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ARTICLE

Bis(chalcogenones) as pincer ligands: Isolation and Heck activity of the selone-ligated unsymmetrical C,C,Se-Pd pincer complex

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The reaction of *meta*-phenylene-bis(1-methyl-1*H*-imidazole-2(3*H*)-selone) with [Pd₂(μ-Cl)₂(2-C₆H₄CH₂NMe₂)₂] in dry benzene and glacial acetic acid resulted in the formation of an unsymmetrical 5,6-membered C,C,Se-Pd(II) pincer complex through C-H bond activation and extrusion of one selenium. This is the first example of a C,C,Se-Pd(II) complex wherein the central Pd(II) is simultaneously coordinated to a selone and a N-heterocyclic carbene. The chelated complex of the type [PdL₂]²⁺[PF₆]⁻ (L = bis(selone)) was isolated from the reaction of the bis(selone) with [PdCl₂(PhCN)₂] and NH₄PF₆. The unsymmetrical pincer complex was studied for Heck activity revealing its application as an acceptable catalyst in coupling of iodobenzene with acrylates and styrene.

Introduction

Palladium complexes of pincer ligands of the type D,C,D (D = N, P, O, S) have attracted considerable current interest in various catalytic reactions.¹ However, the pincer ligands involving Se donors, usually selenoethers, are comparatively few due to difficulty in synthesis, handling and malodorous nature of the organoselenium ligands.² The first important result was demonstrated by Yao *et al.*^{2c} wherein the symmetrical Se,C,Se-Pd(II) catalyst was synthesized through C-H activation of the bis(selonide). The palladium complex was shown to be an excellent Heck catalyst with its ability to couple relatively unreactive aryl bromides and *n*-butyl acrylate with extremely high TON (≈ 240 000) and high yield. The catalytic activity was not only comparable with the analogous P- and S-donor pincers but also outperforming them. Also, the catalytic efficiency of an air and moisture stable unsymmetrical C,N,Se pincer consisting of Schiff-base ligand scaffold was studied in Suzuki-Miyaura C–C coupling.³ A recent review highlights the synthesis and catalytic activity of organochalcogen based Pd(II) complexes including selenium-ligated Pd(II) pincer complexes in Heck catalysis.⁴ More recently, Singh and coworkers have developed a related chelate complex with NHC and selenoether ligand and shown its catalytic activity for Suzuki–Miyaura coupling reactions.⁵

The pincer complexes discussed above have generally more common 5,5-membered ring systems, however, the examples of 6,6-membered Pd(II) pincers are relatively rare,⁶ while there is no evidence of 7,7-membered pincer complexes. We intuited the use of selones as pincer donors instead of selenoethers. It was envisaged that a strong Pd–Se overlap due to the existence of considerable zwitterionic C⁺–Se⁻ character in C=Se may lead to the isolation of stable pincer complexes with higher than five ring members.⁹ Recently, we reported a series of benzimidazol-2-chalcogenones (chalcogen = S, Se, Te). Interestingly, the DFT calculation of the chalcogenoes suggested the characteristic negative charge on the chalcogen atoms.⁷ Even though the transition metal complexes of selones are reported in literature,⁸ the potential of these ligands as pincers has never been explored. Therefore, it was decided to explore the role of bis(chalcogenone) pincer ligands to access 6,6- and 7,7-membered Pd(II) pincer complexes. The present investigation reports the formation of an unprecedented C,C,Se unsymmetrical pincer complex, which was further explored for its catalytic ability in Heck C–C coupling of iodobenzene and alkenes.

Results and discussion

Synthesis of bis(chalcogenones): Bis(selone) **7** was prepared from salt **1**¹⁰ through a reported procedure with slight modification (route A, Scheme 1). The reactions of salts **2-6** with disodium dichalcogenides (prepared *in situ*) in the presence of potassium *t*-butoxide in dry THF afforded bis(chalcogenones) **8-13** (route B).⁷ Bis(chalcogenones) **7-13** were characterized by ¹H, ¹³C, ⁷⁷Se and ¹²⁵Te NMR spectroscopy. The ⁷⁷Se NMR signals for bis(selones) **7, 8** and **10-13** were observed at ~ δ 32, 61, 59, 60, 198 and 102 ppm, respectively while the ¹²⁵Te NMR signal for

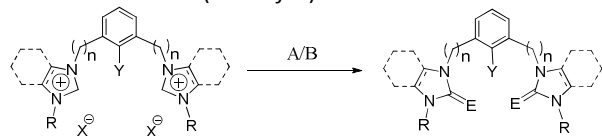
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Electronic Supplementary Information (ESI) available: [NMR Spectra, mass spectra and elemental analysis of the compounds. Crystal packing diagrams, bond lengths and bond angles for **8, 9** and **13**. Cif files for **8, 9, 13, 15** and **16**.]. See DOI: 10.1039/x0xx00000x

bis(tellurone) **9** at δ -129 ppm. Compounds **8**, **9** and **13** were further characterized by single crystal X-ray diffraction studies (*vide infra*).

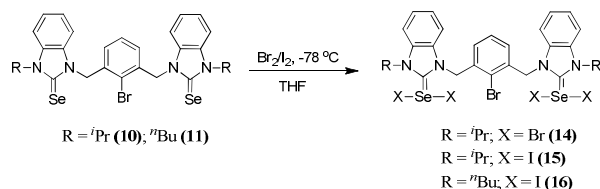


A = (i) 2.2 eq. K_2CO_3 (ii) 2.1 eq. Se; B = (i) Na_2E_2 (E = Se, Te); (ii) KO^tBu

Sr. No.	R	X	Y	n	NHC	Sr. No.	R	Y	n	NHC	E
1	Me	I	H	0	Im	7	Me	H	0	Im	Se
2	ⁿ Bu	Br	H	1	BzIm	8	ⁿ Bu	H	1	BzIm	Se
3	ⁱ Pr	Br	Br	1	BzIm	9	ⁿ Bu	H	1	BzIm	Te
4	ⁿ Bu	Br	Br	1	BzIm	10	ⁱ Pr	Br	1	BzIm	Se
5	^t Bu	Br	Br	1	BzIm	11	ⁿ Bu	Br	1	BzIm	Se
6	Py	Br	Br	1	BzIm	12	^t Bu	Br	1	BzIm	Se
						13	Py	Br	1	BzIm	Se

Scheme 1. Synthesis of pincer bis(chalogenones)

Synthesis of bis(dihaloselones) : Bis(selones) **10** and **11** were further characterized by synthesizing their halogen derivatives (**14-16**) wherein the oxidative addition derivatives were obtained by the reaction of corresponding halogens in THF at -78 °C (Scheme 2). The ^{13}C NMR signals ($\sim \delta$ 150 ppm) and ^{77}Se NMR signals ($\sim \delta$ 160 ppm) of the iodo-derivatives **15** and **16**, suggested that the electron density has been shifted from selenium to carbene carbon with respect to the precursors **10** and **11** respectively.

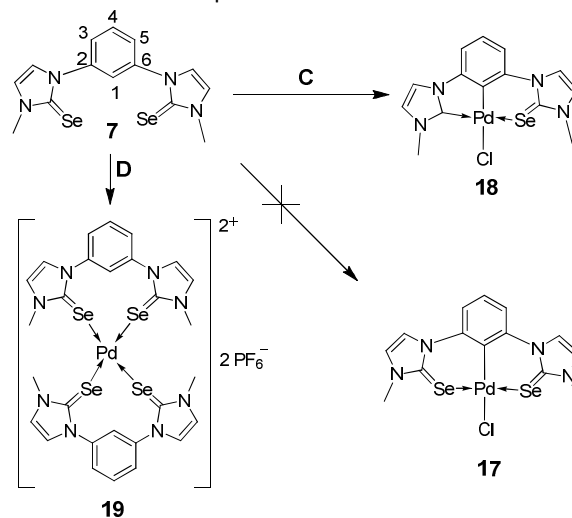


Scheme 2. Synthesis of bis(dihaloselones)

Synthesis of Pd(II) complexes of bis(chalogenones): In an attempt to prepare symmetrical 6,6-membered Pd(II) pincer complex **17**, bis(selone) **7** was refluxed with Pd(II) precursor $[Pd_2(\mu-Cl)_2(2-C_6H_4CH_2NMe_2)_2]^{2c}$ in dry benzene and glacial acetic acid. This resulted in an unprecedented formation of 5,6-membered unsymmetrical C-H activated Pd(II) pincer complex **18** via extrusion of one selenium (route C, Scheme 3). The molecular structure was confirmed by single crystal X-ray crystallography (*vide infra*). The extrusion of selenium may take place via the formation of palladium selenide.^{11a,b} The extrusion leads to almost planar pincer complex accompanied with formation of a 5-membered chelate ring where a NHC is strongly bonded to palladium. The formation of a planar, more rigid structure with one 5-membered chelate ring and NHC as a ligand may be the driving forces for the extrusion of selenium.

Also, cleavage of C=Se bond has been observed in the literature.^{11c} Attempts to prepare analogous symmetrical 6,6-membered PCP-Rh(I) pincer complexes by Chauvin and coworkers were unsuccessful, further demonstrating the difficulty in the synthesis of higher ring system pincer complexes.^{12a} Significantly, **18** is the first example of 5,6-membered selone ligated Pd(II) pincer complex reported to date. The synthesis of symmetrical 7,7-membered Pd(II) pincer complexes was attempted through extension of the same approach to bis(selones) **8** and **9** comprising a methylene spacer. This yielded an intractable mixture of compounds and the attempts to purify, isolate or characterize proved futile. The application of other synthetic strategies such as C-H activation of **8** and **9** through more electrophilic Pd(II) precursors like $Pd(OAc)_2$, $[Pd(CH_3CN)_4(BF_4)_2]$ or more facile oxidative addition of C-Br bond (**10-13**) to Pd(0) precursor $Pd_2(dba)_3$ also proved unsuccessful. Interestingly, Nicasio-Collazo and coworkers who synthesized an unsymmetrical 5,7-membered NNC-Pd(II) pincer, emphasized the difficulty in the synthesis of palladacycles larger than six members due to facile reductive elimination pathway.^{12b}

The cationic Pd(II) complex (**19**) of the type $[PdL_2]^{2+}2[PF_6]^-$ (L = **7**) was isolated by the reaction of **7** with $[PdCl_2(PhCN)_2]$ (2:1 ratio) and NH_4PF_6 (route D, Scheme 3) and characterized with common NMR spectroscopy and single crystal X-ray crystallography (*vide infra*). The reaction of **7** with $[PdCl_2(PhCN)_2]$ in 1:1 ratio and NH_4PF_6 also gives the same product **19** in low yield. However, attempts to isolate cationic Pd(II) complexes of **8-13** with $[PdCl_2(PhCN)_2]$ and NH_4PF_6 resulted in insoluble products, which could not be purified and characterized.



C = (i) $[Pd_2(\mu-Cl)_2(2-C_6H_4CH_2NMe_2)_2]$, benzene, 5 h; D = $[PdCl_2(PhCN)_2]$, NH_4PF_6 (2.2 eq.).

Scheme 3. Synthesis of Pd(II) complexes of bis(selones)

The dissymmetric electronic environment of **18** was evident from the 1H and ^{13}C NMR spectra. As expected the four imidazole protons as well as the two protons (C_3-H and C_5-H) of the phenylene bridge are different from each other. The C_1-H proton peak (7.96 ppm) of phenylene ring of the ligand **7** is

absent in the ^1H NMR of **18**. Interestingly, ^{13}C NMR for **18** exhibits two different methyl carbons at ~ 36 ppm and twelve aromatic carbons as compared to only one methyl peak and seven aromatic carbons in **7**. The observation of ^{13}C peak of C=Se in **18** at 171 ppm and ^{77}Se peak at 97 ppm much downfield with respect to **7** (^{13}C (156 ppm) and ^{77}Se (32 ppm)) is the direct outcome of deshielding effect due to coordinate bonding between Pd and Se thereby reducing the electronic density on the selenium. An downfield shift of ^{77}Se NMR signal (δ 42 ppm) was observed for the complex **19** compared to the bis(selone) **7** (δ 32 ppm).

X-ray crystallography

Compounds **8**, **9** and **13** crystallize in $P2_1/c$ space group with monoclinic crystal system. The molecular structure of compound **8** is shown in Figure 1a. The significant bond distances and angles for **8**, **9** and **13** are mentioned in SI (Table 1). In compound **8** the bond length Se1-C1 (1.833(4) Å) is slightly smaller than the Se2-C20 (1.842(5) Å). Interestingly, the Se2-C20-N4A (131.0(4) $^\circ$) bond angle is significantly higher than related bond angles Se1-C1-N1 (126.6(3) $^\circ$), Se1-C1-N2 (126.4(3) $^\circ$) and Se2-C20-N3 (125.5(3) $^\circ$). In the absence of 1-bromo group on the central aryl ring, the two selenium atoms are *cis* to each other. In compound **9** (Figure 1b) the bond lengths Te1-C1 (2.087(10) Å) and Te2-C20 (2.073(9) Å) are almost equal. Also all Te-C-N (126.00(1) $^\circ$) bond angles are equal. The two tellurium atoms are *cis* to each other with respect to the middle benzene ring. In compound **13**, the bond length Se1-C2B (1.824(4) Å) is slightly smaller than the Se2-C2A (1.836(4) Å) (Figure 1c). However, these bond lengths are comparable with the Se-C bond lengths of related compounds.⁷ The two benzimidazole ring planes are perpendicular to the middle benzene ring plane and also the two selenium atoms are *trans* to each other.

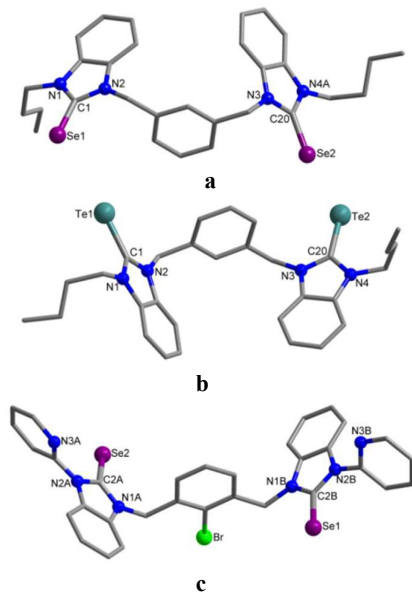


Figure 1. Molecular structures of compounds **8** (a), **9** (b) and **13** (c). Hydrogen atoms are omitted for clarity.

The molecular packing diagrams of compounds **8** and **9** show 1-D network formed by π - π stacking interactions (3.777(1) Å for **8** (Figure 78 in SI) and 3.846(2) Å for **9**, (Figure 79 in SI)). Due to these interactions, the supramolecular structure has been formed. The packing diagram of **13** showed a centrosymmetric pair due to intermolecular secondary Se1 \cdots Br* and Se1* \cdots Br interactions (Figure 80 in SI). One of the selenium atoms interacts with the bromine atom of the other molecule. The Se1 \cdots Br* and Se1*-Br distance (3.668 Å) is significantly higher than the sum of the single bond covalent radii for Se (1.22 Å) and bromine (1.21 Å), but shorter than the sum of van der Waals radii (3.75 Å). Also the C2A- π interactions have been observed which are responsible for the formation of the 1-D network.

The molecular structures of **18** and **19** with atomic numbering scheme are shown in Figure 2.

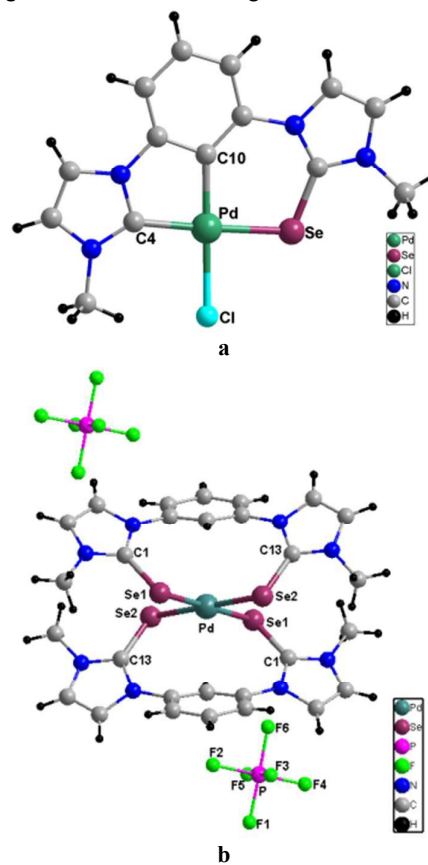


Figure 2. Molecular structures of compounds **18** (a) and **19** (b). Significant bond lengths [Å] and angles [$^\circ$]: 15: Pd-C(10) 2.022(4); Pd-C(4) 2.014(4); Pd-Se 2.3773(5); Pd-Cl 2.3967(10); C(10)-Pd-Cl 178.75(12); C(4)-Pd-Se 176.36(13). 16: Pd-Se(1) 2.4508(5); Pd-Se(2) 2.4553(5) Se(1)-Pd-Se(1)#1 180.000(1).

The crystals of **18** were obtained by slow evaporation of an acetonitrile solution of the compound. The Pd(II) metal centre is bound in a tridentate way to the carbene \wedge C \wedge Se ligand, with the fourth site occupied by a chlorine atom. The geometry of this cyclometalated complex is distorted square planar as the C(4)-Pd-C(10) bond angle of 82.0 $^\circ$ and the C(10)-Pd-Se bond

angle of 95.9° deviate from ideal 90° due to the planar and rigid framework of the carbene[^]C[^]Se ligand (Figure 2a). The Pd–Se bond length of 2.3773(5) Å is significantly shorter than that reported (~ 2.528 Å) for the selenium-ligated palladacycle reported by Singh and coworkers.⁵ Moreover, it is also shorter than Pd–Se bond distances of 2.4508(5) and 2.4553(5) Å observed for chelated complex **19**. The Pd–Cl bond length (2.3967(10) Å) is longer than the value of 2.325(16) Å for the selenium-ligated palladacycle reported by Singh and coworkers.³ This may be due to the increase in s-character in sp² hybridised orbitals of selenium compared to sp³ hybridization in selenoethers. This may facilitate a better overlap with d-orbitals of palladium, resulting in a very strong interaction and thus a shorter bond length.

Complex **19** crystallized as red crystals through slow evaporation of acetonitrile solution of the complex. Complex **19** is symmetrical where Pd(II) metal centre is chelated to two bis(selone) ligands resulting in square planar geometry with Se–Pd–Se bond angle in the range of 88–91° (Figure 2b). The two selone ligands are *anti* with respect to each other and arranged in a zig-zag mode to the central metal. The Pd–Se bond distances 2.4508(5) and 2.4553(5) Å of **19** are comparable to those reported for Pd(II) coordination complexes of N,N-dimethylselenourea.¹³ The two PF₆[−] anions are outside the coordination sphere and are involved in hydrogen bonding through fluorine with protons of the imidazole moiety.

Catalytic activity of **18**

The selone ligated Pd(II) pincer complex **18** was studied as a catalyst for Heck C–C coupling reaction and the optimization and catalytic activity data is mentioned in Table 1.¹⁴ The evaluation of various bases for coupling of iodobenzene with methyl acrylate in DMA (1 mol% catalyst loading) illustrated that Et₃N is a relatively less active base (entry 1), NaOMe and KO^tBu are inactive bases (entries 2 and 3). It was observed that bases like K₂CO₃ and Cs₂CO₃ are more active resulting in 95% and 75% yields (entries 4 and 5) but eventually K₂CO₃ was preferred as base over Cs₂CO₃ for further reactions with less reaction time as well as better yields. The unsuccessful assessment of other solvents like xylene and DMSO (entries 6 and 7) proved that

DMA is a superior solvent for this reaction. The coupling of iodobenzene with *n*-butyl and *t*-butyl acrylates in DMA (1 mol% catalyst loading) resulted in high yields (~ 95%) in comparatively less reaction times (~ 7 h) (entries 8 and 9). Almost analogous high yields were obtained in coupling of iodobenzene with styrene under similar reaction conditions but moderately prolonged reaction time of 20 h (entry 10). Attempts to couple less reactive substrates like bromobenzene with acrylates proved futile (entry 11). The catalytic activity of **18** is observed to be high with respect to reactive substrates like iodobenzene, but has no activity as compared to other selenium-ligated Pd(II) pincer complexes studied which show better activity for less reactive and inexpensive substrates like ArBr and ArCl.^{2c,3}

Conclusions

In summary, we have demonstrated the application of bis(chalcogenone) ligands for synthesizing unsymmetrical, rigid and selone ligated 5,6-membered C,C,Se-Pd(II) pincer complex through C–H bond activation. The synthesis of 7,7-membered pincer complexes was unsuccessful plausibly due to facile reductive elimination pathways. The pincer complex has Pd in dissymmetric electronic environment with very short Pd–Se and long Pd–Cl bond. The complex showed good Heck activity with respect to reactive substrates like iodobenzene.

Experimental section

All reactions were carried out under nitrogen or argon atmosphere using standard Schlenk techniques. Solvents were purified and dried by standard procedures and were distilled prior to use. Melting points were recorded on a Veego VMP-I melting point apparatus in capillary tubes and were uncorrected. The ¹H (400 MHz) and ¹³C (100.56 MHz) NMR spectra were recorded on Varian VXR 400S and Bruker AV 400 spectrometers at 25 °C. The ⁷⁷Se (57.22 MHz and 76.3 MHz) and ¹²⁵Te (94.79 MHz and 157.97 MHz) NMR spectra were recorded on a Varian VXR 300S and Bruker AV 400 spectrometers. Chemical shifts are cited with respect

Table 1. Catalytic activity of **18 in Heck C–C coupling of aryl halides and acrylates.**

Entry	Aryl Halide	Alkene	Product	Base	Solvent	Temp	Time	Yield
1	Iodobenzene	Methyl acrylate	Methyl cinnamate	Et ₃ N	DMA	140 °C	48 h	<5%
2	Iodobenzene	Methyl acrylate	Methyl cinnamate	NaOMe	DMA	140 °C	48 h	-
3	Iodobenzene	Methyl acrylate	Methyl cinnamate	KO ^t Bu	DMA	140 °C	48 h	-
4	Iodobenzene	Methyl acrylate	Methyl cinnamate	K ₂ CO ₃	DMA	140 °C	7 h	95%
5	Iodobenzene	Methyl acrylate	Methyl cinnamate	Cs ₂ CO ₃	DMA	140 °C	48 h	75%
6	Iodobenzene	Methyl acrylate	Methyl cinnamate	K ₂ CO ₃	Xylene	135 °C	48 h	-
7	Iodobenzene	Methyl acrylate	Methyl cinnamate	K ₂ CO ₃	DMSO	180 °C	48 h	-
8	Iodobenzene	<i>n</i> -Butyl acrylate	<i>n</i> -Butyl cinnamate	K ₂ CO ₃	DMA	140 °C	8 h	96%
9	Iodobenzene	<i>t</i> -Butyl acrylate	<i>t</i> -Butyl cinnamate	K ₂ CO ₃	DMA	140 °C	7 h	95%
10	Iodobenzene	Styrene	Stilbene	K ₂ CO ₃	DMA	140 °C	20 h	94%
11	Bromobenzene	Methyl acrylate	Methyl cinnamate	K ₂ CO ₃	DMA	140 °C	48 h	-

to Me₄Si as internal standard (¹H, ¹³C) and Me₂Se (⁷⁷Se) and Me₂Te (¹²⁵Te) as external standards. Elemental analyses were performed on a Carlo Erba Model 1106 elemental analyzer. The ESI mass spectra were recorded on a Q-ToF micro (YA-105) mass spectrometer.

Synthesis of salts 1: Salt **1** was obtained by stirring a mixture of acetonitrile solution of 1,3-di(1*H*-imidazol-1-yl)benzene (1.35 g, 6.42 mmol) with methyl iodide (5 eq.) (4.55 g, 2 mL, 32.1 mmol) at room temperature for 8 h by slightly modifying a reported procedure.¹⁰ The white precipitate formed was washed with diethyl ether and dried. Yield: 2.95 g (93%). ¹H NMR (400 MHz, DMSO): δ (ppm) 9.80 (s, 2H), 8.36 (m, 2H), 8.25 (m, 1H), 8.00-7.90 (m, 4H), 3.95 (s, 6H). ¹³C NMR (100 MHz, DMSO): δ (ppm) 136.3, 135.6, 132.2, 124.7, 122.8, 121.0, 115.9.

General procedure for the synthesis of salts 2-6: Salts **2-6** were synthesized by dissolving 2,6-bis(bromomethyl)-1-bromophenylene (1 eq.) in 1,4-dioxane and the corresponding *N*-alkyl or *N*-aryl benzimidazole (2.2 eq.). The reaction mixtures were refluxed for 14 h under nitrogen atmosphere. The white solids formed were filtered and washed with THF and diethyl ether to afford salts **2-6**.

2: The reagents used are 2,6-bis(bromomethyl)benzene (2.01 g, 7.59 mmol) and *N*-butyl benzimidazole (2.91 g, 16.71 mmol). Yield: 4.6 g (99%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 11.13 (s, 2H), 8.30 (s, 1H), 8.04 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 7.7 Hz, 2H), 7.59-7.51 (m, 4H), 7.29 (t, *J* = 7.7 Hz, 1H), 5.92 (s, 4H), 4.63 (t, *J* = 7.3 Hz, 4H), 2.06-1.99 (m, 4H), 1.48-1.39 (m, 4H), 0.95 (t, *J* = 7.7 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 141.8 (NCN), 134.0, 131.1, 130.8, 129.8, 129.7, 129.4, 127.1, 126.9, 114.3, 112.8, 66.8, 50.2, 47.5 (1,4-dioxane), 30.9, 19.6, 13.3. Anal. Calcd. for C₃₀H₃₆Br₂N₄ + 1H₂O (%): C, 57.15; H, 6.08; N, 8.89. Found: C, 57.35; H, 6.04; N, 8.24.

3: The reagents used were 2,6-bis(bromomethyl)-1-bromophenylene (4.59 g, 13.38 mmol) and *N*-*iso*-propyl benzimidazole (4.71 g, 29.43 mmol). Yield: 7.8 g (88%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.88 (s, 2H), 9.82 (d, *J* = 6.4 Hz, 2H), 8.10 (d, *J* = 8.2 Hz, 2H), 7.78-7.70 (m, 2H), 7.66-7.61 (m, 2H), 7.50-7.42 (m, 3H), 5.97 (s, 4H), 5.21-5.10 (m, 2H), 1.76 (d, *J* = 6.7 Hz, 12H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 142.4 (NCN), 135.6, 133.1, 132.6, 132.5, 130.3, 128.6, 128.4, 126.1, 115.4, 115.1, 68.2, 53.2, 52.8, 22.4. Anal. Calcd. for C₂₈H₃₁Br₃N₄ (%): C, 50.70; H, 4.71; N, 8.45. Found: C, 49.70; H, 4.20; N, 8.99.

4: The reagents used are 2,6-bis(bromomethyl)-1-bromophenylene (0.50 g, 1.45 mmol) and *N*-butyl benzimidazole (0.51 g, 2.91 mmol). Yield: 0.84 g (87%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 11.12 (s, 2H), 8.04 (d, 2H), 7.75 (d, 2H), 7.69 – 7.50 (m, 4H), 7.29 (s, br, 3H), 5.92 (s, 4H), 4.62 (t, *J* = 7.2 Hz, 4H), 2.02 (quint, *J* = 7.2 Hz, 4H), 1.44 (sext, *J* = 7.2 Hz, 4H), 0.91 (t, *J* = 7.2 Hz, 6H). ¹³C NMR (CDCl₃): δ 141.8, 133.9, 131.1, 130.8, 129.8, 129.6, 129.3, 127.1, 126.9, 114.3, 112.8, 50.2, 47.5, 30.9, 19.6, 13.3.

5: The reagents used are 2,6-bis(bromomethyl)-1-bromophenylene (1.55 g, 4.52 mmol) and *N*-*tert*-butyl benzimidazole (1.73 g, 9.94 mmol). Yield: 2.6 g (83%). Mp. 227-229 °C. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.84 (s, 2H), 8.30 (d, *J* = 8.7 Hz, 2H), 7.72-7.68 (m, 4H), 7.60 (t, *J* = 7.1 Hz, 2H), 7.43 (t, *J* = 8.6 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 2H), 6.02 (s, 4H), 1.95 (s, 18H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 142.9 (NCN), 135.6, 133.9, 132.0, 131.7, 130.1, 128.2, 128.1, 125.3, 118.0, 117.9, 115.3, 63.3, 52.7, 29.4, 29.3, 29.2. Anal. Calcd. for C₃₀H₃₅Br₃N₄ + 1H₂O (%): C, 50.80; H, 5.26; N, 7.90. Found: C, 50.78; H, 4.46; N, 8.54.

6: The reagents used are 2,6-bis(bromomethyl)-1-bromophenylene (5.00 g, 14.57 mmol) and *N*-pyridyl benzimidazole (6.15 g, 31.5 mmol). Yield: 9.58 g (84%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 10.69 (s, 2H), 8.80 (d, *J* = 2.7 Hz, 2H), 8.51 (d, *J* = 8.3 Hz, 2H), 8.30 (t, *J* = 7.3 Hz, 1H), 8.12 (d, *J* = 8.2 Hz, 2H), 7.95 (d, *J* = 8.3 Hz, 2H), 7.81-7.72 (m, 6H), 7.49-7.42 (m, 4H), 6.07 (s, 4H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 149.3 (NCN), 147.1, 143.2, 140.5, 133.6, 131.3, 130.5, 129.6, 128.5, 127.8, 127.4, 125.2, 123.9, 117.3, 116.1, 114.0, 51.2. Anal. Calcd. for C₃₂H₂₅Br₃N₆ (%): C, 52.41; H, 3.44; N, 11.46. Found: C, 51.76; H, 2.92; N, 12.54.

Synthesis of bis(selone) 7: A mixture of **1** (1.43 g, 2.89 mmol), Se powder (0.48 g, 6.0 mmol) and K₂CO₃ (0.88 g, 6.36 mmol) was refluxed in dry methanol (50 mL) for 6 h. After which the solvent was evaporated and the residual solid was extracted with chloroform. The chloroform extract was concentrated to 4 mL and 1 mL of methanol was added to yield a white crystalline solid of **7**. (0.644 g, 56%) Mp. 247 °C (dec.). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 129.7, 126.3, 124.6, 120.9, 120.3, 37.6. ⁷⁷Se NMR (57 MHz, CDCl₃): δ (ppm) 32.2. Anal. Calcd. for C₁₄H₁₄N₄Se₂ (%): C, 42.44; H, 3.56; N, 14.14. Found: C, 42.64; H, 3.66; N, 14.67. HRMS: (*m/z*) 398.9647 [M + 1]⁺.

General procedure for the synthesis of bis(chalcogenones) 8-13:

Bis(chalcogenones) **8-13** were synthesized by addition of respective salts **2-6** (1 eq.) into a brownish red solution of Na₂E₂ (3 eq.; E = Se, Te) (prepared *in situ*) under nitrogen atmosphere and the reaction mixture was stirred for 8-10 h at the room temperature. Potassium *tert*-butoxide was added to the reaction mixture and the reaction was further stirred for 5-7 h at room temperature. The reaction mixture was quenched by adding water (50 mL) and extracted with diethyl ether/chloroform, dried over sodium sulfate. Combined organic layer was evaporated under reduced pressure to obtain bis(chalcogenones) **8-13**.

8: Yield: 0.47 g (58%). Mp. 120-122 °C. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.44 (s, 1H), 7.24 (m, 6H), 7.11 (m, 5H), 5.67 (s, 4H), 4.47 (t, *J* = 7.7 Hz, 4H), 1.87 (m, 4H), 1.49 (m, 4H), 1.00 (t, *J* = 7.4 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 167.2 (NCN), 136.2, 133.3, 132.9, 129.5, 127.3, 127.2, 123.5, 110.5, 109.7, 50.1, 47.0, 30.3, 20.3, 13.9. ⁷⁷Se NMR

(57 MHz, CDCl₃): δ (ppm) 60.7. Anal. Calcd. for C₃₀H₃₄N₄Se₂ (%): C, 59.21; H, 5.63; N, 9.21. Found: C, 59.61; H, 5.49; N, 9.95.

9: Yield: 0.61 g (34%). Mp. 160-162 °C. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.43 (s, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.29-7.10 (m, 9H), 5.75 (s, 4H), 4.55 (t, *J* = 7.7 Hz, 4H), 1.94-1.86 (m, 4H), 1.56-1.46 (m, 4H), 1.02 (t, *J* = 7.3 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 146.2 (NCN), 135.6, 134.2, 133.8, 129.4, 127.3, 123.8, 123.7, 111.2, 110.4, 53.2, 50.2, 30.6, 20.2, 13.9. ¹²⁵Te NMR (126.2 MHz, CDCl₃): δ (ppm) -129.1. HRMS: (*m/z*) 711.0993 [M]⁺.

10: Yield: 0.35 g (54%). Mp. 114-116 °C. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.55 (d, *J* = 8 Hz, 2H), 7.22 (m, 4H), 7.10 (d, *J* = 8 Hz, 2H), 6.98 (t, *J* = 7.8 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 2H), 5.92 (m, 2H), 5.90 (s, 4H), 1.67 (d, *J* = 7.1 Hz, 12H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 167.2 (NCN), 135.1, 133.5, 131.5, 128.1, 126.9, 123.5, 123.3, 122.3, 111.5, 110.7, 52.3, 50.9, 20.3, 20.2, 15.4. ⁷⁷Se NMR (57 MHz, CDCl₃): δ (ppm) 59.3. Anal. Calcd. for C₂₈H₂₉BrN₄Se₂ (%): C, 51.00; H, 4.43; N, 8.50. Found: C, 50.67; H, 4.50; N, 8.06.

11: Yield: 0.85 g (57%). Mp. 193-195 °C. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.96 (d, *J* = 7.6 Hz, 1H), 7.35-7.17 (m, 4H), 7.04 (d, *J* = 8 Hz, 1H), 6.66 (dd, *J* = 0.8 Hz, 7.2 Hz, 1H), 5.79 (s, 2H), 4.50 (t, *J* = 7.6 Hz, 2H), 1.91 (m, 2H), 1.50 (m, 2H), 1.02 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 167.5 (NCN), 135.1, 133.2, 132.9, 128.0, 127.0, 123.8, 123.7, 122.3, 110.4, 109.8, 50.5, 47.0, 30.3, 20.3, 13.9. ⁷⁷Se NMR (57 MHz, CDCl₃): δ (ppm) 60.2. Anal. Calcd. for C₃₀H₃₃BrN₄Se₂ (%): C, 52.42; H, 4.84; N, 8.15. Found: C, 52.56; H, 4.58; N, 8.94.

12: Yield: 0.58 g (87%). Mp. 203 °C (decomposed). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.86 (m, 2H), 7.16 (m, 4H), 7.03 (m, 2H), 6.95 (t, *J* = 7.7 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 2H), 5.99 (s, 4H), 2.23 (s, 18H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 165.9 (NCN), 134.9, 133.9, 133.4, 127.9, 126.6, 123.4, 123.1, 122.2, 114.5, 110.6, 64.6, 50.2, 30.8. ⁷⁷Se NMR (57 MHz, CDCl₃): δ (ppm) 197.6. Anal. Calcd. for C₃₀H₃₃BrN₄Se₂ (%): C, 52.42; H, 4.84; N, 8.15. Found: C, 52.22; H, 4.77; N, 6.73.

13: Yield: 0.7 g (74%). Mp. 240-242 °C. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.73 (dd, *J* = 4.9 Hz, *J* = 1.9 Hz, 2H), 8.16 (d, *J* = 8.3 Hz, 2H), 8.01 (dt, *J* = 7.6 Hz, *J* = 1.8 Hz, 2H), 7.48 (m, 2H), 7.42 (m, 2H), 7.25 (m, 4H), 7.12 (m, 2H), 7.05 (t, *J* = 7.7 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 2H), 5.98 (s, 4H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 168.2 (NCN), 150.3, 149.4, 138.4, 134.8, 133.5, 133.0, 128.2, 127.2, 124.6, 124.4, 124.2, 123.9, 111.9, 110.4, 50.7. ⁷⁷Se NMR (57 MHz, CDCl₃): δ (ppm) 102.1. Anal. Calcd. for C₃₂H₂₃BrN₆Se₂ (%): C, 52.69; H, 3.18; N, 11.52. Found: C, 52.21; H, 4.76; N, 6.73.

General procedure for the synthesis of bis(dihaloselenones) 14-16:

The bis(selenones) **10** or **11** (1 eq.) were taken in dry THF (15 mL) and iodine/bromine (2 eq.) in THF were added at -78 °C under nitrogen atmosphere. The reaction mixtures were stirred for 16-20 h at room temperature. The reaction mixtures were concentrated in vacuum and *n*-pentane (15-

20 mL) was added. Crystalline compounds were obtained at -30 °C.

14: Yield: 0.65 g (87%). Mp. 208 °C (decomposed). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.92 (d, *J* = 7.7 Hz, 2H), 7.58 (m, 4H), 7.45 (d, *J* = 7.7 Hz, 2H), 7.22 (d, *J* = 7.0 Hz, 2H), 7.16 (t, *J* = 6.2 Hz, 1H), 6.19 (s, 4H), 5.95 (m, 2H), 1.92 (d, *J* = 7.0 Hz, 12H). ⁷⁷Se NMR (57 MHz, CDCl₃): δ (ppm) 290.4. ESI-MS: *m/z* 738.9 [M-Br₃]⁺, 685.9 [M-C₄H₁₀Br₃]⁺, 581.1 [M-Br₅]⁺; Anal. Calcd. for C₂₈H₂₉Br₅N₄Se₂ (%): C, 34.35; H, 2.99; N, 5.72. Found: C, 34.17; H, 2.84; N, 6.00.

15: Yield: 0.12 g (68%). Mp. 119-129 °C. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.86 (d, *J* = 6.7 Hz, 2H), 7.53 (m, 4H), 7.45 (d, *J* = 7 Hz, 2H), 7.17 (t, *J* = 7.8 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 2H), 6.00 (s, 4H), 5.79 (t, *J* = 7.1 Hz, 2H), 1.87 (d, *J* = 7.1 Hz, 12H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 150.0 (NCN), 133.6, 133.5, 131.1, 129.4, 128.7, 127.1, 126.6, 122.8, 114.2, 113.6, 55.8, 53.2, 20.7. ⁷⁷Se NMR (57 MHz, CDCl₃): δ (ppm) 154.6.

16: Yield: 0.42 g (81%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.80 (d, *J* = 8 Hz, 1H), 7.48-7.34 (m, 4H), 7.05 (t, *J* = 8 Hz, 1H), 6.38 (d, *J* = 8 Hz, 1H), 5.85 (s, 2H), 4.51 (t, *J* = 7.2 Hz, 2H), 1.79 (m, 2H), 1.40 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 156.4 (NCHN), 134.7, 132.5, 127.9, 126.6, 125.3, 121.9, 112.1, 111.9, 50.8, 47.1, 30.0, 19.4, 13.6. ⁷⁷Se NMR (57 MHz, CDCl₃): δ (ppm) 166.09. Anal. Calcd. for C₃₀H₃₃BrI₄N₄Se₂ (%): C, 30.15; H, 2.78; N, 4.69. Found: C, 30.07; H, 2.46; N, 5.21.

Synthesis of 18: The reaction mixture of **7** (0.215 g, 0.54 mmol) and [Pd₂(μ -Cl)₂(2-C₆H₄CH₂NMe₂)₂] (0.179 g, 0.32 mmol) in benzene (30 mL) and glacial acetic acid was refluxed for 5 h. The reaction mixture was evaporated to dryness and washed with diethyl ether to isolate the crude product. The solid was extracted with chloroform, filtered through celite pad. The solvent was evaporated and the residue was treated with diethyl ether to yield a reddish brown solid. Yield: 0.105 g (42%). Mp. 205 °C (dec.). ¹H NMR (400 MHz, DMSO): δ (ppm) 8.21 (d, *J* = 2.4 Hz, 1H), 8.09 (d, *J* = 1.9 Hz, 1H), 7.77 (d, *J* = 2.3 Hz, 1H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 1.9 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 4.10 (s, 3H), 3.74 (s, 3H). ¹³C NMR (100 MHz, DMSO): δ (ppm) 171.6, 148.4, 143.1, 139.2, 132.7, 125.9, 123.4, 122.6, 119.4, 117.1, 115.1, 111.2, 37.1, 36.6. ⁷⁷Se NMR (57 MHz, DMSO): δ (ppm) 97.8. ESI-MS: *m/z* 422.9 [M-Cl]⁺, 343.0 [M-(Se+Cl)]⁺, 317.0 [M-(Pd+Se+Cl)]⁺. Anal. Calcd. for C₁₄H₁₃ClN₄PdSe (%): C, 36.70; H, 2.86; N, 12.23. Found: C, 36.82; H, 2.95; N, 12.60.

Synthesis of 19: To a solution of selone **7** (0.133 g, 0.33 mmol) in acetonitrile, PdCl₂(PhCN)₂ (0.064 g, 0.16 mmol) and NH₄PF₆ (0.061 g, 0.36 mmol) were added and the mixture was refluxed with stirring for 3 h. The reaction mixture was then evaporated to dryness and the residual solid was washed with methanol followed by diethyl ether. The solid was extracted with acetonitrile and filtered. The filtrate was evaporated to dryness to yield a reddish brown solid. Yield: 0.165 g (83%). Mp. 217 °C (dec.). ¹H NMR (400

Table 2. Details of the X-ray data collection parameters.

Compound	8	9	13	18	19
Formula	C ₃₀ H ₃₃ N ₄ Se ₂	C ₃₀ H ₃₄ N ₄ Te ₂	C ₃₂ H ₂₃ BrN ₆ Se ₂	C ₁₄ H ₁₃ ClN ₄ PdSe	C ₂₈ H ₂₈ F ₁₂ N ₈ P ₂ PdSe ₄
Mr	607.52	705.81	729.39	458.09	1188.76
System	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P 21/c	P 21/c	P 1 21/c 1	P 21/c	P 21/c
a[Å]	9.74100(10)	9.7586(3)	13.4416(4)	8.0559(2)	6.82075(19)
b[Å]	21.5258(5)	21.6201(13)	20.7586(7)	13.1124(3)	10.9648(3)
c[Å]	13.7748(2)	14.0678(5)	12.6712(4)	13.8977(3)	25.1631(6)
α[°]	90.00	90.00	90.00	90.00	90.00
β[°]	94.4040(10)	93.418(3)	107.462(4)	96.673(2)	95.769(2)
γ[°]	90.00	90.00	90.00	90.00	90.00
V[Å ³]	2879.81(8)	2962.8(2)	3372.69(19)	1458.10(6)	1872.38(9)
Z	4	4	4	4	2
Size [mm ³]	0.48 x 0.41 x 0.24	0.44 x 0.39 x 0.22	0.49 x 0.32 x 0.15	0.4159 x 0.1574 x 0.1395	0.3662 x 0.1823 x 0.0907
ρ _{calcd} [Mg/m ³]	1.401	1.582	1.436	2.087	2.109
μ [mm ⁻¹]	3.391	1.993	3.406	14.786	10.132
Reflections collected	11694	12138	36999	8995	6718
Observed reflns [R(int) = 0.0615]	5827	5995	11354	2978	3731
R ₁ observed reflns	0.0636	0.0896	0.0493	0.0402	0.0450
wR ₂ , all	0.1959	0.2995	0.1285	0.1107	0.1226

MHz, CD₃CN): δ (ppm). 7.95 (t, *J* = 1.2 Hz, 2H), 7.75 (t, *J* = 8.7 Hz, 2H), 7.66 (d, *J* = 1.5 Hz, 4H), 7.56 (d, *J* = 8.1 Hz, 4H), 7.41 (d, *J* = 1.9 Hz, 4H), 3.53 (s, 12H). ⁷⁷Se NMR (57 MHz, CDCl₃): δ (ppm) 42.8. Anal. Calcd. for C₂₈H₂₈F₁₂N₈P₂PdSe₄ (%): C, 28.29; H, 2.37; N, 9.43. Found: C, 28.41; H, 2.11; N, 8.71.

X-Ray crystallographic study

The single crystal X-ray diffraction measurements were performed on an Oxford Diffraction Gemini diffractometer. The data were corrected for Lorentz, polarization, and absorption effects. The structures were determined by routine heavy-atom methods using SHELXS 97¹⁵ and Fourier methods and refined by full-matrix least squares with the non-hydrogen atoms anisotropic and hydrogen with fixed isotropic thermal parameters of 0.07 Å² using the SHELXL 97¹⁶ program. The hydrogens were partially located from difference electron density maps, and the rest were fixed at predetermined positions. Scattering factors were from common sources.¹⁷ Details of the X-ray data collection parameters are given in Table 2.

General method for optimization of the catalytic reaction condition using gas chromatography

A two-necked round-bottomed flask was charged with aryl halide (1 mmol), alkene (1.5 mmol), catalyst **18** (1 mol %), base (2 mmol) and solvent (5 mL) and the reaction mixture was heated in a preheated oil bath for a specified time at the given temperature. After completion of the reaction, it was cooled to room temperature. The reaction mixture was filtered through a celite pad and washed with water and extracted with dichloromethane. The organic layer was dried over anhydrous sodium sulfate and filtered. The sample was injected in the gas chromatographic column

using microsyringe and run for 30 min under preset temperature program. Yields were calculated from the conversion of the aryl halides.

General method for Heck coupling of iodobenzene and bromobenzene

A round-bottom flask was charged with aryl halide (1 mmol), alkene (1.5 mmol), catalyst **18** (1 mol %), base (2 mmol), and solvent (5 mL) the reaction mixture was heated in a preheated oil bath for a given time at specified temperature. After completion of the reaction, it was worked up as described above and purified by column chromatography (silica: 60-120, hexane-ethyl acetate).

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The reaction of *meta*-phenylene-bis(1-methyl-1*H*-imidazole-2(3*H*)-selone) with $[\text{Pd}_2(\mu\text{-Cl})_2(2\text{-C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_2]$ in dry benzene and glacial acetic acid resulted in the formation of an unsymmetrical 5,6-membered C,C,Se-Pd(II) pincer complex.

