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Palladacycles of unsymmetrical (N,C⁻,E) (E = S / Se) pincers based on indole: Synthesis, structure and catalysis of Heck coupling and allylation of aldehydes

Mahabir P. Singh, Fariha Saleem, Gyandshwar K. Rao, S. Kumar, Hemant Joshi and Ajai K Singh*.

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Unsymmetrical (N,C,E)-type pincer ligand precursors [**L1** and **L2 :** E = S / Se] with indole core were synthesized for the first time by condensation of 1-(2-phenylsulfanyl/selenylethyl)-1H-indole-3-carbaldehyde with benzyl amine. The synthetic protocols are easy and give good yields (>85%). The **L1** and **L2** on reaction with sodium tetrachloropalladate(II) in the presence of CH_3COONa result in complexes [Pd(**L1**/**L2**−H)Cl] (**1 / 2**), where they bind in a tridentate (N,C⁻, E) mode. The **L1** and **L2**, their aldehyde precursors and Pd(II)-complexes, **1** and **2** have been characterized with ^{1}H, $^{13}C\{^{1}H\}$and $^{77}Se\{^{1}H\}$ NMR and HR-MS. Palladium(II) complexes **1** and **2** and precursor aldehydes of **L1** and **L2** were authenticated with single crystal X-ray diffraction. The catalytic activities of complexes **1** and **2** were investigated for Heck coupling and allylation of aldehydes. The two reactions require 0.1−0.3 and 1 mol% loading of complexes as catalysts, respectively.

Introduction

The interest in research on metal complexes of pincer ligands continues[1] due to their versatile applications,[2] arising from their stability and unique reactivity resulting probably due to tridentate coordination mode of such ligands and the presence of a metal–carbon σ-bond[3] in many cases. The fine tuning of steric and electronic properties of metal–pincer ligand complexes and consequently their catalytic properties is possible by changing donor atoms, substituent on them and central ring system.[4] The donor groups attached to arms of known pincer ligands include PR_2, AsR_2, NR_2, OR, SR and SeR. Benzene, pyridine or triazole is a core structural unit in many of them.[5] The known unsymmetrical pincer structures are fewer in number than symmetrical ones (both arms identical), which are easy to synthesize. In unsymmetrical pincer ligands two arms differ in one or more of the following three ways: (i) donor atoms in them (ii) substituents on donor atoms and (iii) length of linkers between donor atom and core.[6] When donor atoms are different (i.e. E and E′), metal complex of an unsymmetrical pincer has M–E and M–E′ bonds of different strength. In this situation out of two donor atoms, the one forming more labile bond may dissociate from the metal leaving the relatively inert one bonded, resulting in a condition favorable for catalytic activity.[7] However, major problem with unsymmetrical pincer ligands is their syntheses, as most of such ligands reported so far, are designed by less convenient multi step reactions, which consequently result in low overall yield.[5h] However, catalytic efficiencies of unsymmetrical pincer-palladacycles for some chemical processes are better than those of symmetric ones.[7] Thus, unsymmetrical pincer ligands may be envisaged as important candidates for designing of new and efficient catalysts for organic synthesis. Recently, Pd(II) complexes of chalcogen donor containing symmetrical pincer ligands have emerged as a family of efficient catalysts for various organic transformations including C-C coupling.[8]

The C-H of indole's five membered ring is more acidic than those of benzene. Consequently M-C bond of indole based pincer is expected to be stronger than that of its benzene analogue. Thus ligands with indole as a pincer core are worth exploring, as they have been scantly explored so far. Only one example of (S,C,S) pincer having this core and non-identical arms is known.[9] Herein, first examples of indole core based unsymmetrical (N,C,E) type (E = S / Se) pincer ligand precursors **(L1** and **L2,** Scheme 1), which have different arms as well as donor atoms and their Pd(II) complexes are reported. Interestingly these ligands make both five and six membered chelate rings. Such kind of pincers known, are fewer in number[10] than those which make two five or six membered rings.[1,5-6] The applications of these complexes in catalysis of Heck coupling and allylation of aldehydes have been found promising and are described here.

Heck coupling continues to get attention of both industry and academia[11] due to its synthetic importance. The designing of various pincer and bulky electron-rich phosphine ligands has fuelled investigations on it.[12] High stability of palladium-pincer ligand complexes has made them important for Heck reaction under strident conditions.[1f] In 2003 Szabó and co-workers reported pincer ligand based palladium complexes as highly active and selective catalysts for allylation of aldehydes or activated imines with allylstannanes and showed better results compared to bis(allyl)palladium intermediates.[13a,b] The homoallylic alcohols obtained by allylation of aldehydes are used extensively in the synthesis of biologically active compounds and natural products.[13c-e] For allylation of aldehydes and Heck coupling no complex of palladium(II) with indole based pincer ligand is in our knowledge. The **1** and **2** are probably the first examples.

Results and discussion

The syntheses of **L1** and **L2** and their Pd(II)-complexes (**1** - **2**) are summarized in Scheme 1. 1-(2-Chloroethyl)-1H-indole-3-carbaldehyde (**A**) was synthesized by reacting indole-3-carboxaldehyde with 1,2-dichloroethane (DCE) in the presence of K_2CO_3 and *n*-Bu_4NBr using a reported procedure[14] with some modifications. The nucleophiles PhS^- and $PhSe^-$, generated in

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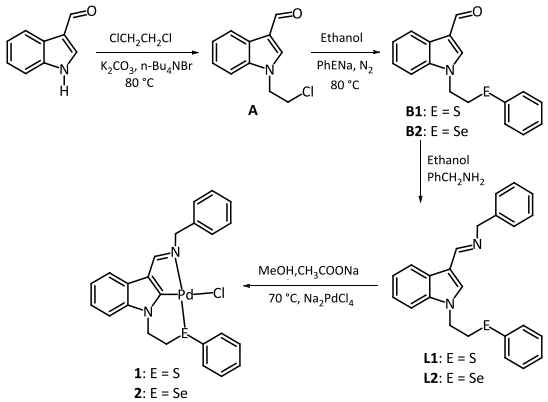
situ by reaction of PhSH with NaOH and reduction of diphenyl diselenide with $NaBH_4$ in EtOH under inert atmosphere respectively, on reaction with compound **A** formed 1-(2-phenylsulfanylethyl)-1H-indole-3-carbaldehyde and 1-(2-phenylselanylethyl)-1H-indole-3-carbaldehyde respectively. These aldehydes on condensation with benzyl amine resulted in (N,C,E)-type pincer ligand precursors **L1** and **L2,** which on palladation with Na_2PdCl_4 in the presence of CH_3COONa in methanol formed complexes **1** and **2** respectively. The **L1** and **L2** have good solubility in common organic solvents: *viz.*, $CHCl_3$, CH_2Cl_2 and EtOAc but their palladium complexes are soluble in them moderately.



Scheme 1. Synthesis of **L1** and **L2** and their complexes, **1** and **2**

NMR spectra

The pincer ligand precursors **L1** and **L2** and their diamagnetic palladium(II) complexes (**1** and **2**) were characterized with ^1H, $^{13}C\{^1H\}$, and $^{77}Se\{^1H\}$ NMR spectroscopy and mass spectrometry (See 'ESI' for scans of various spectra; Figs S4–S29). The NMR and mass spectral data are consistent with the structures depicted for them in Scheme 1. The singlet of CH (imine) in ^1H NMR spectra of **L1** and **L2** appearing at 8.56 and 8.41 ppm respectively, on complexation has been found shifted to 7.86 and 7.88 ppm, shielded by ~0.70 and 0.52 ppm respectively. In $^{13}C\{^1H\}$ NMR spectra, the CH carbon signals appearing at 155.8 ppm for **L1** and **L2** both, are deshielded by ~10 ppm on complexation, appearing at 166.1 and 165.8 ppm in the spectra of **1** and **2** respectively. The signal in $^{77}Se\{^1H\}$ NMR spectrum of **2** appears at 316.0 ppm. It is deshielded by ~30.8 ppm with respect to that of free **L2** (285.2 ppm), implying coordination of Se with palladium.[15]

Crystal structures

Aldehydes **A** and **B1** and complexes **1** and **2** were authenticated by X-ray diffraction on their single crystals. The crystals of **A** and **B1** were obtained by slow evaporation of their solutions made in EtOH. Ethyl acetate – chloroform (1:1) mixture was used to grow single crystals of **1** and **2** in a similar fashion. Figs. 1−4 show the molecular structure of **A**, **B1**, **1** and **2** respectively with selected bond lengths and angles. Their crystal data and structure refinement parameters are given in Tables S1 and S2 of ESI.

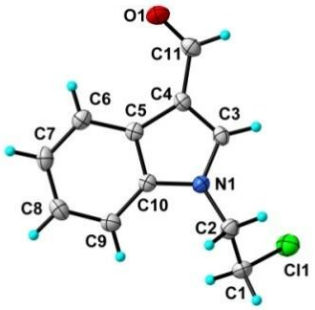


Fig. 1 Molecular structure of **A**. Selected bond distances (Å). Cl(1)−C(1) 1.784(3); N(1)−C(3) 1.358(3); N(1)−C(10) 1.392(3); N(1)−C(2) 1.459(3); C(8)−C(7) 1.393(4); C(11)−O(1) 1.212(3). Selected bond angles (°): C(3)−N(1)−C(10) 108.59(19); C(10)−N(1)−C(2) 125.5(2); O(1)−C(11)−C(4) 126.2(3); N(1)−C(3)−C(4) 110.4(2); C(6)−C(7)−C(8) 121.3(2).

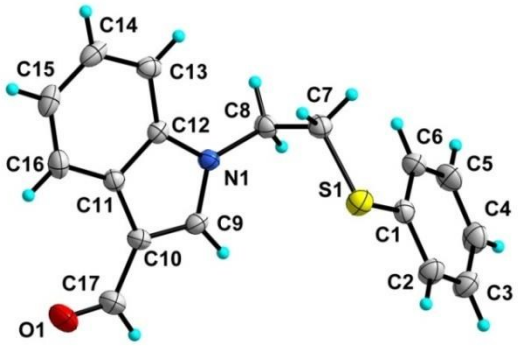


Fig. 2 Molecular structure of **B1**. Selected bond distances (Å). S(1)−C(1) 1.770(3); S(1)−C(7) 1.792(3); N(1)−C(9) 1.352(3); N(1)−C(12) 1.395(3); N(1)−C(8) 1.451(3); C(1)−C(6) 1.381(4); C(17)−O(1) 1.215(4). Selected bond angles (°): C(1)−S(1)−C(7) 103.82(15); C(9)−N(1)−C(12) 108.1(2); C(9)−N(1)−C(8) 126.4(2); C(12)−N(1)−C(8) 125.4(2); C(6)−C(1)−C(2) 117.9(3).

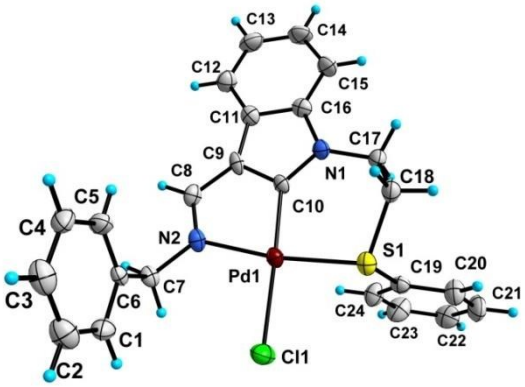


Fig. 3 Molecular structure of **1**. $CHCl_3$ molecule is omitted for clarity. Selected bond distances (Å): Pd(1)−C(10) 1.957(8); Pd(1)−N(2) 2.082(7); Pd(1)−S(1) 2.283(2); Pd(1)−Cl(1) 2.376(2). Selected bond angle (°):C(10)−Pd(1)−N(2) 79.1(3); C(10)−Pd(1)−S(1) 93.4(2); N(2)−Pd(1)−S(1) 171.4(2); C(10)−Pd(1)−Cl(1) 174.4(2).

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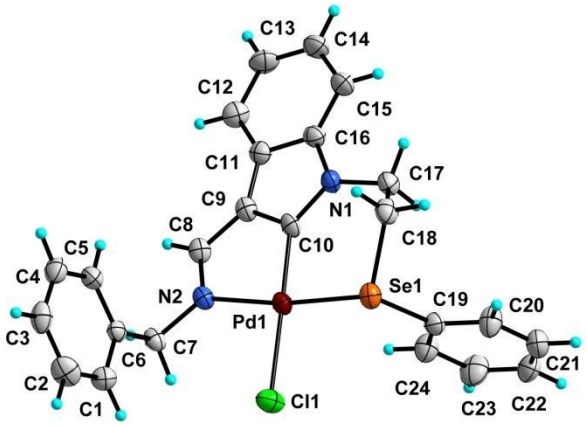


Fig. 4 Molecular structure of **2**. $CHCl_3$ molecule is omitted for clarity. Selected bond distances (Å): Pd(1)−C(10) 1.942(7); Pd(1)−N(2) 2.070(5); Pd(1)−Se(1) 2.3654(10); Pd(1)−Cl(1) 2.358(2). Selected bond angle (°): C(10)−Pd(1)−N(2) 79.5(3); C(10)−Pd(1)−Se(1) 94.2(2); N(2)−Pd(1)−Se(1) 172.18(15); C(10)−Pd(1)−Cl(1) 175.4(2).

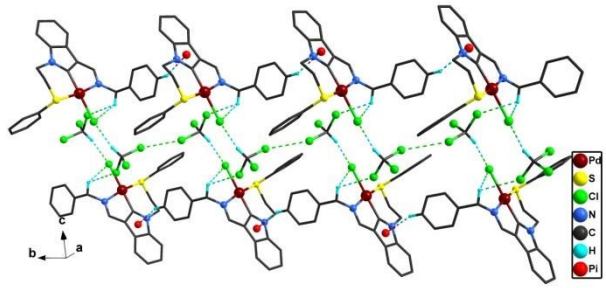


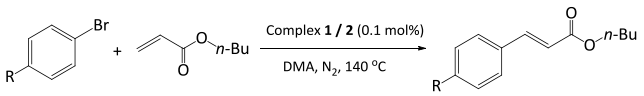
Fig. 5 Non-covalent C−H···Cl interaction in **1**

In Tables S3−S6 of ESI more selected bond lengths and angles for **A, B1**, **1** and **2** are given. Both complexes crystallize with one molecule chloroform (per molecule of **1** or **2**)

Palladium has a distorted square planar geometry in both complexes **1** and **2** with Cl and C(indolyl) disposed *trans* to each other. The Pd−N bond lengths in **1** and **2** (2.082(7) and 2.070(5) Å respectively) are consistent with the reported value, 2.056(4) for a palladacycle of (N, Se, C^-) ligand.[16a] The Pd−C bond distances 1.957(8) and 1.942(7) Å in **1** and **2** respectively are somewhat shorter than the values 1.973(5)[16a] and 1.970(7) Å[16b] reported for Pd−C bonds of palladacycles of reduced chalcogenated Schiff bases. The Pd−Cl bond lengths, 2.376(2) and 2.358(2) Å for **1** and **2** respectively are consistent with each other and somewhat longer than the reported values 2.325(16)[16a] and 2.319(2) Å[16b] for palladacycles of reduced chalcogenated Schiff bases. The Pd−S (2.285(2) Å) and Pd−Se (2.3654(10) Å) bond distances of complexes **1** and **2** are consistent with the values reported for palladium(II)-complexes of 1-phenylthio-2-arylthioethane [2.285(14) Å][16c] and tridentate selenated Schiff base [2.3669(11) Å][16d] respectively. The C−H···Cl and C−H···π secondary interactions in the two complexes result in three dimensional structures (Fig. 5 and Fig. S1 in ESI). Distances of non-covalent interactions of precursor aldehyde of **L1** and **L2** and complexes **1** and **2** are given in ESI (Tables S7 and S8). The C−H···Cl interactions are intra as well as intermolecular and chlorine atoms of both $CHCl_3$ and complex are involved. Chloroform intercalates chains of complexes formed due to C−H···π interactions. The precursor aldehydes **A** and **B1** have O···H secondary interactions which result in three dimensional structural network (ESI: Figs. S2-S3)

Applications of complexes 1 and 2 in Heck coupling and allylation of aldehydes

The catalytic properties of complexes **1** and **2** have been studied for Heck coupling of various aryl bromides with *n*-butylacrylate (Scheme 2). K_2CO_3 has been found best base for this purpose. Optimum reaction temperature and time were found 140 °C and 24 h respectively.



Scheme 2. Heck coupling Catalyzed with **1** and **2**

The coupling of 4-bromoanisole with *n*-butylacrylate was carried out under N_2 atmosphere using complex **1** as a catalyst for optimization of solvent for reaction. The results are summarized in Table 1. The stability of complexes under ambient conditions was found good but for good conversions, the coupling reactions were carried out under nitrogen atmosphere.

Table 1. Optimization of reaction conditions[a] for Heck coupling

Entry No.	Solvent	Base	% Yield[b]
1	DMF	K_2CO_3	26
2	DMA	K_2CO_3	49
3	NMP	K_2CO_3	29
4	DMF+ Water	K_2CO_3	< 10
5	Toluene	K_2CO_3	< 10

[a]*Reaction conditions*: 4-bromoanisole, 1.0 mmol, *n*-butylacrylate, 1.2 mmol, K_2CO_3, 2.0 mmol, solvent, 3 mL, complex catalyst, 0.1 mol%, temperature 140 °C. [b]isolated yield.

The yield of coupled product was found maximum in the presence of 0.1 mol% of **1**, when *N*,*N*-dimethyl acetamide (DMA) was used as a solvent (Table 1; Entry 2). In DMF, *N*-methyl-2-pyrrolidone (NMP) and toluene, the yield of coupled product diminished significantly (Table 1). The coupling in DMA of 4-bromoanisole with *n*-butylacrylate resulted in 49% yield (Table 2; Entry 1) in 24 h at 0.1 mol% of **1**. On increasing the catalyst loading to 0.3 mol% the yield of coupled product increased to 94% in the same reaction time. The yields of coupled

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products were good for 0.1 mol% catalyst loading when an electron withdrawing group was present in ArBr at a position *para* to bromo (Table 2; Entry 6 and 7). For example for reaction of 1-bromo-4-nitrobenzene / 4-bromobenzaldehyde with *n*-butylacrylate in the presence of 0.1 mol % catalyst loading coupled product resulted in yield up to 95%. No product was obtained when attempts were made to couple chlorobenzene with *n*-butylacrylate in the presence of even 1 mol % of **1**/**2.**

Table 2. Heck C−C coupling reaction catalyzed with palladacycle[a]

Entry No.	Aryl halide	Complex **1** Yield[b]	Complex **2** Yield[b]
1	4-Bromoanisole	49/94[c]	55
2	4-Bromoacetophenone	89	95
3	4-Bromotoluene	33/96[c]	60
4	Bromobenzene	91	90
5	1-Bromo-4-nitrobenzene	95	96
6[d]	4-Bromobenzaldehyde	93	95

[a]*Reaction conditions*: Aryl bromide, 1.0 mmol, *n*-butylacrylate, 1.2 mmol, K_2CO_3, 2.0 mmol, reaction time, 24 h, DMA, 3 mL, complex catalyst 0.1 mol%, bath temperature 140 °C. [b]Isolated yield after column chromatography, [c]complex catalyst equiv. to 0.3 mol% of Pd, [d]bath temperature, 110 °C.

Scheme 3. Allylation of aldehydes catalyzed with **1** and **2**

Allylation (Scheme 3) of aryl as well as heteroaryl aldehydes was explored in the presence of **1** and **2** as catalyst. The results are summarized in Table 3. DMF was found best solvent and 1 mol% of each complex as optimum loading for the catalytic process. The yield of allylated product was dependent on electron withdrawing / donating properties of the substituents present at a position *ortho* / *para* to CHO, as the catalytic activity enhanced in the presence of electron withdrawing group. For deactivated 4-methoxybenzaldehyde, the reaction in the presence 1 mol% of catalyst **1,** resulted in its low conversion (51%; Table 3: Entry 6) to allylated product. Allylation of heteroaryl halides was achieved with excellent yields (Table 3: Entry 7 and 8). Among Pd based catalysts for Heck coupling, Pd complexes of pincer ligands have been reported very promising. Therefore, complexes **1** and **2** of (N,C$^-$,E)-pincer ligands, are compared with Pd-complexes of other pincer ligands. They have been found competitive or better in efficiency for Heck coupling than many pincer ligand based palladium catalysts reported to be efficient.[17a-c] Palladium-complexes of some (O,N,N) (**I**)[17a] and (N,C$^-$,N) (**II**)-pincer ligands[17b] are reported as good catalysts for coupling of aryl iodides and but not as effective ones for nonactivated bromobenzene substrates.

Table 3. Allylation of aldehydes catalyzed with complexes 1 and 2 [a]

Entry No.	Aryl aldehyde	Complex **1** Yield[b]	Complex **2** Yield[b]
1	4-Bromobenzaldehde	77	80
2	2-Bromobenzaldehde	93	90
3	4-Chlorobenzaldehyde	95	92
4	Benzaldehyde	94	96
5	4-Methylbenzaldehyde	72	95
6	4-Methoxybenzaldehyde	51	50
7	Furfural	77	80
8	Pyridine-2- carbaldehyde	95	95

[a]*Reaction conditions:* Aryl / heteroaryl aldehyde, 1.0 mmol, allyltributyl stannane, 1.2 mmol, DMF, 2 mL, reaction time 16 h, bath temperature 50 °C. [b]Isolated yield after column chromatography, complex catalyst equiv. to 1 mol% of Pd

.

Some complexes of category **II** are reported little active for Heck coupling at 0.1 mol % catalyst loading, found to be good for **1** and **2**. The optimum loading for good conversion in case of some complexes of type **I** is up to 5 mol %, much higher than those of present (N,C$^-$,E)-pincer complexes for similar conversions. In comparison to (NHC)-pincer complex[17c] of Pd reported for catalysis of Heck-coupling at 0.5 mol % loading (reaction time 20 h, temp. 165 °C), **1** and **2** appear to be better as required catalyst loading is only 0.1 mol% at 140 °C (bath temperature). The 0.5 mol % Pd-(N,C,P)-pincer complex[17d] required for catalysis of Heck coupling of bromoanisole is somewhat higher than 0.3 mol % of present complexes **1** and **2** needed for the coupling of same substrate. Palladium complexes of (C,N,C) pincer ligands[17e] based on NHC moieties and (N,C,N)[17f] pincers having bis(azole) framework are more catalytically efficient for activated aryl bromides than unactivated ones when their loading is 1 mol %, more than the optimum loading of the present pincer complexes. Palladium complex of (N,C,N)-pincer having hexahydro-1H-pyrrolo[1,2-c]imidazolone group in its two side arms, as a catalyst[17g] shows good conversion of aryl iodides in Heck coupling at a loading of 0.1 mol %, but fails in case of ArBr, which undergoes Heck coupling easily in the presence of **1** and **2**. With respect to palladium complex of symmetric (Se,C,Se)-pincer[18a] reported for allylation of *p*-anisaldehyde, the catalytic efficiency of **1** and **2** appears to be comparable as required catalyst loading is 1 mol % in both the cases. The reaction time, 18 h and temperature, 60 °C for Pd complex of (Se, C, Se) pincer are also not much different from those of **1** and **2**. Palladacycle of (P,C,P)-pincer[4c] catalyzes allylation at 0 ºC to room temperature but for good conversion, 5 mol% catalyst loading and 18-120 h reaction time are required. However, with **1** and **2** allylation in good yield is achieved with 1 mol % loading of catalyst at 50-55 ºC in 16 h. Palladium(II) complex of unsymmetrical (C,N,N)-pincer[18b] has been reported as effective catalyst for allylation of

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p-anisaldehyde at 5 mol % loading (reaction time 24 h and temperature 50 ºC). The present (N,C⁻,E)-pincer palladacycles do allylation of *p*-anisaldehyde at 1 mol % loading under almost similar reaction conditions. For allylation of *p*-anisaldehyde 2.5 mol % loading of (P,P,P)-pincer based Pd catalyst[18c] was found insufficient but good conversion resulted with 5 mol % of (P,C,P)-pincer Pd-catalyst.[18d] Thus present complexes **1** and **2** may be placed among efficient catalysts known for Heck coupling and allylation.

Generally for Heck coupling Pd(0)/Pd(II) mechanism is believed, particularly for pincer palladacycles.[12] Under harsh and basic reaction conditions pincer palladacycle undergoes reduction and dispenses catalytically active Pd(0) complex with the cleavage of the Pd-C bond.[1f] The catalytic efficiencies of these Pd(0) species is finely tuned by ligands and consequently pincer complexes differ in activity. Palladium(0) complex enters in the catalytic cycle which includes oxidative addition, β-hydride elimination and base-promoted reductive elimination. In our case also Pd(0)/Pd(II) mechanism appears to be operative, as with onsetting of catalytic process, colour of reaction mixture changes most probably due to the formation of Pd(0) based species.

Szabó and co-workers have suggested mechanism for allylation of aldehydes and imines catalyzed with pincer complexes of palladium.[18d] η^1-Allyl-coordinated pincer species is generated in first step through transmetalation of allylstannane with catalyst. Nucleophilic σ-allylpalladium species undergoes addition to aldehyde (via a cyclic transition state with the metal) and in final step alkoxide-coordinated palladium undergoes exchange reaction with $SnBu_3X$ to give homoallyl alcohol. Presumably a similar mechanistic process occurs in our case also.

4. CONCLUSION

The precursors of unsymmetrical (N,C⁻,E)-pincer ligands based on indole core have been synthesized for the first time. The protocols are easy and give good yields. These precursors on reaction with sodium tetrachloropalladate(II) in the presence of CH_3COONa have resulted in [**Pd(L1/L2−H)Cl**] **(1 / 2)** where ligands bind in a tridentate (N,C⁻,E) mode, making five and six membered chelate rings (one each). Such pincer complexes of palladium are known scantly. The precursor aldehydes, ligand precursors **L1** and **L2** and complexes of **L1/L2−H** have been characterized with multinuclear NMR spectroscopy and mass spectrometry. Both Pd(II) complex **1** and **2** and two precursor aldehydes have been characterized with single crystal X-ray diffraction. The catalytic properties of the two complexes have been investigated for Heck coupling and allylation of aldehydes. Optimum loading of **1** or **2** as catalyst has been found 0.1−0.3 and 1 mol% for catalysis of Heck coupling and allylation respectively. A range of functional groups present on substrates is tolerable in the two catalytic reactions.

Experimental

Materials and instrumentation. Tributylstannane, diphenyl diselenide, sodium borohydride and sodium tetrachloropalladate were procured from Sigma-Aldrich (USA). Indole-3-carboxaldehyde, thiophenol, dichloroethane, *n*-butylacrylate, bases, aldehydes and aryl bromides were procured from local sources. Commercial nitrogen gas was used after passing it successively through traps containing solutions of alkaline anthraquinone, sodium dithionite, alkaline pyrogallol, concentrated H_2SO_4 and KOH pellets. The products of catalytic Heck coupling and allylation were authenticated by matching their ^{1}H NMR data with those reported in the literature. Yields of isolated coupled products [purity ≥ 95% established by ^{1}H NMR] are reported. The ^{1}H, ^{13}C{^{1}H}, and ^{77}Se{^{1}H} NMR spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300.13, 75.47, and 57.24 MHz, respectively with chemical shifts reported in ppm relative to internal standards. Carbon-13 DEPT NMR experiments were used routinely to determine the number of hydrogen atoms linked to carbon atoms. Melting points were determined in an electrically heated apparatus by taking the sample in a glass capillary sealed at one end. High-resolution mass spectral (HR-MS) measurements were performed with an instrument Bruker Micro TOF-Q II, based on electron spray ionization (10 eV, 180 °C source temperature, and sodium formate as calibrant), taking the sample in CH_3CN. Suitable single crystals of **1** and **2** were obtained by slow evaporation of their solutions made in ethylacetate – chloroform (1:1) mixture. The slow evaporation of solutions of **A** and **B1** made in ethanol also gave their single crystals. X-ray diffraction data for all these crystals were collected at 298(2) K on a Bruker AXS SMART Apex CCD diffractometer using Mo-Kα (0.71073 Å) radiation. Frames were collected at T = 298 K by ω, φ, and 2θ- rotations with full quadrant data collection strategy (four domains each with 600 frames) at 10s per frame with SMART. The measured intensities were reduced to F^2 and corrected for absorption with SADABS.[20] Structure solution and refinement were carried out with the SHELXTL package by direct methods.[21] Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in idealized positions and a riding model was used for the refinement. Images were created with the program Diamond.

Synthesis of 1-(2-chloro-ethyl)-1H-indole-3-carbaldehyde. Indole-3-carbaldehyde (2.18 g, 15 mmol), 1,2-dichloroethane (75 mL), *n*-Bu_4NBr (4.83 g, 15 mmol), K_2CO_3 (18 g) and 40 mL of distilled water were taken in a 250 mL round bottom flask. The mixture was heated on an oil bath maintained at 80 °C with vigorous stirring for 2 h. The reaction mixture was cooled and diluted with 100 mL of water and extracted with dichloromethane (2 × 50 mL). The organic layer was washed with water (5 × 50 mL) and dried over anhydrous sodium sulfate. The solvent of extract was evaporated off under reduced pressure on a rotary evaporator to get 1-(2-chloroethyl)-1H-indole-3-carbaldehyde as yellow solid which was recrystallized with hot ethanol to get white solid.

A: white solid; Yield 2.95 g, (95%). Anal. Found: C, 63.60; H, 4.83; N, 6.73%. Calcd for $C_{11}H_{10}ClNO$: C, 63.62; H, 4.85; N, 6.75%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS): δ (ppm): 3.81 (t, 2H, J = 6.0 Hz, H_1), 4.46 (t, 2H, J = 6.0 Hz, H_2), 7.25–7.29 (m, 3H), 7.73 (s, 1H), 8.25–8.28 (m, 1H), 9.96 (s, 1H, H_{11}). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 ºC, TMS): δ (ppm): 42.1, 48.5, 109.5, 118.3, 122.2, 123.0, 124.1, 125.2, 136.6, 139.0, 184.6.

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Synthesis of 1-(2-phenylsulfanyl/selanylethyl)-1H-indole-3-carbaldehyde. 1-(2-Chloroethyl)-1H-indole-3-carbaldehyde (2.07g, 10 mmol) dissolved in 20 mL of ethanol was added drop wise to a solution of PhSNa or PhSeNa generated in situ by the reaction of NaOH (0.40 g, 10.0 mmol) with thiophenol (1.10 g, 10.0 mmol) or $NaBH_4$ (0.37 g, 10 mmol) reduction of diphenyldiselenide (1.52 g, 5 mmol) at 80 °C under nitrogen atmosphere. The reaction mixture was heated on an oil bath kept at 80 °C for 6 h. It was allowed to cool to room temperature, poured in 100 mL of distilled water and extracted with chloroform (100 mL). The extract was washed with water (3 × 50 mL) and dried over anhydrous sodium sulfate. The solvent was evaporated off under reduced pressure on a rotary evaporator to obtain the product **B1** or **B2**.

B1: Light yellow solid; Yield: 2.6 (93%). Anal. Found: C, 72.50; H, 5.35; N, 4.95%. Calcd for $C_{17}H_{15}NOS$: C, 72.57; H, 5.37; N, 4.98%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS): δ (ppm): 3.22 (t, 2H, J = 6.9 Hz, H_7), 4.24 (t, 2H, J = 6.9 Hz, H_8), 7.12–7.26 (m, 8H), 7.55 (s, 1H), 8.18–8.21 (m, 1H), 9.85 (s, 1H, H_{17}). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 ºC, TMS): δ (ppm) 33.6, 46.4, 109.6, 118.2, 122.2, 122.9, 124.0, 125.3, 127.1, 129.2, 130.3, 133.8, 136.7, 138.6, 184.5.

B2: Light yellow solid; Yield: 2.95g (90%). Anal. Found: C, 62.28; H, 4.64; N, 4.21%. Calcd for $C_{17}H_{15}NOSe$: C, 62.20; H, 4.61; N, 4.27%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS): δ (ppm): 3.17 (t, 2H, J = 6.9 Hz), 4.31 (t, 2H, J = 6.9 Hz), 7.08–7.18 (m, 1H), 7.15–7.23 (m, 5H), 7.37–7.40 (m, 2H), 7.55 (s, 1H), 8.17–8.23 (m, 1H), 9.85 (s, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 ºC, TMS): δ (ppm) 26.5, 47.3, 109.6, 118.2, 122.2, 122.9, 124.0, 125.4, 127.8, 128.0, 129.4, 133.3, 136.7, 138.2, 184.4. ^{77}Se{^{1}H} NMR ($CDCl_3$, 25 °C, Me_2Se): δ (ppm): 287.2.

Synthesis of benzyl-[1-(2-phenylsulfanyl/selanylethyl)-1H-indol-3-ylmethylene]amine (L1/L2) 1-(2-Phenylsulfanyl/selanylethyl)-1H-indole-3-carbaldehyde (2.0 mmol) was stirred in dry ethanol (5 mL) at room temperature for 0.5 h. Benzylamine (0.214 g, 2.0 mmol) dissolved in dry ethanol (2 mL) was added to it drop wise with stirring. The reaction mixture was stirred further at room temperature for 12 h. It was then cooled in refrigerator overnight. The precipitate was filtered off and washed with cold ethanol.

L1: White solid; Yield: 0.65 g (88%). Anal. Found: C, 77.83; H, 5.90; N, 7.52%. Calcd for $C_{24}H_{22}N_2S$: C, 77.80; H, 5.98; N, 7.56%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS): δ (ppm): 3.29 (t, 2H, J = 6.9 Hz, H_{18}), 4.32 (t, 2H, J = 7.5 Hz, H_{17}), 4.83 (s, 2H, H_7), 7.20–7.42 (m, 14H), 8.34–8.37 (m, 1H), 8.56 (s, 1H, H_8). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 ºC, TMS): δ (ppm) 33.8, 46.0, 65.5, 109.1, 114.8, 121.3, 122.2, 123.0, 126.4, 126.6, 127.0, 127.8, 128.3, 129.2, 130.3, 131.6, 134.4, 136.6, 140.5, 155.8. HR-MS [M + H] (m/z) = 371.1578; calcd. value for $C_{24}H_{23}N_2S$ = 371.1576 (ppm error δ: 0.3).

L2: White solid; Yield: 0.71 g (85%). Anal. Found: C, 69.01; H, 5.36; N, 6.77%. Calcd for $C_{24}H_{22}N_2Se$: C, 69.06; H, 5.31; N, 6.71%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS): δ (ppm): 3.07 (t, 2H, J = 7.5 Hz, H_{18}), 4.19 (t, 2H, J = 7.5 Hz, H_{17}), 4.70 (s, 2H, H_7), 7.00–7.03 (m, 1H), 7.08–7.18 (m, 6H), 7.21–7.31 (m, 5H), 7.37–7.43 (m, 2H), 8.22–8.25 (m, 1H), 8.41 (s, 1H, H_8). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 ºC, TMS): δ (ppm) 26.7, 46.7, 65.4, 109.1, 114.6, 121.2, 122.1, 123.0, 126.3, 126.5, 127.6, 127.7, 128.3, 128.4, 129.3, 131.4, 133.2, 136.5, 140.4, 155.8. ^{77}Se{^{1}H} NMR ($CDCl_3$, 25 °C, Me_2Se): δ (ppm): 285.2. HR-MS [M + H] (m/z) = 419.1012; calcd. value for $C_{24}H_{23}N_2S$ = 419.1022 (ppm error δ: 2.4).

Synthesis of palladium complexes 1 and 2. A solution of ligand **L1** or **L2** (0.2 mmol) made in 20 mL of methanol was heated at 70 °C for 15 minutes. Anhydrous sodium acetate (0.02 g, 0.24 mmol) was added to it with stirring and the reaction mixture was further stirred for 15 min. Sodium tetrachloropalladate(II) (0.059 g, 0.2 mmol) was added to the reaction flask and the resulting mixture was further heated at 70°C for 6 h. The solvent of the mixture was removed completely on a rotary evaporator. The green residue was dissolved in 30 mL of chloroform and filtered through celite. The volume of solution was reduced to ~3 mL and it was mixed with 50 mL of hexane to obtain complex **1** or **2** as yellowish green colored powder.

Complex 1: Yellowish green solid; Yield: 0.082 g (80%). m.p. 153 °C(d). Anal. Found: C, 56.32; H, 4.17; N, 5.42%. Calcd for $C_{24}H_{21}ClN_2PdS$: C, 56.37; H, 4.14; N, 5.48%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS): δ (ppm): 3.29 (br, 2H, H_{18}), 4.37 (br, 2H, H_{17}), 5.06 (br, 2H, H_7), 7.05–7.16 (m, 3H), 7.30–7.52 (m, 9H), 7.86 (s, 1H, H_8), 8.01–8.03 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 ºC, TMS): δ (ppm): 37.8, 42.5, 60.3, 109.0, 117.6, 120.5, 120.6, 122.1, 125.8, 127.4, 127.6, 128.7, 129.1, 129.8, 130.9, 134.0, 136.5, 138.4, 165.6, 166.1. HR-MS [M − Cl] (m/z) = 475.0474; calcd. value for $C_{24}H_{21}N_2PdS$ = 475.0463 (ppm error δ: 2.2).

Complex 2: Yellowish Green Solid; Yield: 0.093 g (83%). m.p. 165 °C(d). Anal. Found: C, 51.60; H, 3.82; N, 5.00%. Calcd for $C_{24}H_{21}ClN_2PdSe$: C, 51.63; H, 3.79; N, 5.02%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS): δ (ppm): 3.04–3.13 (m, 1H), 3.25–3.26 (m, 1H), 3.82–3.91 (m, 1H), 4.67–4.72 (m, 1H), 4.81–4.85 (m, 1H), 4.97–5.12 (m, 1H), 7.03–7.16 (m, 3H), 7.26–7.52 (m, 9H), 7.88 (s, 1H, H_8), 8.00–8.03 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 ºC, TMS): δ (ppm): 29.3, 43.3, 60.1, 109.1, 117.5, 120.6, 121.3, 122.0, 124.2, 125.8, 127.4, 128.7, 129.1, 130.0, 130.5, 134.8, 136.7, 138.5, 165.0, 165.8.^{77}Se{1H} NMR ($CDCl_3$, 25 °C, Me_2Se): δ (ppm): 316.0. HR-MS [M − Cl] (m/z) = 522.9893; calcd. value for $C_{24}H_{21}N_2PdS$ = 522.9931 (ppm error δ: 3.8).

General procedure for Heck coupling. Aryl bromide (1.0 mmol), *n*-butylacrylate (1.2 mmol) and K_2CO_3 (2.0 mmol) were added to a 50 mL three neck round bottom flask and purged with nitrogen. An appropriate amount of complex (**1** or **2**) from a stock solution made in DMA was added drop wise and the reaction mixture was heated for 24 h on an oil bath maintained at 140 °C. The mixture was cooled, diluted with 20 mL of water and extracted with ethylacetate (2 × 25 mL). The organic layer was washed with water (3 × 50 mL), dried over Na_2SO_4 and its solvent evaporated off on a rotary evaporator. The crude product obtained as a residue was purified by column chromatography on silica gel using ethylacetate and hexane as eluent.

General procedure for allylation. Solution of aldehyde (1 mmol) and Pd complex **1** or **2** (1.0 mol%) in DMF (2 mL) was flushed with nitrogen for 10 min. Allyltributyltin (1.2 mmol) was added drop wise and the reaction mixture was stirred at 50 °C (oil

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bath temperature) for 24 h. After cooling, the reaction was quenched by the addition of 10% aqueous KF solution (30 mL) and the reaction mixture stirred further at room temperature for 3 h. Thereafter the mixture was extracted with ethyl acetate (2 × 25 mL). The organic layer was washed with water (2 × 50 mL), dried over Na_2SO_4 and its solvent evaporated off on a rotary evaporator. The residue (crude product) was purified by column chromatography on silica gel using ethylacetate and hexane as eluent.

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Notes and references

Department of Chemistry, Indian Institute of Technology Delhi, New Delhi 110016, India.

**Corresponding author. Fax: +91-01- 26581102; Tel: +91-011-26591379;E-mail:aksingh@chemistry.iitd.ac.in, ajai57@hotmail.com (A. K. Singh)*

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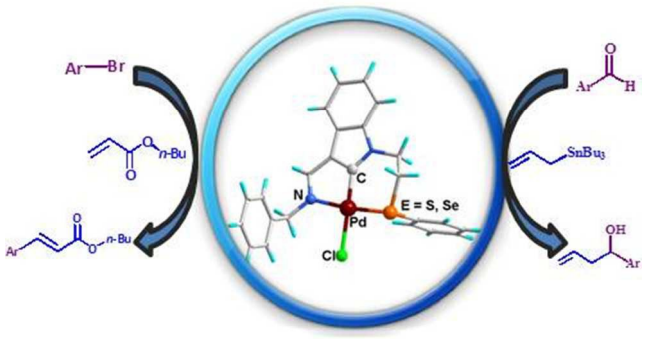
Palladacycles of unsymmetrical (N,C ⁻,E) (E = S / Se) pincers based on indole: Synthesis, structure and catalysis of Heck coupling and allylation of aldehydes

Mahabir P. Singh, Fariha Saleem, Gyandshwar K. Rao, S. Kumar, Hemant Joshi and Ajai K. Singh*



Palladacycles of Schiff bases of 1-(2-phenylsulfanyl/selenylethyl)-1H-indole-3-carbaldehyde with benzyl amine catalyze Heck coupling and allylation at 0.1-0.3 and 1.0 mol% respectively.