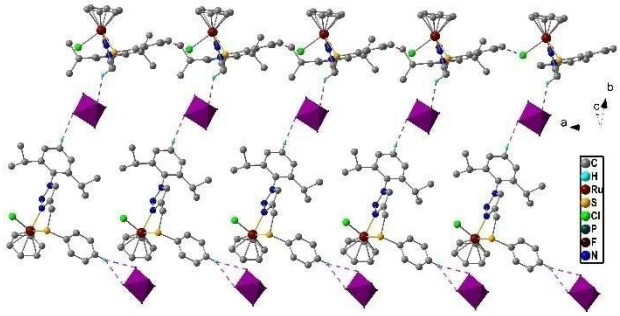

Fig. 7 Non-covalent interactions in **3**

sandwich complex of Ru(II) with 1-benzyl-4-[(phenylthio)-methyl]-1*H*-1,2,3-triazole [2.3847(11) Å][11a] The Ru–Se bond distance (2.4741(6) Å) in **4** is similar to the values reported for $[(\eta^6\text{-}C_6H_6)RuCl(N\text{-}\{2\text{-}(phenylseleno)ethyl\}pyrrolidine)]^+$ (2.480(11) Å)[39] and $[(\eta^6\text{-}C_6H_6)Ru(2\text{-}MeSC_6H_4CH{=}NCH_2CH_2\text{-}SeC_6H_5)]^{2+}$ (2.4848(8) Å).[40] The Ru−N bond distances of cation of **3** and **4** (2.082(3) Å and 2.081(3) Å respectively) are

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consistent with that of cation $[(\eta^6\text{-}C_6H_6)Ru(2\text{-}MeSC_6H_4CH{=}N{-}CH_2CH_2SC_6H_5)]^{2+}$ (2.073(6) Å).[40] The PF_6^- anion has been found to be involved in C−H···F secondary interactions in the crystals of **3** and **4** resulting in chain type structures as shown in Figs. 7 and 8.

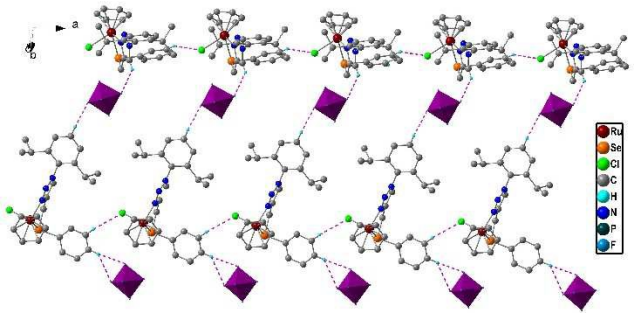

Fig. 8 Non-covalent interactions in **4**

Catalysis of Suzuki–Miyaura coupling (SMC)

Palladium(II) complexes **1** and **2** catalyze SMC efficiently in water used many times for it as a co-solvent with DMF, EtOH, dioxane and THF.[23c,41] No significant gain in catalytic activity was observed in mixtures of water with DMF and EtOH, using SMC reaction conditions optimized in water or attempting fresh optimization. The reports on the use of discrete Pd(II) complexes as a catalyst for SMC in water are scanty.[5,15,23c,41a,b,42,43] In the present study, 4-bromobenzaldehyde was reacted with

Table 1 Suzuki-Miyaura C−C coupling reactions catalyzed with **1**–**2**[a]

Ar−Br + $PhB(OH)_2$ → Ar−Ph

Entry No.	Aryl bromide	1 Mol%	1 time	1 Conversion[b] /Yield[c]	2 Mol%	2 time	2 Conversion[b] /Yield[c]
1	4-Bromobenzaldehyde	0.01	30min	99/91	0.01	3 h	81/70
2	4-Bromobenzaldehyde	0.001	15 h	71	0.01	12 h	99/-
3	4-Bromobenzonitrile	0.01	90min	70/62	0.1	90min	65/52
4	4-Bromonitrobenzene	0.01	30min	99/93	0.01	3h	99/89
5	4-Bromoacetophenone	0.01	30min	99/90	0.1	5h	99/86
6	4-Bromobenzoic acid	0.01	30min	99/88	0.01	30min	99/93
7	4-Bromotoluene	0.1	12h	63/52	0.1	12h	51/42
8	4-Bromoanisole	0.1	6h	99/93	1	12h	35/-

[a]Reaction conditions: ArBr (1.0 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (2.0 mmol), water (3 mL), temperature of bath 100 °C, [b]NMR conversion in %, [c]Isolated yield in %.

phenylboronic acid to optimize the reaction conditions (monitoring conversion with ^{1}H NMR). Among bases K_2CO_3 was found most suitable. On completion of the coupling reaction the coupled product was isolated. In Table 1 optimum mol% of catalyst required, reaction time, % isolated yield and % conversion estimated at the end of reaction with ^{1}H NMR are reported. Isolated yields are lower than conversions, as expected, but both show similar trends with substrates. These results indicate that in SMC catalyzed with **1** and **2** the coupling of several aryl bromides can be successfully achieved in a short time without any additive or phase transfer catalyst such as tetrabutylammonium bromide (TBAB). The complex **1** at 0.01 mol% loading catalyzes SMC of 4-bromobenzaldehyde with phenylboronic acid at 100 °C in presence of K_2CO_3, resulting in ~99% conversion (Table 1 Entry1) into cross-coupled product in 30 min. The conversion to the same coupled product was 71% when this SMC reaction was carried out for 15 h at 0.001 mol% catalyst loading (Table 1: Entry 2). On using **2** (0.01 mol%) as a catalyst for the same SMC under identical reaction conditions, the conversion was 81% for reaction time of 3 h and 99% for 12h (Table 1: Entries 1 and 2). Among other aryl bromides the activated ones gave good conversion when SMC was carried out for 1-2 h in the presence of **1**, however the reaction time increased with **2** for coupling of the same substrate (Table 1, Entries 3-6). 4-Bromonitrobenzene, 4-bromoacetophenone and 4-bromobenzoic acid were converted into coupled product within 30 min when 0.01 mol% loading of **1** was used for the coupling. When complex **2** was used as a catalyst for SMC of these substrates, increase in the catalyst amount/reaction time was necessary for good conversion (Table 1, Entries 4-6). The conversion of deactivated aryl bromides *viz*. 4-bromotoluene and 4-bromoanisole into coupled product was 51-99% when long reaction time and high catalyst loading (0.1-1 mol%) were used for SMC. The conversion of 4-bromoanisole into coupled product is ~99% in 6 h at 0.1 mol% loading of **1,** whereas 1.0 mol% loading of catalyst **2** results only 35% conversion under identical reaction conditions (Table 1, Entry 8). The conversion of 4-bromotoluene catalyzed with **1** and **2** at 0.1 mol% loading into coupled product is 63 and 51% respectively (Table 1, Entry 7).

Catalysis of Sonogashira coupling

The catalytic performance of Pd(II) complexes **1**−**2** has been explored for Sonogashira (C_{sp^2}–C_{sp}) coupling. To the best of our knowledge no Pd(II) complex of 1,2,3-triazole based organochalcogen ligand has been used to catalyze this coupling so far, and the present one is the first attempt. The base and solvent were optimized by choosing 4-bromobenzaldehyde as a substrate and **1** as a catalyst. The conversions were monitored with ^{1}H NMR. Among bases the (Table 2) best results were

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

Br−C_6H_4−CHO + PhCCH → CHO−C_6H_4−CCPh

Entry No.	Solvent	Base	Conversion[b] (%)
1	DMA	K_2CO_3	55
2	DMF	K_2CO_3	99/87[c]
3	DMSO	K_2CO_3	27
4	DMA	KOH	40
5	DMF	KOH	--
6	DMSO	NaOH	--
7	DMF	Cs_2CO_3	<10
8	EtOH	K_2CO_3	26

[a]Reaction conditions: 1.0 mmol of 4-bromobenzaldehyde, 1.1 mmol of phenylacetylene, 2.0 mmol of base, 1 mol % complex **1**, 2 mol% of CuI, 3 mL solvent, N_2 atmosphere, temperature of bath, 120 °C and reaction time 12 h, [b] % conversion by NMR, [c]Isolated yield in %.

obtained with K_2CO_3 and DMF was found to be best solvent. Presence of CuI (2−4 mol%) as a co-catalyst and N_2 atmosphere were found necessary to get good conversion. The scope of substrates was explored under optimized reaction conditions monitoring conversion with ^{1}H NMR. In case of 4-bromobenzaldehyde conversion at 120 °C into the coupled

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product was ~99% when loading of **1** as a catalyst was 1 mol%.

Table 3 Sonogashira coupling reaction catalyzed with complexes **1** and **2**[a]

$R{-}C_6H_4{-}Br + PhCCH \rightarrow R{-}C_6H_4{-}CCPh$

Entry No.	Aryl halide	**1** Mol%	t (h)	Conversion[b] Yield[c]	**2** Mol%	t (h)	Conversion[b] Yield[c]
1	4-Bromobenzaldehyde	1	8	99/87	1	12	60/52
2	4-Bromobenzaldehyde	0.1	12	84	0.1	12	40
3	4-Bromobenzonitrile	2	12	99/91	2	12	99/88
4	4-Bromoacetophenone	0.1	12	60/43	1	12	74/61
5	4-Bromonitrobenzene	2	8	98/85	2	12	87/80
6[d]	4-Bromotoluene	2	12	61/53	2	12	43/31
7[d]	4-Bromoanisole	2	12	40/32	2	12	--

[a]Reaction conditions: 1.0 mmol of ArBr, 1.1 mmol of phenylacetylene, 2.0 mmol of base (K_2CO_3), [d]CuI equiv. to 4 mol%, 3 mL DMF solvent, temperature of bath 120 °C, % conversion by NMR[b], [c]Isolated yield in %.

When Sonogashira coupling of 4-bromobenzaldehyde was carried out in the presence of 1 mol% of **1** in copper free condition, no conversion of substrate was noticed. The catalytic role of Pd was ascertained by performing the coupling reaction without palladium catalyst. The possibility of palladium free catalysis was ruled out as only homo-coupled product of phenylacetylene (PhCCCCPh) was obtained (Glaser-type reaction),[19b,21c,d] in the absence of Pd. Moreover, the present Sonogashira coupling reactions being amine-free (K_2CO_3 is the base in the present case) may be labeled as more environmentally friendly, as the amines are not considered environmentally benign.[21b] The % conversion (monitored with ^{1}H NMR) and isolated yield(%) for the catalytic coupling of various substrates are given in Table 3. The 0.1-2 mol% of Pd and 2 mol% of copper iodide were required to get good conversion into couple product, of electronically activated aryl bromides (Table 3, Entries 1−5). 4-Bromobenzaldehyde and 4-bromoacetophenone were converted 84 and 60% respectively into the coupled product at 0.1 mol% loading of **1** (Table 3, Entries 2 and 4). For the same substrate activity of **2** was lower than that of **1** e.g. 1 mol% of palladium was necessary to get 74% of 4-bromoacetophenone converted into the coupled product (Table 3, Entry 4). The 2 mol% of **1/2** gave almost complete conversion of 4-bromobenzonitrile and 4-bromonitrobenzene into the coupled products (Table 3, Entries 3 and 4). In the case of deactivated aryl bromides *viz.* 4-bromotoluene and 4-bromoanisole conversion/yield of the cross-coupled product was low even when 2 mol% loading of **1** was used. On increasing the amount of co-catalyst, CuI to 4 mol%, with 2 mol% of Pd catalyst, conversion was achieved up to 61% for these substrates (Table 3, Entries 6 and 7). In case of 4-bromoanisole coupling was negligible in the presence of **2**.

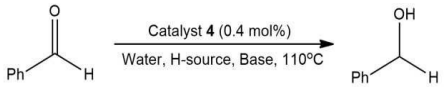
The nature of catalyst in the two coupling processes was investigated by mercury and triphenylphosphine poisoning tests[43] The reaction of 4-bromobenzaldehyde with phenylboronic acid (SMC)/phenylacetylene (Sonogashira coupling) was carried out in the presence of **1** as described in the ESI. The results given in Table S7 and S8 (ESI) reveal that catalytic processes are not quenched in the presence of Hg(0)/PPh_3 but do not reach to completion, indicating that they are partially poisoned by Hg / PPh_3 and small contribution of heterogeneous pathway may exist.

The **1** and **2** can survive at reaction temperatures of coupling reactions. Thus Pd(0)/Pd(II) in solution is most likely pathway for these coupling reaction.

Catalysis of transfer hydrogenation (TH)

The Ru(II) complexes **3** and **4** (0.1−0.4 mol%) were explored for catalytic transfer hydrogenation (TH) of carbonyl compounds in water using millimole amount of glycerol as a hydrogen-source. Reaction conditions were optimized in water by choosing benzaldehyde as a model substrate and **4** as a catalyst. At reaction temperature of 110 °C, combination of glycerol/2-propanol and KOH was found best, as conversion achieved was maximum (Table 4: glycerol: 95%, Entry 1; 2-propanol: 93%, Entry 6). TH reaction was ineffective in the presence of KOH when citric and acetic acids were used as H-sources (Table 4, Entries 7 and 8). Ascorbic acid is somewhat better than these two acids (Table 4, Entry 2). High amount of 2-propanol or HCOOH with weak base HCOONa also gave somewhat good results (Table 4, Entries 3 and 4). In comparison to 2-propanol which gave results comparable to glycerol, the later was preferred as it is considered a green solvent.[33a,35] The combination of glycerol with HCOONa

Table 4 Optimization of reaction conditions for catalytic transfer hydrogenation of carbonyl compounds using **4**[a]



Entry No.	Base/amount(mmol)	*H*-source/amount(mmol)	Conversion[b] (%)
1	KOH/1	Glycerol/2	95/89[c]
2	KOH/1	Ascorbic acid /5	50
3	HCOONa/2	HCOOH/10	55
4	HCOONa/2	2-Propanol/10	90
5	HCOONa/2	Glycerol/2	<10
6	KOH/1	2-Propanol /2	93
7	KOH/1	Citric acid/2	<10
8	KOH/1	Acetic acid /5	25

[a]Reaction conditions: 1.0 mmol of benzaldehyde, 0.4 mol % of Ru(II) complex **4**, 3 mL of water, temperature 110 °C, reaction time 6 h. [b] % conversion by NMR, [c]Isolated yield in %.

base does not work in the present case (Table 4, Entry 5). The reaction of benzaldehyde was carried out under optimized conditions in the presence of catalyst **4** without any hydrogen source, to check possibility of KOH-promoted TH. After 8 h of reaction, conversion was <10%, affirming the role of the Ru as a catalyst. The conversions in catalytic reactions monitored with ^{1}H NMR spectra and isolated yields of coupled products are given in Table 5. The scope of substrates for the catalytic TH with **3** and **4** was studied and results are given in Tables 5. Activity of both **3** and **4** is highest for benzaldehyde (isolated yield up to ~99%, Table 5, Entry 1). The conversion of acetophenone is ~ 99% with **4** and 70% with **3** (Table 5, Entry 4). The complex **4** is efficient for catalytic TH of furfuraldehyde, 4-chlorobenzaldehyde and 4-bromobenzaldehyde but activity of **3** is lower (Table 5, Entry 5-7) than that of **4** under identical reaction conditions. The combination of glycerol-water was not effective for 4-bromoacetophenone and benzophenone as no conversion to reduced product was achieved. In 2-propanol, used as a solvent

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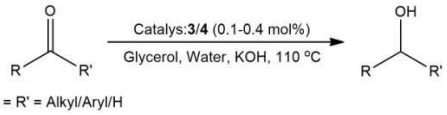
and H-source their conversions were good (Table 5, Entries 3 and 9). The comparison of the performance of **3** and **4** as catalysts for TH, made with other catalysts reported to work in water, is a mixed bag. The loading for good conversion[in H_2O-MeOH mixture; base: HCOONa) required for catalyst, [Ru(η^6-arene)(dhbp)Cl]$^+$, (dhbp = 6,6′-dihydroxy-2,2′-bipyridyl)[44] is 1 mol%, higher than those of present complexes. The reaction time 16 h, is also long. The TH activity of **3** and **4** in water-glycerol is better than those of [(η^5-Cp*/η^6-benzene)Ru(**L**)Cl]PF_6 (**L**=2-(pyridine-2-ylmethylsulfanyl)benzoic acid).[33a]

Table 5 Catalytic transfer hydrogenation of carbonyl compounds using complexes **3** and **4**[a]



Entry No.	Aldehyde/Ketone	3 Mol%	3 t(h)	3 Conversion[b] Yield[c]	4 Mol%	4 t(h)	4 Conversion[b] Yield[c]
1	Benzaldehyde	0.4	6	99/93	0.4	8	95/89
2	Benzophenone	0.4	8	--	0.4	8	--
3[d]	Benzophenone	0.1	3	99/90	0.2	5	93/84
4	Acetophenone	0.4	6	70/59	0.2	6	99/87
5	Furfuraldehyde	0.4	15	71/61	0.4	10	80/72
6	4-Chlorobenzaldehyde	0.4	18	<10	0.2	8	83/71
7	4-Bromobenzaldehyde	0.4	12	62/48	0.4	6	99/88
8	4-Bromoacetophenone	0.4	12	--	0.4	8	35/-
9[d]	4-Bromoacetophenone	0.1	6	95/88	0.4	3	99/85

[a]Reaction conditions: 1.0 mmol of carbonyl compound, 1.0 mmol of KOH, 3 mL of water, 2.0 mmol of glycerol, temperature 110 °C. [b]% Conversion determined with NMR. [c]Isolated yield, [d]reaction was performed in 2-propanol.

Using HCOONa as a hydrogen source at pH 4 in water, [Ru(η^6-arene)(dmobpy)Cl]$^+$(dmobpy = 4,4′-dimethoxy-2,2′-bipyridine)[45] shows better catalytic efficiency than **3** and **4**. The optimum loading of [(*p*-cymene)Ru(NHC)][46] as a TH catalyst in 2-propanol is reported higher than those of **3** and **4,** but with a short reaction time ≤1 h. The optimum loading of Ru(II) complexes of 1,3,5-triaza-7-phosphaadamantane (PTA) for biphasic TH in aqueous medium[47] is reported higher than those of **3** and **4**. The catalytic TH efficiency of $RuCl_2(TPPMS)_2$] (TPPMS = 4-(diphenylphosphino)benzenesulfonic acid)[48] in aqueous medium is comparable to those of **3** and **4**. Thus Ru complexes, **3** and **4** can be rated as efficient TH catalysts, as yields/conversions are better in a short time and optimum catalyst loading is low relative to several Ru species mentioned above. The performance of **3** and **4** may be partly ascribed to overall strong ligating characteristics of **L1** and **L2** and their steric influence. During TH reaction in glycerol, its dehydrogenation gives dihydroxyacetone (^{1}H NMR: δ 4.4 and 3.5 ppm) in a very low yield which is very difficult to isolate economically.[35,49] However its recovery is not of great concern due to low cost of glycerol. In ^{1}H NMR spectrum of reaction mixture recorded after 1 h of setting of TH reaction a broad singlet appears between −8 to −11.0 ppm, indicating the presence of H^-. Thus present catalytic TH probably proceeds *via* formation of Ru−H bond.[50] High electron donating ability of Se and S makes metal center electron rich which probably promotes the formation of metal-hydride species during the catalysis. Thus in TH catalyzed with **3** and **4**, the formation of Ru−H bond containing intermediate and the absence of the NH group in the ligand together suggest that a conventional mechanism *via* alkoxide formation[51] is most plausible.

The possibility in the present catalytic TH reaction, of heterogeneous pathway due to formation of Ru NPs from **3** or **4,** was explored using mercury and PPh_3 poisoning test.[35,43,52] The poisoning reagents were added to three TH reactions when they progressed simultaneously under optimal conditions for 1, 2 and 3 h respectively, and the reactions continued further for optimum time (details in ESI). The results are given in ESI (Table S9). The presence of Hg (Ru:Hg ; 1:500) in the TH of benzaldehyde catalyzed with **4** (0.1 mol%) did not show significant inhibition of conversion. In the presence of 5.0 equiv of PPh_3, only slight decrease in percent conversion was noticed. Thus, the present catalytic TH proceeds homogeneously and formation of Ru NPs is negligible.

DFT calculations

Density functional theory (DFT) calculations made for **1**−**4** are consistent with their structures and support experimental results on their catalytic activity. For Pd(II) complexes **1** and **2,** the HOMOs (highest occupied molecular orbitals), constituted by interaction of a *d*-orbital of Pd(II) and *p*-orbital of chlorine, are positioned primarily on Pd and Cl atoms. In HOMO−1 the metal *d*-orbital, *p*-orbitals of S/Se, chlorine and nitrogen (coordinated one) of triazole ring have contribution. The HOMOs of Ru(II) complexes **3** and **4** are essentially similar and positioned primarily over Ru(II) and the η^6-benzene ring and to some extent on S/Se, N, and Cl donor atoms. The *d*-orbitals of Ru(II)

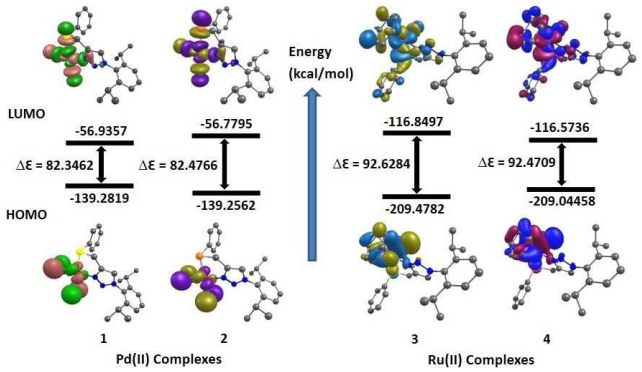


Fig. 9 Frontier molecular orbital diagrams of complexes **1**−**4**

interacting with π-orbitals of η^6-benzene ring and *p*-orbitals of chlorine, nitrogen, and sulfur/selenium atoms compose their HOMOs (Fig. 9). In simplistic terms catalytic activity of the complexes may be correlated to their HOMO−LUMO energy gap. Its low value results in high activity.[54,11a,b] Therefore between complex **1** and **2**, lower HOMO−LUMO energy gap (calculated by DFT) in **1** makes it more catalytically active than **2** (Fig. 9), as found experimentally in SMC and Sonogashira coupling reactions. HOMO−LUMO energy gap for Ru(II)

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complexes is lower for **4** than that of **3**. Therefore Se analog (Fig. 9) shows higher catalytic activity for TH in comparison to that of S one. However, variation in catalytic activities of various complexes observed experimentally is moderate only but consistent with DFT calculations.

The experimentally observed and DFT calculated Pd−Cl, Pd−N, Ru−Cl, Ru−N and Ru−S/Se bond distances and various bond angles are reasonably consistent (ESI; Tables S2-S5 and S6). However, calculated and observed Pd− S/Se bond distances differ.

Conclusions

The complexes (**1**−**4)** have been synthesized by reacting appropriate metal precursors with click generated ligands 1-(2,6-diisopropylphenyl)-4-(phenylthio / selenomethyl)-1*H*-1,2,3-triazole (**L1** / **L2**). The complexes and their ligands have been characterized with multinuclear NMR spectroscopy and HR-MS. The single crystal structures of **1**−**4** reveal geometry around Pd in **1** and **2** as distorted square planar. In case of **3** and **4** there is a pseudo octahedral "piano-stool" disposition of donor atoms around Ru. The complexes **1** and **2** efficiently catalyze SMC (in aqueous medium) and Sonogashira coupling reactions. The catalyst loading of 0.1−0.01 mol% is optimum for SMC, while for Sonogashira coupling loading of 0.1−2 mol% of Pd is essential. The ruthenium(II) complexes **3** and **4** have been explored as catalysts for transfer hydrogenation (TH) of aldehydes and ketones in aqueous media using glycerol as a hydrogen source. The optimum loading of **3** and **4** required for TH is 0.1−0.4 mol%. The poisoning experiments for TH show that catalytic process is nearly homogenous. The coupling reactions are also inferred overwhelmingly homogeneous on the basis of poisoning experiments. The nature of the chalcogen appears to affect the catalytic efficiency of complexes **1**−**4**. In view of literature reports[15] the effect of steric bulkiness of dipp group present on ligands on catalytic efficiency, can not be rule out. The results of DFT calculations are consistent with the experimental results on activity of these complexes for SMC and Sonogashira coupling *i.e*. **1** in which palladium is coordinated with sulfur is more efficient than **2**. The catalytic activity of Ru complexes **3** and **4** for TH is also consistent with DFT calculations.

Experimental

Diphenyldiselenide, $NaBH_4$, propargyl bromide, 2,6-diisopropylaniline, phenyl acetylene and NH_4PF_6 procured from Sigma-Aldrich (USA) were used as received. Phenylboronic acid, thiophenol, aryl halides, aldehyde and ketones were procured locally. Bis(acetonitrile)dichloropalladium(II) was prepared by refluxing palladium chloride in acetonitrile. The reported methods were used to synthesize $[\{(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)\}_2]$,[55a] propargyl phenyl sulfide/selenide.[55b] Solvents were dried or distilled before use by standard procedures.[55c] The reported methods were used to synthesize 2-azido-1,3-diisopropyl-benzene from 2,6-diisoropylaniline.[56] The ligand precursors were purified by column chromatography using silica gel (60−120 mesh) and *n*-hexane and its mixtures with chloroform/ethyl acetate in variable proportions as eluent. All reactions were carried out in glassware dried under ambient conditions. 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 commercial nitrogen gas was passed successively through traps containing solutions of alkaline anthraquinone-sodium dithionite, alkaline pyrogallol, concentrated. H_2SO_4 and KOH pellets, before use. Nitrogen atmosphere was created using Schlenk techniques.

Physical measurements

^1H, $^{13}C\{^1H\}$ and $^{77}Se\{^1H\}$ NMR spectra were recorded on a Bruker Spectrospin DPX 300 NMR spectrometer at 300.13, 75.47 and 57.24 MHz respectively. In ^1H and $^{13}C\{^1H\}$ NMR chemical shifts (in ppm) are reported relative to the internal standard tetramethylsilane (TMS). ^{13}C DEPT NMR was used routinely to determine the number of hydrogen atoms linked to a carbon atom. IR spectra in the range 4000−400 cm^{-1} were recorded on a Nicolet Protége 460 FT-IR spectrometer as KBr pellets. 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). The powder XRD data of complexes (**1-4**) were collected on a Rigaku Ultima IV diffractometer using Cu-Kα at room temperature over a 2θ range of 5° to 70°. In Fig. S21 (ESI) the powder diffraction patterns are shown.

Single-crystal data were collected with a Bruker AXS SMART Apex CCD diffractometer using Mo-Kα (0.71073 Å) radiation. The software SADABS[57a] was used for absorption correction and SHELXTL for space group, structure determination, and refinement.[57b,c] Hydrogen atoms have been included in idealized positions with isotropic thermal parameters set at 1.2 times those of the carbon atoms to which they were attached. The least-squares refinement cycles on F^2 were performed until the model converged. High-resolution mass spectral (HR-MS) measurements were made with a Bruker Micro TOF-Q II machine using electron spray ionization (10 eV, 180 °C source temperature and sodium formate as a calibrant) and dissolving the sample in CH_3CN. HR-MS was simulated using program developed by Scientific Instrument Services.[58] All DFT calculations were carried out at the Supercomputing Facility for Bioinformatics and Computational Biology, IIT Delhi, with the GAUSSIAN-03[59] programs. The geometries of complexes **1**−**4** have been optimized at the B3LYP[60] level using an SDD basis set for metal atoms and chalcogen and 6-31G* basis sets for C, N, and H. Geometry optimizations have been 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: A round-bottom reaction flask was charged with 2-azido-1,3-diisopropylbenzene (0.203 g, 1.0 mmol) 30 mL of CH_3CN and propargyl phenyl sulfide (0.148 g, 1.1 mmol)/propargyl phenyl selenide (0.195 g, 1.1 mmol). In two separate test tubes, each of $CuSO_4{\cdot}5H_2O$ (0.249 g, 1.0 mmol) and sodium ascorbate (80 mol%, 0.158 g) was dissolved in 3 mL of

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distilled water separately. Both solutions were mixed, and the resulting dark brown mixture was quickly added to the reaction flask and the reaction mixture stirred for 24 h at 90° C under nitrogen atmosphere. After 24 h same amount of $CuSO_4 \cdot 5H_2O$ and sodium ascorbate was added again to the reaction mixture, and it was stirred further for next 24 h at 90° C. Thereafter, solvent of the reaction mixture was reduced to minimum level. The mixture was poured into water (30 mL) and extracted with $CHCl_3$ (3 × 25 mL). Organic layers were combined together and washed with water (30 mL), 20% ammonia solution (30 mL) and brine (30 mL) successively. The organic phase was dried over anhydrous Na_2SO_4 and its solvent evaporated under reduced pressure on a rotary evaporator to give **L1** and **L2** as yellow solid. Their further purification was done by column chromatography on silica gel using hexane-ethyl acetate mixture (95:5) as an eluent.

L1; Yellow solid, Yield: (0.287 g, 82%); m.p. 119 °C. Anal. Found: C, 71.14; H, 6.89; N, 11.31 %. Calcd. for $[C_{21}H_{25}N_3S]$: C, 71.75; H, 7.17; N, 11.95 %.^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS); δ (ppm): 0.98−1.25 (m, 12H, $-H_3C(5)$), 2.03−2.08 (m, 2H, >HC(4)), 4.32 (s, 2H, $-H_2C(9)-$), 7.14−7.44 (m, 9H, ArH). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 23.7−23.8 (C5), 28.0 (C9), 28.6 (C4), 123.5, 124.9, 126.4, 128.6, 129.9, 130.7, 132.9, 134.6, 144.4, 145.7. IR (KBr; cm^{-1}): 480 (*w*), 557 (*w*), 713 [*m*; ν_{C-H} (*aromatic*)], 1116 (*m*), 1382 (*w*), 1452 [*m*; ν_{C-C} (*aromatic*)], 1637 [*m*; $\nu_{N=N}$], 2358 (*w*), 2831 [*m*; ν_{C-H} (*isopropyl*)], 2925 [*s*; ν_{C-H} (*aliphatic*)], 3081 [*m*; ν_{C-H} (*aromatic*)]. HR-MS [M+Na] (m/z) = 374.1659; Calcd. value for $C_{21}H_{25}N_3SNa$ = 374.1661 (error δ: 0.6 ppm).

L2; Light yellow solid, Yield: (0.338 g, 85%); m.p. 110 °C. Anal. Found: C, 63.24; H, 6.19; N, 10.53 %. Calcd. for $[C_{21}H_{25}N_3Se]$: C, 63.31; H, 6.32; N, 10.55 %. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS); δ (ppm): 1.05−1.11 (m, 12H, $-H_3C(5)$), 2.05−2.14 (m, 2H, >HC(4)), 4.29 (s, 2H, $-H_2C(9)-$), 7.23−7.51 (m, 9H, ArH). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 20.4 (C4), 23.9−24.0 (C5), 28.2 (C9), 123.6, 124.7, 127.4, 129.0, 129.3, 130.6, 133.1, 133.3, 145.3, 146.0. $^{77}Se\{^1H\}$ NMR (57 MHz, $CDCl_3$, 25 °C, Me_2Se): δ (ppm) 366.3. IR (KBr; cm^{-1}): 466 (*w*), 692 (*m*), 740 [*m*; ν_{C-H} (*aromatic*)], 1050 (*s*), 11179 (*s*), 1361 [*w*], 1470 [*s*; ν_{C-C} (*aromatic*)], 1575 [*m*; $\nu_{N=N}$], 2334 (*w*), 2870 [*m*; ν_{C-H} (*isopropyl*)], 2967 [*s*; ν_{C-H} (*aliphatic*)], 3119 [*m*; ν_{C-H} (*aromatic*)]. HR-MS [M + H] (m/z) = 400.1299; Calcd. value for $C_{21}H_{26}N_3Se$ = 290.1032 (error δ : -2.9 ppm).

Synthesis of Pd-complexes 1 and 2: To a solution of 0.2 mmol of **L1** (0.070 g) or **L2** (0.079 g) in CH_3CN (5 mL) was added a solution of $[(CH_3CN)_2PdCl_2]$ (0.052 g, 0.2 mmol) made in 5 mL of CH_3CN. The reaction mixture was stirred for 5 h at room temperature. The solvent was removed from the pale yellow coloured solution under reduced pressure and the residue was washed with diethyl ether (5 mL) and dried in vacuo.

Complex 1; Yellow solid, Yield: (0.485 g, 92%); m.p. 278 °C(d). Anal. Found: C, 47.70; H, 4.69; N, 7.87 %. Calcd. for $[C_{21}H_{25}Cl_2N_3PdS]$: C, 47.69; H, 4.76; N, 7.95 %. ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS); δ (ppm): 0.98 (s, 12H, $-H_3C(5)$), 1.89 (s, 2H, >HC(4)), 4.37−4.78 (m, 2H, $-H_2C(9)-$), 7.35−7.53 (m, 6H, ArH), 7.84−8.13 (m, 2H, ArH), 8.78 (s, 1H, HC(7)). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm): 23.4 (C5), 23.7 (C4), 27.8 (C9), 123.8, 124.1, 126.2, 128.9, 129.3, 130.5, 131.8, 132.1, 134.8, 145.2. IR (KBr; cm^{-1}): 474 (*w*), 574 (*w*), 748 [*m*; ν_{C-H} (*aromatic*)], 807 [*m*; ν_{C-H} (*aromatic*)], 1062 (*m*), 1255 (*m*), 1469 [*s*; ν_{C-C} (*aromatic*)], 1573 [*m*; $\nu_{N=N}$], 2360 (*m*), 2361 (*w*), 2869 [*m*; ν_{C-H} (*isopropyl*)], 2963 [s; ν_{C-H} (*aliphatic*)], 3076 [*m*; ν_{C-H} (*aromatic*)]. HR-MS [M+H−2Cl] (m/z) = 458.0874; Calcd. value for $C_{21}H_{26}N_3PdS$ = 458.0884 (error δ: 2.1 ppm).

Complex 2; Yellow solid, Yield: (0.50 g, 87%); m.p. 272 °C(d). Anal. Found: C, 43.17; H, 4.15; N, 6.39 %. Calcd. for $[C_{21}H_{25}Cl_2N_3PdSe]$: C, 43.81; H, 4.38; N, 7.30 %. ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS); δ (ppm): 1.0 (s, 12H, $-H_3C(5)$), 1.56−2.0 (m, 2H, >HC(4)), 4.36−4.90 (m, 2H, $-H_2C(9)-$), 7.40−7.69 (m, 6H, ArH), 7.77−7.90 (m, 2H, ArH), 8.70 (s, 1H, HC(7)). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6, 25 °C, TMS): δ(ppm): 23.4 (C5), 23.7 (C4), 28.0 (C9), 124.0, 129.1, 129.2, 129.9, 130.2, 130.3, 131.9, 132.7, 145.0, 145.2. $^{77}Se\{^1H\}$ NMR (57 MHz, DMSO-d_6, 25 °C, Me_2Se): δ (ppm) 466.5. IR (KBr; cm^{-1}): 469 (*w*), 576 (*w*), 742 [*m*; ν_{C-H} (*aromatic*)], 869 [*m*; ν_{C-H} (*aromatic*)], 1062 (*m*), 1254 (*m*), 1470 [*s*; ν_{C-C} (*aromatic*)], 1566 [*m*; $\nu_{N=N}$], 2360 (*m*), 2353 (*w*), 2867 [*m*; ν_{C-H} (*isopropyl*)], 2962 [*s*; ν_{C-H} (*aliphatic*)], 3073 [*m*; ν_{C-H} (*aromatic*)].

Syntheses of ruthenium complexes 3 and 4: To a solution of 0.2 mmol of **L1** (0.07 g,) or **L2** (0.065 g) made in CH_3OH (5 mL) was added a solution of $[\{(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)\}_2]$ (0.05 g, 0.1 mmol) made in CH_3OH (5 mL), and the mixture was stirred for 8 h at room temperature. The resulting orange solution was filtered, and the volume of the filtrate reduced up to ~1 mL with rotary evaporator. Solid NH_4PF_6 (0.032 g, 0.2 mmol) was added to the concentrate with stirring and the resulting orange microcrystalline solid filtered, washed with 5 mL of ice cold CH_3OH, and dried in vacuo.

Complex 3; Yield: (0.561 g, 79%); m.p. 234 °C(d). Anal. Found: C, 45.50; H, 4.34; N, 5.97 %. Calcd. for $[C_{27}H_{31}N_3ClRuS][PF_6]$: C, 45.60; H, 4.39; N, 5.91 %.^{1}H NMR (300 MHz, CD_3CN, 25 °C, TMS); δ (ppm): 1.18−1.34 (m, 12H, $-H_3C(5)$), 2.32−2.41 (m, 2H, >HC(4)), 4.07−4.32 (m, 2H, $-H_2C(9)-$), 7.46−7.72 (m, 8H, ArH), 8.18 (s, 1H, HC(7)). $^{13}C\{^1H\}$ NMR (75 MHz, CD_3CN, 25 °C, TMS): δ (ppm): 22.7−22.8−23.4−23.6 (C5), 28.6−28.8 (C4), 36.5 (C9), 87.51 (C14) 124.4−124.5, 126.6, 129.6, 130.3, 131.6, 132.2, 132.3, 134.9, 145.6−145.8, 147.2. IR (KBr; cm^{-1}): 483 (*w*), 558 (*w*), 757 [*m*; ν_{C-H} (*aromatic*)], 842 [*s*; ν_{P-F}], 1094 (*w*), 1181 (*w*), 1471 [*m*; ν_{C-C} (*aromatic*)], 1574 [*b*; $\nu_{c=c}$], 1624 [*w*; $\nu_{N=N}$], 2362 (*w*), 2873 [*m*; ν_{C-H} (*isopropyl*)], 2949 [*s*; ν_{C-H} (*aliphatic*)], 3093 [*m*; ν_{C-H} (*aromatic*)]. HR-MS (CH_3CN; m/z): [M−PF_6] (m/z) = 566.0970; Calcd. value for $C_{27}H_{31}ClN_3RuS$ = 566.0963 (error δ: -0.3 ppm).

Complex 4; Yield: (0.614 g, 81%); m.p. 230 °C(d). Anal. Found: C, 42.80; H, 4.14; N, 5.47 %. Calcd. for $[C_{27}H_{31}N_3ClRuSe][PF_6]$: C, 42.78; H, 4.12; N, 5.54 %.^{1}H NMR (300 MHz, CD_3CN, 25 °C, TMS); δ (ppm): 1.33−1.63 (m, 12H, $-H_3C(5)$), 2.21−2.34 (m, 2H, >HC(4)), 3.91−4.15 (m, 2H, $-H_2C(9)-$), 7.44−7.70 (m, 8H, ArH), 8.12 (s, 1H, −HC(7)). $^{13}C\{^1H\}$ NMR (75 MHz, CD_3CN, 25 °C, TMS): δ (ppm): 22.7−22.8−23.7−23.72 (C5), 28.6 (C4), 28.8 (C9), 86.9 (C14) 124.4−124.5, 127.0, 130.0, 130.7, 130.9, 131.1, 132.1, 132.2, 145.6−145.8, 148.0. $^{77}Se\{^1H\}$ NMR (57 MHz, CD_3CN, 25 °C, Me_2Se): δ (ppm) 452.0. IR (KBr; cm^{-1}):

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471 (*w*), 557 (*w*), 742 [*m*; ν_{C-H} (*aromatic*)], 843 [*s*; ν_{P-F}], 1091 (*m*), 1241 (*m*), 1470 [*m*; ν_{C-C} (*aromatic*)], 1627 [*w*; $\nu_{N=N}$], 2361 (*w*), 2874 [*m*; ν_{C-H} (*isopropyl*)], 2968 [*s*; ν_{C-H} (*aliphatic*)], 3099 [*m*; ν_{C-H} (*aromatic*)]. HR-MS (CH_3CN; m/z): [M−PF_6] (m/z) = 614.0410; Calcd. value for $C_{27}H_{31}ClN_3RuSe$ = 614.0417 (error δ: 1.0 ppm).

Procedure for Suzuki-Miyaura C−C coupling reaction catalyzed with 1 and 2

Aryl bromide (1.0 mmol), phenylboronic acid (0.147 g, 1.2 mmol), K_2CO_3 (0.276 g, 2.0 mmol), water (3 mL) and a palladium complex **1** or **2** (0.01-1 mol%) were charged in a round bottom flask. It was placed on an oil bath maintained at 100 °C under aerobic condition and its content stirred. The progress of reaction was monitored by ^{1}H NMR spectroscopy to estimate conversions. When maximum conversion of ArBr into coupled product occurred, the reaction mixture was cooled to room temperature. It was mixed with water (20 mL) and extracted with diethyl ether (3×10 mL). For benzoic acid derivatives the reaction mixture was mixed with 20 mL of water acidified with 20% HCl and extracted with ethyl acetate (3×10 mL). Organic phase was dried over anhydrous Na_2SO_4. Its solvent was removed on rotary evaporator to isolate coupled product and its yield was determined. Further purification (if required) was done by column chromatography on silica gel (60−120 mesh) using ethyl acetate-hexane mixture as an eluent, before yield calculation. The coupled products were authenticated by matching their NMR data with the literature reports.[23b,c]

4−Phenylbenzaldehyde: Light yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): 7.39−7.50 (m, 3H), 7.62−7.65 (m, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.4 Hz, 2H), 10.05 (s, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): *δ* 127.3, 127.6, 128.4, 128.9, 130.2, 135.1, 139.7, 147.1, 191.9

4-Phenylbenzonitrile: Pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): *δ* 7.34−7.44 (m, 3H), 7.49−7.52 (m, 2H), 7.54−7.60 (m, 4H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): 110.3, 118.5, 126.7, 127.2, 128.3, 128.7, 132.1, 138.5, 145.0

4-Nitrobiphenyl: Pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): 7.40−7.51 (m, 3H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.71 (d, 2H, *J* = 9.0 Hz), 8.26 (d, 2H, *J* = 9.0 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): 123.1, 127.0, 127.2, 127.6, 128.8, 129.0, 138.6, 146.9, 147.5

4−Acetylbiphenyl: White solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): 2.61 (s, 3H), 7.38−7.48 (m, 3H), 7.60−7.68 (m, 4H), 8.01 (d, 2H, *J* = 8.4 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): 26.5, 127.1, 127.2, 128.1, 128.8, 128.8, 135.7, 139.7, 145.6, 197.6

4-Carboxylicbiphenyl: White solid. ^{1}H NMR (300 MHz, DMSO, 25 °C); *δ* (ppm): 7.39−7.52 (m, 3H), 7.72 (d, *J* = 6.9 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 8.02 (d, *J* = 8.4 Hz, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO, 25 °C, TMS); *δ* (ppm): *δ* 126.8, 127.0, 128.3, 129.1, 129.6, 130.0, 139.0, 144.3, 167.2

4-Methylbiphenyl: Colourless solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): 2.37 (s, 3H), 7.22 (d, 2H, *J* = 7.8 Hz), 7.27−7.32 (m, 1H), 7.37−7.42 (m, 2H), 7.48 (d, 2H, *J* = 8.1 Hz), 7.55−7.58 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): 21.0, 126.9, 126.9, 128.6, 129.4, 136.9, 138.3, 141.1

4-Methoxybiphenyl: White solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): 3.81 (s, 3H), 6.96 (d, 2H, *J* = 8.4 Hz), 7.28−7.30 (m, 1H), 7.39 (t, 2H, *J* = 7.2 Hz), 7.50−7.55 (m, 4H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): 55.2, 114.1, 126.6, 126.7, 128.1, 128.7, 133.7, 140.7, 159.1

General procedure for Sonogashira coupling reaction catalyzed with 1 and 2

The round bottom flask charged with aryl bromide (1.0 mmol), phenyl acetylene (0.112 g, 1.1 mmol) and K_2CO_3 (0.276 g, 2.0 mmol) and 3 mL of DMF was degassed with N_2 to protect reaction mixture from moisture. Thereafter palladium complex **1** or **2** (0.1–2 mol%) and CuI (2–4 mol%) were added and the mixture was heated at 120° C for 12 h under nitrogen atmosphere. The progress of reaction was monitored by ^{1}H NMR spectroscopy to estimate conversions. When maximum conversion of ArBr into coupled product occurred, the reaction mixture was cooled to room temperature and extracted with ethylacetate (2×15 mL). The extract was washed with brine (2×10 mL) and aqueous ammonia (10 mL). After drying over anhydrous Na_2SO_4 its solvent was evaporated off with rotary evaporator. The resulting residue was purified by column chromatography using silica gel (60−120 mesh) and *n*-hexane and its mixtures with chloroform/ethyl acetate in variable proportions as eluent. The yield was calculated. The authentication by matching ^{1}H and $^{13}C\{^1H\}$ NMR with literature data was carried out for each coupled product.[22a,d]

4-(Phenylethynyl)benzaldehyde**:** Light yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): 10.03 (s, 1H), 7.87 (d, 2H, *J* = 8.2 Hz), 7.67 (d, 2H, *J* = 8.2 Hz), 7.57-7.53 (m, 2H), 7.39-7.36 (m, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): 191.8, 135.8, 132.5, 132.2, 130.02, 130.0, 129.3, 128.9, 122.9, 93.8, 88.9

1-Nitro-4-(phenylethynyl)benzene: Light-yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): 7.36− 7.39 (m, 3H), 7.54−7.56 (m, 2H), 7.64−7.66 (m, 2H), 8.22 (d, 2H, J = 8.7 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): 86.5, 93.7, 121.1, 122.6, 127.5, 128.3, 129.3, 130.8, 131.2, 145.9

4-(Phenylethynyl)benzonitrile: Yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): 7.36−7.40 (m, 3H), 7.53−7.56 (m, 2H), 7.59−7.64 (m, 4H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): 86.7, 92.7, 110.4, 117.5, 121.1, 127.2, 127.4, 128.1, 130.7, 131.03, 131.05

1-Methoxy-4-(phenylethynyl)benzene: Light-yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): 3.82 (s, 3H), 6.85−6.89 (m, 2H), 7.29−7.35 (m, 3H), 7.45−7.52 (m, 4H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): 54.2, 87.0, 88.3, 112.9, 114.3, 122.5, 126.9, 127.3, 130.4, 132.0, 158.6

1-Methyl-4-(phenylethynyl)benzene: White solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): 2.35 (s, 3H), 7.14 (d, J = 7.8 Hz, 2H), 7.30−7.35 (m, 3H), 7.42 (d, 2H, J = 7.2 Hz), 7.50−7.53 (m, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): 21.2, 88.4, 89.3, 119.9, 123.2, 127.8, 128.0, 128.8, 131.2, 131.3, 138.1

Procedure for catalytic transfer hydrogenation (TH)

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In a round bottom flask an aldehyde (or a ketone) (1.0 mmol), KOH (0.056 g, 1.0 mmol), glycerol (0.184 g, 2.0 mmol) and a complex **3**/**4** (0.1–0.4 mol %) were mixed in water (3 mL) and the mixture heated at 110 °C for optimum time (Table 5). The conversion into corresponding alcohol was monitored by ^{1}H NMR. After maximum conversion, the resulting product was extracted with diethyl ether (2×5 mL) from the reaction mixture. The organic phases were combined, dried over Na_2SO_4 and its solvent was evaporated off with a rotary evaporator. The resulting product was isolated and purified by column chromatography using silica gel (60−120 mesh) and *n*-hexane and its mixtures with chloroform/ethyl acetate in variable proportions as eluent. The yield was calculated. The products were analyzed with ^{1}H and ^{13}C{^{1}H } NMR spectra to authenticate them.[35]

Phenylmethanol: Colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS); δ (ppm): 2.30 (br s, 1H, -OH), 4.62 (s, 2H), 7.23−7.32 (m, 5H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C, TMS); δ (ppm): 65.2, 127.0, 127.6, 128.5, 140.9

1-Phenylethanol: Colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS); δ (ppm): 1.51 (d, 3H, J = 6.3), 4.87−4.93 (m, 1H), 7.28−7.39 (m, 5H); ^{13}C{^{1}H} (75 MHz, $CDCl_3$) δ 25.1, 70.3, 124.4, 127.4, 128.4, 148.8

Diphenylmethanol: White solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS); δ (ppm): 2.29 (d, 1H), 5.81 (d, 1H), 7.23−7.60 (m, 10H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C, TMS); δ (ppm): 76.2, 126.5, 127.5, 128.5, 143.8

(4-Chlorophenyl)methanol: White solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS); δ (ppm): 1.78(b, 1H, -OH), 4.68 (d, 2H, J = 4.8), 7.28−7.36 (m, 4H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C, TMS); δ (ppm): δ 64.5, 128.2, 128.6, 133.4, 139.2

Furan-2-ylmethanol: Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS); δ (ppm): 2.39 (b, 1H, -OH), 4.57 (s, 2H), 6.26−6.34 (m, 2H), 7.38 (s, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C, TMS); δ (ppm): 57.3, 107.7, 110.3, 142.5, 154.0.

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Notes and References

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† Electronic Supplementary Information (ESI) available: Spectral data of **L1** and **L2** and **1**–**4**; single crystal data of complexes **1**–**4** (CCDC 1472950-1472953), See DOI: 10.1039/b000000x/

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"Click" generated 1,2,3-triazole based organosulfur/selenium ligands and their Pd(II) and Ru(II) complexes: their synthesis, structure and catalytic applications

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Sonogashira and Suzuki-Miyaura coupling were catalyzed with Pd(II) complexes (0.001-2 mol%) and transfer hydrogenation (in water-glycerol) with Ru(II) complexes (≤ 0.4 mol%)