Inorganica Chimica Acta 362 (2009) 3208–3218

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Palladium(II), platinum(II), ruthenium(II) and mercury(II) complexes of potentially tridentate Schiff base ligands of (E, N, O) type (E = S, Se, Te): Synthesis, crystal structures and applications in Heck and Suzuki coupling reactions

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ARTICLE INFO

Article history:
Received 12 September 2008
Received in revised form 14 February 2009
Accepted 20 February 2009
Available online 9 March 2009

Keywords:
Chalogenated Schiff bases
Tridentate ligands
Metal complexes
Structure elucidation
Homogeneous catalysis
2-Hydroxybenzophenone

ABSTRACT

Schiff bases of 2-hydroxybenzophenone (HBP) $(C_6H_5)(2\text{-}HOC_6H_4)C{=}N(CH_2)_nEAr$ (**L1**/**L2**: E = S, Ar = Ph, n = 2/3; **L3**/**L4**: E = Se, Ar = Ph, n = 2/3; **L5**/**L6**: E = Te, Ar = 4-$MeOC_6H_4$, n = 2/3) and their complexes [PdCl(**L**-H)] (**L** = **L1**–**L6**; **1**, **2**, **3**, **5**, **7**, **11**), [PtCl(**L3**-**H**/**L5**-H)] (**4**/**8**), $[PtCl_2$(**L4**/**L6**$)_2]$ (**6**/**12**), [(p-cymene)RuCl(**L5**/**L6**)]Cl (**9**/**13**) and $[HgBr_2$(**L5**/**L6**$)_2]$ (**10**/**14**) have been synthesized and characterized by proton, carbon-13, selenium-77 and tellurium-125 NMR, IR and mass spectra. Single crystal structures of **L1**, **1**, **3**, **4**, **5** and **7** were solved. The Pd–E bond distances (Å): 2.2563(6) (E = S), 2.3575(6)–2.392(2) (E = Se); 2.5117(5)–2.5198(5) (E = Te) are near the lower end of the bond length range known for them. The Pt–Se bond length, 2.3470(8) Å, is also closer to the short values reported so far. The Heck and Suzuki reaction were carried out using complexes **1**, **3**, **5** and **7** as catalysts under aerobic condition. The percentage yields for *trans* product in Heck reaction were found upto 85%.

1. Introduction

A variety of 2-hydroxybenzophenones have been found suitable precursors for 3-substituted benzofurans [1]. Hydroxylated benzophenone derivatives used as UV stabilizers and in hair and skin sunscreen composition [2–4], have estrogenic and anti-androgenic activities [5–7]. Antiplaque oral composition containing a 2-hydroxybenzophenone has been reported [8]. Schiff bases of 2-hydroxybenzophenone are continued to be explored as ligands [9–15] as some of their complexes have interesting features and properties like chirality and catalytic activity [16]. Schiff bases of 2-hydroxybenzophenone have also been found to have potential as corrosion inhibitors [17] and catalyst for polymerization [18]. Schiff bases and related compounds continue to be of current interest for catalyst designing. Thiosemicarbazones [19,20] as well as salicylaldehyde derived chalcogenated Schiff bases [21,22] are known as efficient ligands for the palladium-catalyzed Heck and Suzuki reactions under aerobic condition. Recently use of 2-hydroxyacetphenone derived selenated Schiff bases as ligands in Heck reaction has been reported by us [23]. However, we are unaware of any chalcogenated Schiff base of 2-hydroxybenzophenone (HBP), which has been studied so far as a ligand. The presence of chalcogen atom may tune the properties of their complexes in a new direction. Therefore first examples of Schiff bases of 2-hydroxybenzophenone (HBP) containing chalcogen functionalities, **L1**–**L6** (Scheme 1) are reported here. Their complexes with Pd(II), Pt(II), (p-cymene)Ru(II) and Hg(II) have been synthesized. The ligands and complexes have been characterized using multinuclei NMR, IR and mass spectral data. The single crystal structures of palladium(II) complexes of **L1**, **L3**, **L4** and **L5**, platinum(II) complex of **L3** and Schiff base **L1** have been solved and reported in this paper. The Pd (II) complexes of **L1**–**L5** show potential as homogeneous catalysts for Heck and Suzuki (under aerobic condition) reactions with good yields (upto ~85%). The results of these investigations are included in the present paper.

2. Results and discussion

2.1. General

The syntheses of ligands **L1**–**L6** made by further standardizing general procedures [21,23,24,30,34] and their complexes are given in Scheme 1. The complexes formed with the four metal ions do not change on varying the metal:ligand ratio during their synthesis. The complexes **6** and **12** may be mixtures of *cis*–*trans* isomeric

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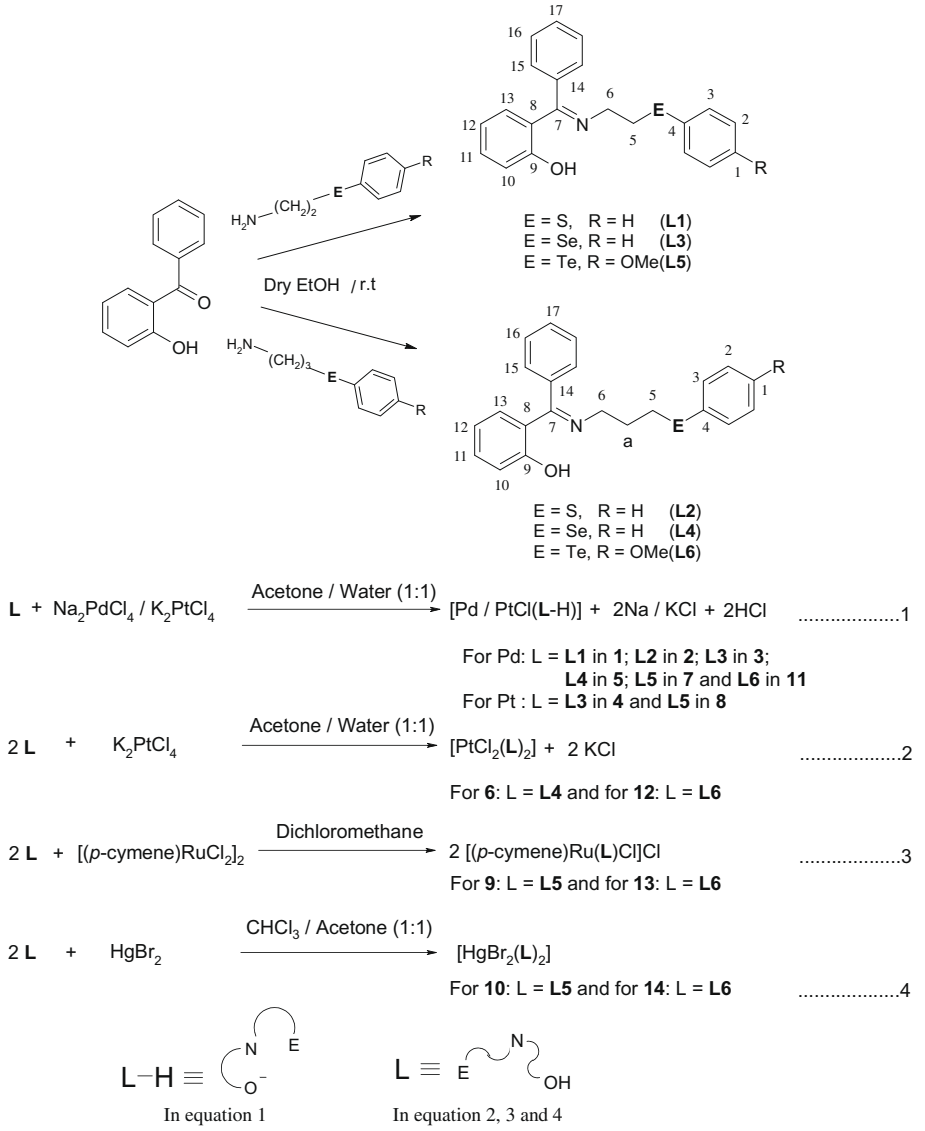
doi:10.1016/j.ica.2009.02.031



Scheme 1.

forms but attempt to separate them did not succeed. The ligands and complexes **1**–**14** are stable and can be stored under ambient conditions up to six months. They have good solubility in $CHCl_3$, CH_2Cl_2, CH_3CN, CH_3OH, C_2H_5OH and acetone but are sparingly soluble in hexane. The complexes are non-ionic in nature except **9** and **13**, which have molar conductance values at room temperature in CH_3CN, 44.0 and 52.0 S cm^2 mol^{-1}, respectively, less than the Λ_M value expected for a 1:1 electrolyte (120–160 S cm^2 mol^{-1}). However, Λ_M values of **9** and **13** in CH_2Cl_2 at room temperature are 26.0 and 32.0 S cm^2 mol^{-1}, respectively (Λ_M = 22.0–27.0 S cm^2 mol^{-1} for a 1:1 electrolyte in CH_2Cl_2). The **L5** and **L6** can behave as hemilabile ligands. Therefore lower values in MeCN may be due to partial substitution of weak Ru···N (see Section 2.4) bond with Ru–Cl. The CH_3CN is a good coordinating solvent therefore the possibility of following equilibrium also exists.

$$[(p\text{-cymene})\mathrm{Ru(Te,N)Cl}]\mathrm{Cl} \rightleftharpoons [(p\text{-cymene})\mathrm{Ru(Te)Cl_2}] + \mathrm{CH_3CN} \rightleftharpoons [(p\text{-cymene})\mathrm{Ru(Te)(CH_3CN)Cl}]\mathrm{Cl}$$

L5/**L6** coordinated through Te and N = (Te, N) and Te = (Te)

In IR spectra of all the complexes except those of **6**, **10**, **12** and **14**, >C=N– stretching frequency has been observed red shifted (16–39 cm^{-1}) with respect to that of corresponding ligand, indicating the involvement of its nitrogen in coordination or weak interaction. The bands at 3300–3400 cm^{-1} in IR spectra of ligand and some complexes are due to ν(OH), as they are intramolecularly hydrogen bonded. The mass spectra of few representative complexes for which crystals could not be grown were recorded. The appearance of molecular ion peak in the spectra of **6** and **12** supports their 1:2 (M:L) stoichiometry. The presence of peaks in mass spectra of complexes **9** and **10** for [MH$^+$–Cl] and [M$^+$–Br], respectively, concurs with the stoichiometries (M:L) 1:1 for Ru and 1:2 for Hg. The [MH$^+$–Cl] peak in the spectra of Ru-complex, further suggests that one of Ru–Cl bond is weak and consequently Ru appears to alternate coordination with Cl and nitrogen of >C=N group, which is supported by NMR and IR spectral data [25].

2.2. NMR spectra of ligands

In ^{77}Se{^{1}H}NMR spectra of **L3** and **L4** the difference in the positions of signals (Table 1) was found small (~8 ppm). The signals in ^{125}Te{^{1}H}NMR spectra of **L5** and **L6** has been found deshielded by 52.5 ppm and unchanged, respectively, with respect to that of precursor 2-(4-methoxyphenyltelluro)ethylamine and 3-(4-methoxy-

Table 1
$^{125}Te/^{77}Se$ NMR of metal complexes of **L3**–**L6**.

S. no.	Complex	Chemical shift δ (ppm) in $^{125}Te/^{77}Se$ NMR	Change in chemical shift relative to ligand (ppm)
1	PdCl(**L3**-H)] (**3**)	440.0	+158.5
2	[PtCl(**L3**-H)] (**4**)	389.7	+108.2
3	[PdCl(**L4**-H)](**5**)	273.7	−16.2
4	$[PtCl_2(\mathbf{L4})_2]$ (**6**)	339.2 and 340.1	+49.3 and +50.2
5	[PdCl(**L5**-H)] (**7**)	755.4	+308.8
6	[PtCl(**L5**-H)] (**8**)	631.2	+184.5
7	[(*p*-cymene)RuCl**L5**]Cl (**9**)	505.5	+58.9
8	$[HgBr_2\ (\mathbf{L5})_2]$ (**10**)	361.7	−84.9
9	[PdCl(**L6**-H)] (**11**)	472.9	+11.10
10	$[PtCl_2(\mathbf{L6})_2]$ (**12**)	563.4 and 578.5	+101.6 and +116.7
11	[(*p*-cymene)RuCl**L6**]Cl (**13**)	534.6	+72.8
12	$[HgBr_2\ (\mathbf{L6})_2]$ (**14**)	356.1	−105.7

phenyltelluro)propylamine which is corroborated by $^{13}C\{^1H\}$ NMR spectra. In $^{13}C\{^1H\}$ NMR spectra of all the six ligands, the position of signal of C_7 has been found shielded by ~26–27 ppm in comparison to that of precursor 2-hydroxybenzophenone [26]. The position of N–CH_2 carbon signal of precursor amine shows a deshielding of the order of ~9 ppm on the formation of Schiff base. The CH_2E carbon signal (E = Chalcogen) in the spectra of ligands containing E–$(CH_2)_2$–N = system appears shielded (<6 ppm) with respect to that of corresponding precursor amine and the value of shielding follows the order S < Se < Te. In the spectra of ligands containing E–$(CH_2)_3$–N = system, the position of CH_2E signal remains almost unchanged with respect to that of precursor amine. In spectra of the six ligands the δ value of C_4 and C_5 atom signal follows the order S > Se > Te. The signal of C_{14} appears almost at the same position in the spectra of **L1**–**L6** but shielded (~4 ppm) with respect to that of 2-hydroxybenzophenone. The signals of H_5 in ^1H NMR spectra of ligands containing E–$(CH_2)_2$–N= system are deshielded by 0.12–0.20 ppm with respect to those containing E–$(CH_2)_3$–N=, but their δ values are in the order S > Se > Te. The signal of –OH proton has been observed beyond 15 ppm due to intramolecular H-bonding O–H···N (see Supplementary material).

2.3. Palladium and platinum complexes

All palladium complexes are of type [PdCl(**L**-H)] (**L** = **L1**–**L6**), in which the ligands coordinate in an uni-negative tridentate mode as corroborated by single crystal structures of **1**, **3**, **5** and **7**. Platinum(II) forms two type of species [PtCl(**L**-H)] (**4** and **8**), which are similar to Pd-complexes and $[PtCl_2(\mathbf{L})_2]$ (**6** and **12**), in which the ligands probably coordinate through chalcogen atom. The greater softness of Pt(II) may be a possible reason for the difference. The signals (Table 1) in $^{77}Se\{^1H\}$ spectra of Pd-complex **3** and Pt-complexes **4** and **6** and $^{125}Te\{^1H\}$ NMR spectra of Pd-complexes **7** and **11** and Pt-complexes **8** and **12** have been found deshielded with respect those of free ligands. When one chelate ring around Pd is five membered, the deshielding is much large (Table 1) in magnitude. In $^{77}Se\{^1H\}$ NMR spectrum of **6** and $^{125}Te\{^1H\}$ NMR spectrum of **12**, two signals appear which are close by (Table 1), probably indicating the presence of both *cis* and *trans* isomeric forms together in solution. The Pd-complex **5** is an exception as shielding of 16.2 ppm is observed in this case which does not concur with deshielding (6.9 ppm) observed earlier in a similar case, [PdCl{PhSe-$(CH_2)_3$-N=C(CH_3)-C_6H_4-2-O^-}] [23]. In $^{13}C\{^1H\}$NMR spectra of all Pd and Pt-complexes signals of C_5 (CH_2E; E = S, Se or Te) show deshielding (upto 12.42 ppm) with respect those of free ligands, supporting bonding through chalcogen atom as indicated by $^{77}Se\{^1H\}$ and $^{125}Te\{^1H\}$ NMR spectra. The signal of C_{14} shows deshielding upto 3.42 ppm (relative to corresponding ligand) on formation of all Pd-complexes and Pt-complexes **4** and **8** indicating involvement of >C=N group in bonding. In case of **6** and **12** signal of C_{14} appears almost unshifted as >C=N group is not involved in bonding. In the spectra of all Pd-complexes and Pt-complexes **4** and **8** signals of carbon atom of =NCH_2 group have been always found deshielded (upto 14.03 ppm) with respect to those of corresponding free ligands. In case of Pt species **6** and **12** no shift in the position of =NCH_2 signal is observed as ligands are coordinating through chalcogen atom. For ligands having E–$(CH_2)_2$–N= system (**1**, **3** and **7**), the magnitude of deshielding of =NCH_2 (relative to free ligand) is between 10.19 and 13.00 ppm whereas for E–$(CH_2)_3$–N= (**2**, **5** and **11**), it is between 3.61 and 7.82 ppm. The signal of –OH has not been observed in ^1H NMR spectra of **1**–**5**, **7**, **8** and **11**, indicating that –OH group coordinates in deprotonated form O^-. The signal of C_9 directly attached to OH group also shifts low field (upto 3.43 ppm) in $^{13}C\{^1H\}$NMR spectra, on the formation of these complexes. On complexation with Pd/Pt the signal of C_4 is expected to show deshielding (with respect to those of free ligands) as observed for **7** and **11** (4.87 and 5.08 ppm, respectively) and **6**, **8** and **12** (1.58–3.38 ppm). Surprisingly shielding was observed in the case of other Pd/Pt-complexes (**1**: 6.36; **2**: 7.12; **3**: 3.91, **4**: 4.87 and **5**: 3.08 ppm).

In all Pd-complexes and Pt-complexes **4** and **8** two protons of each CH_2 group become diastereotopic. The two H_5 protons in ^1H NMR spectra of **1**, **3**, **4**, **5**, **7**, **8** and **11** show two signals (assigned on the basis of HMQC experiment), each corresponds to one proton. Generally, one of these two is shielded (upto 1.12 ppm) and the other is deshielded (upto 0.45 ppm) in comparison to that of corresponding free ligand, except in the case of **5** in which both the signals are deshielded with respect to that of free **L4**. Instead of expected [26] doublet of doublet of doublet (ddd) for H_5 protons, the ^1H NMR spectra of **1**, **4**, **5**, **7** and **8** have one signal as a triplet of doublet (two $^3J_{(H-C5-C6-H)}$ are similar but $\ll {}^2J_{(H-C5-H)}$) and the other as a doublet of triplet. The dihedral angle ~180° between one out of four pairs of vicinal protons makes two $^3J_{(H-C5-C6-H)}$ different. One $^3J_{(H-C5-C6-H)}$ is $\approx {}^2J_{(H-C5-H)}$ and the other $^3J_{(H-C5-C6-H)}$ much smaller in magnitude. In ^1H NMR spectra of **3** and **11** there are two multiplets for H_5 whereas in the spectra of **2**, there is only one signal for H_5 (complex multiplet), which is deshielded by 0.26 ppm in comparison to that of free **L2**. The two =NCH_2 protons (H_6) like H_5 protons also give two signals (one for each proton) in ^1H NMR spectra of **1**, **3**, **4**, **7**, **8** and **11**. In the spectra of **2** and **5**, signals of both the protons (H_6) appear as one complex multiplet. The signals of H_6 protons in the spectra of **1**–**5**, **7**, **8** and **11** were assigned on the basis of HMQC experiments. In ^1H NMR spectra of **1**, **3** and **4** one signal is shielded (upto 0.22 ppm) and the other is deshielded (upto 0.74 ppm) in comparison to those of the corresponding ligands. For **7**, **8** and **11**, both =NCH_2 signals are deshielded (upto 1.75 ppm) with respect to those of corresponding free ligands. Most probably in case of **6** and **12** ligands are coordinating through chalcogen atom, resulting these complexes in solution as a

mixture of *cis* and *trans* isomeric forms. Thus signals of H_5 and H_6 protons appear as complex multiplet, virtually unshifted with respect to those of free ligands in ^{1}H NMR spectra of **6** and **12**. For details of proton NMR spectral data see Supplementary material.

2.4. Ruthenium and mercury complexes

The deshielding of signals in ^{125}Te{^{1}H}NMR spectra of Ru-complexes (with respect to those of free ligands) is in the order **13** > **9** (Table 1). The signals of C_4 and C_5 (CH_2Te) in ^{13}C{^{1}H}NMR spectra are deshielded in the spectra of both Ru-complexes (upto 11.54 ppm) in comparison to those of free ligands, supporting the ligation of Ru through Te. The signal of carbon atom of =NCH_2 group shows shielding (upto 3.30 ppm) with respect to those of free ligands, for **9** and **13** both and the signals of C_{14} appear almost at positions similar to those of free ligands, ruling out coordination of Ru with >C=N. However presence of [MH^+−Cl] ion peak in high resolution mass spectra and molar conductances of **9** and **13** indicate the possibility of weak interaction between Ru and >C=N. The presence of OH signal in the ^{1}H NMR spectra and almost unshifted signal of C_9 in ^{13}C{^{1}H}NMR spectra for both **9** and **13** (relative to corresponding free ligands), suggest that OH group does not coordinate with Ru in both the species.

In ^{1}H NMR spectra of **9** and **13**, H_5 protons give two multiplets, assigned on the basis of HMQC experiments. In case of **9**, the two multiplets of H_5 are deshielded (~0.20–0.43 ppm) but for **13**, one is almost unshifted while the other is deshielded by 0.43 ppm in comparison to those of corresponding free ligands. The =NCH_2 protons (H_6) give two different signals in case of **9** but both are shielded (0.12 and 0.35 ppm) in comparison to those of free **L5**. In the spectrum of **13**, signals of both the protons of =NCH_2 appear as a complex multiplet, which is slightly shielded (0.08 ppm) with respect to that of free ligand. This supports possible weak interaction between Ru and nitrogen of >C=N group mentioned earlier. For details of proton NMR spectral data see Supplementary material.

In ^{125}Te{^{1}H}NMR spectra of Hg-complexes shielding of signals (Table 1) relative to those of free ligands has been observed as reported earlier for d^{10} systems [27–29]. The signal of C_4 is slightly deshielded in ^{13}C{^{1}H} NMR spectra of both **10** (1.74 ppm) and **14**(1.45 ppm) but signal of C_5 (CH_2E) is deshielded (relative to that of free ligand) by 11.64 and 13.20 ppm, respectively, for **10** and **14**, indicating formation of Te–Hg bond. The deshielding (upto 0.46 ppm) of H_5 signals in ^{1}H NMR spectra of both the complexes relative to those of free ligands further supports it. In ^{13}C{^{1}H}NMR spectra, of **10** and **14**, the signals of C_{14} appear almost unshifted. The signals of C_6 (=NCH_2) show shielding (upto 2.66 ppm) with respect to those of free ligands. Both these observations rule out the possibility of Hg···N interaction which is supported by ^{1}H NMR spectra of **10** and **14**, as triplet of =NCH_2 (H_6) is nearly unshifted or shielded in both the cases in comparison to those of free ligands. The presence of OH signal in the ^{1}H NMR spectra and no change in the position of C_9 signal (relative to those of free **L5** and **L6**) in ^{13}C{^{1}H}NMR spectra of both **10** and **14** suggest that OH group probably does not coordinate with Hg in these species. For details of proton NMR spectral data see Supplementary material.

2.5. Crystal structures

Molecular structure of **L1** is shown in Fig. 1 and bond lengths and angles are available in supplementary crystallographic data (CIF files). S–C bond lengths 1.764(4)/1.833(4) Å are consistent with the earlier reports 1.771(6)/1.794(6) Å on PhS-$(CH_2)_2$-N=C(CH_3)-C_6H_4-2-OH [30]. The bond distances S–C(Ar) is somewhat shorter than S–C(alkyl) distance as expected. C(16)–S(1)–C(15) was found to be 105.39(18)° which is also consistent with

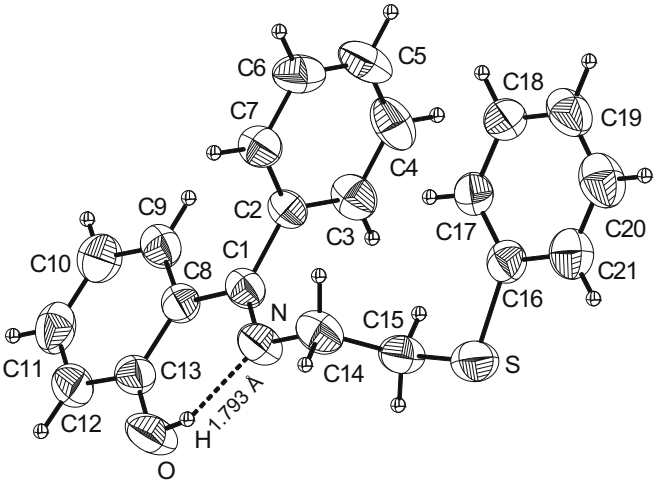


Fig. 1. ORTEP diagram of **L1** with 50% probability ellipsoids.

the earlier reports of 104.1(3)° for PhS-$(CH_2)_2$-N=C(CH_3)-C_6H_4-2-OH [30]. The intramolecular hydrogen bonding O–H···N exists in the structure of **L1**. The molecular structure of **1** with its selected bond distances and angles related to Pd is shown in Fig. 2. The coordination geometry around Pd is almost square planar. The ligand coordinated with Pd in a monoanionic tridentate (S, N, O^-) mode forms six membered chelate ring via O^- and N and five membered via S and N. The Pd–N bond length (2.002(2) Å) in **1** is longer than 1.965(2) Å reported [20] for [PdCl{EtNHC(=S)NH-N=CH-C_6H_4-2-O^-}] (**15**) but the Pd–O distance (1.9862(16) Å) in **1** is slightly shorter than 2.019(2) Å reported [20] for **15**. The bond distances Pd–S (2.2563(6) Å) and Pd–Cl (2.3159(7) Å) of **1** are consistent with the earlier reported values [20] for **15** [Pd–S = 2.2456 (9) and Pd–Cl = 2.3078(8) Å] and [$PdCl_2${4-MeO-$C_6H_4TeCH_2CH_2$-SEt}] [Pd–S = 2.268(4) and Pd–Cl 2.316(4) Å] [31]. The Pd–S bond distance of *cis*-Pd(SNNMe_2-S)($AsPh_3$)Cl_2 (2.249(1) Å) [32] is also in agreement with that of **1**. The Pd–S bond length (2.352 Å) of *trans*-[Pd(SCN)$_2$[P(OPh)$_3$]$_2$] [33], is longer than that of **1**, probably due to the *trans* influence of sulphur.

The molecular structures of **3** and **5** with selected bond lengths and angles related to Pd are shown in Figs. 3 and 4, respectively.

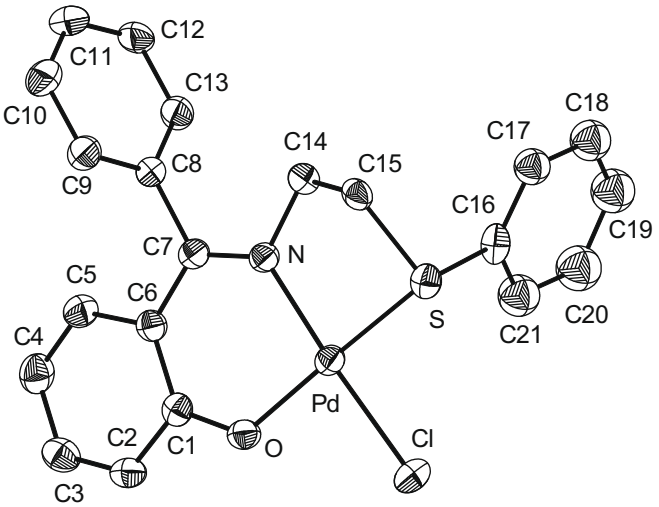


Fig. 2. ORTEP diagram of **1** with 50% probability ellipsoids; bond lengths (Å): Pd–S, 2.2563(6); Pd–O, 1.9862(16); Pd–N, 2.002(2); Pd–Cl, 2.3159(7); bond angles (°): O–Pd–N 93.26(7); O–Pd–S, 175.26(5); N–Pd–S, 89.00(6); O–Pd–Cl, 88.75(5); N–Pd–Cl, 176.77(5); S–Pd–Cl, 89.18(2).

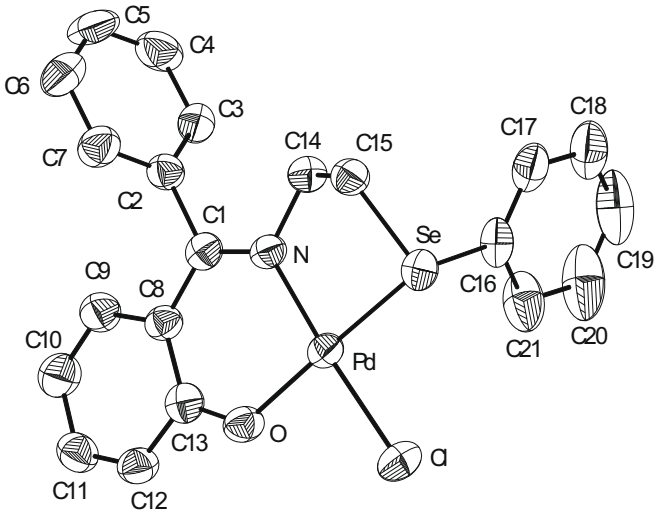


Fig. 3. ORTEP diagram of **3** with 50% probability ellipsoids; bond lengths (Å): Pd–Se, 2.3575(6); Pd–O, 1.993(3); Pd–N, 2.010(4); Pd–Cl, 2.3150(13); bond angles (°): Se–Pd–O, 173.92(9); Se–Pd–N, 89.98(11); Se–Pd–Cl, 87.97(4); O–Pd–N, 93.32(14); O–Pd–Cl, 89.03(10); N–Pd–Cl, 176.02(11).

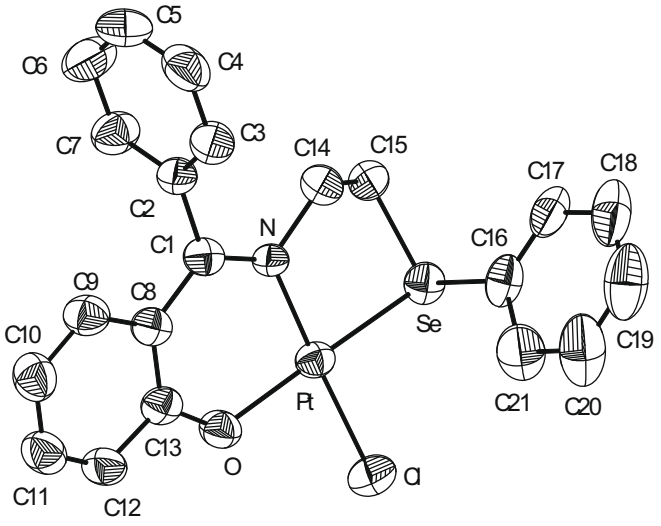


Fig. 4. ORTEP diagram of **4** with 50% probability ellipsoids; bond lengths (Å): Pt–Se, 2.3470(8); Pt–N, 1.992(5); Pt–O, 2.005(4); Pt–Cl, 2.3132(19); bond angles (°): N–Pt–Se, 89.75(15); O–Pt–Se, 174.63(15); Cl–Pt–Se, 89.22(6); N–Pt–O, 93.6(2); N–Pt–Cl, 177.41(17); O–Pt–Cl, 87.56(14).

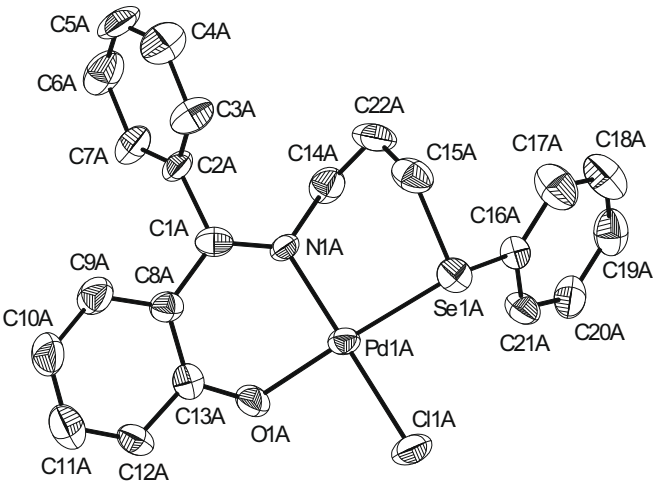


Fig. 5. ORTEP diagram of **5** with 50% probability ellipsoids; bond lengths (Å): Pd(1A)–Se(1A), 2.3855(19); Pd(1A)–N(1A), 1.986(6); Pd(1A)–O(1A), 1.995(6); Pd(1A)–Cl(1A), 2.284(3); bond angles (Å): N(1A)–Pd(1A)–Se(1A), 94.25(19); Cl(1A)–Pd(1A)–Se(1A), 86.19(7); O(1A)–Pd(1A)–Se(1A), 173.95(17); N(1A)–Pd(1A)–O(1A), 89.1(3); N(1A)–Pd(1A)–Cl(1A), 178.12(19); O(1A)–Pd(1A)–Cl(1A), 90.66(17).

The unit cell of **5** has two nearly similar molecules and therefore given bond lengths/angles are average values in this case. The coordination geometry around Pd is nearly square planar in **3** and **5** both. The ligands are coordinated with Pd via Se, N and O^- in both the complexes forming a six membered chelate ring with O^- and N=C< and a five membered with Se and N=C< in **3**, and two six membered chelate rings in the case of **5**. The Pd–Se, Pd–N, Pd–O and Pd–Cl bond distances 2.3575(6), 2.010(4), 1.993(3), 2.3150(13) Å, respectively, in case of **3** and 2.3855(19), 1.986(6), 1.995(6), 2.284(3) Å, respectively, in case of **5**, are consistent with the earlier reports [23] for [PdCl{PhSe-$(CH_2)_2$-N=C(CH_3)-C_6H_4-2-O^-}] [Pd–Se=2.3669(11), Pd–N = 2.003(7), Pd–O = 1.977(6) and Pd–Cl = 2.305(2) Å] and [PdCl{PhSe-$(CH_2)_2$-N = C(CH_3)-C_6H_3-3-R-2-O^-}] [R = $CH(CH_2CH_3)_2$; Pd–Se = 2.365(1), Pd–N = 1.985(4), Pd–O = 2.017(4) and Pd–Cl = 2.323(2) Å] [22]. The Pd–N, Pd–O and Pd–Cl bond distances of **3** and **5** are also consistent with the earlier reports [Pd–N = 2.01(1), Pd–O = 2.03(1), Pd–Cl = 2.290(4) Å] for Pd(II) complex of a (Te, N, O^-) type ligand [34]. The Pd–Se bond lengths of complexes **3** and **5**, 2.3575(6) and 2.3855(19) Å, respectively, are shorter than those reported for [Pd(PEt_3)$_2$(SePh)(-PO(OPh)$_2$)] (2.518(9) Å) [35] and [Pd($Me_2PCH_2CH_2PMe_2$)(Me)(SeC_6H_4-4-Cl)] (2.4483(8) Å) [36]. The possible reason for shortening of Pd–Se bond in **3** and **5** may be the tridentate-coordination mode of **L3** and **L4** which makes two chelate rings and consequently forces Se to bind with Pd(II) some what more strongly in comparison to those complexes in which selenium ligand is monodentate one. Similar observations have been made for (N, Se, O^-) ligands earlier [22–23]. However, it is also noticeable that Pd–Se bond length 2.3575(6) Å in **3** is shorter than Pd–Se bond distance of 2.392(2)/2.3789(18) Å of **5**, where both chelate rings are six membered. The bond angles at N (114.58(15)–12.09 (16)°) are consistent with its trigonal pyramidal geometry (see Fig. 5).

In **7** also the ligand is coordinated with Pd in a tridentate (Te, N, O^-) mode forming a six membered chelate ring with O^- and N and a five membered ring with Te and N (see ORTEP diagram in Fig. 6 with selected bond lengths and angles related to Pd). The unit cell of **7** has two nearly similar molecules and therefore given bond lengths/angles are average values. The lengths of Pd–Te, Pd–N, Pd–O and Pd–Cl bonds of **7**, 2.5158(5), 2.020(3), 2.026(3), 2.3222(12) Å, respectively, are consistent with the earlier report [34] for [PdCl{MeO-*p*-C_6H_4-Te-$(CH_2)_2$-N=C(CH_3)-C_6H_4-2-O^-}] [Pd–Te = 2.504(1), Pd–N = 2.01(1), Pd–O = 2.03(1) and Pd–Cl = 2.290(4) Å]. The Pd–Te bond length in the present complex 2.5158(5) Å is shorter in comparison to earlier reports, 2.5873(2) Å for di[bis(2-{1,3-dioxan-2-yl}ethyl)telluride)dichloropalladium(II) [37] and 2.5865(2)–2.6052(2) Å for di[*N*-{2-(4-methoxyphenyltelluro)ethyl} morpholine]dichloropalladium(II) [38]. This is due to combined effect of tridentate nature of present ligand and the absence of strong *trans* influence in **7**. On comparing Pd–N, Pd–O, Pd–Cl, Pd–Se and Pd–Te bond lengths of **1**, **3**, **5** and **7** with sum of their covalent radii 2.03, 2.01, 2.27, 2.44 and 2.64 Å, respectively, the bonding between **L3**/**L4**/**L5**/**L5** and Pd seems to be strong in nature. The geometry around chalcogen atoms in **1**, **3**, **5** and **7** is pyramidal [bond angles (°): S, 94.87 (8) to 107.01 (9); Se, 91.93(15) to 107.9; Te, 88.05 to 101.74(12)].

In Fig. 6 the molecular structure of **4** with its selected bond lengths and angles related to Pt is given. The geometry around Pt

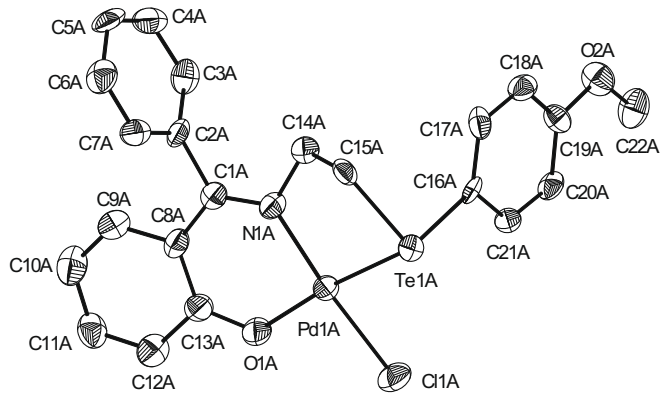


Fig. 6. ORTEP diagram of **7** with 70% probability ellipsoids; bond lengths (Å): Pd(1A)–Te(1A), 2.5158(5); Pd(1A)–N(1A), 2.020(3); Pd(1A)–O(1A), 2.026(3); Pd(1A)–Cl(1A), 2.3222(12); bond angles (°): Te(1A)–Pd(1A)–N(1A), 90.91(10); Te(1A)–Pd(1A)–O(1A), 175.18(8); Te(1A)–Pd(1A)–Cl(1A), 86.76(3); N(1A)–Pd(1A)–O(1A), 92.27(13); N(1A)–Pd(1A)–Cl(1A), 175.93(10); O(1A)–Pd(1A)–Cl(1A), 90.27(9).

is nearly square planar. The Pt–Se bond length, 2.3470(8) Å, is consistent with the earlier reported values in the case of $[(CH_3SeCH_2CH_2CH(COOMe)NH_2)PtCl_2]$ (2.3697(8) Å) [39] and $[PtCl\{C_6H_5\text{-}Se\text{-}(CH_2)_2\text{-}N{=}C(CH_3)\text{-}C_6H_4\text{-}2\text{-}O^-\}]$ (2.3543(16) Å) [23], but is shorter than those reported for *cis*-$[Pt(SePh)_2(PPh_3)_2]$ (2.4970(9)/2.4604(10) Å) [40] and *trans*- $[Pt(SePh)_2$(2,9-dimethyl-1,10-phenanthroline)(MeOOCCH=CHCOOMe)] (2.5197/2.5142 Å) [41]. This may be attributed to tridentate-coordination mode of **L3** in **4**, as in the case of Pd(II) complexes. The absence of the *trans* influence may also contribute, particularly in comparison to *trans*-$[Pt(SePh)_2$(2,9-dimethyl-1,10-phenanthroline)-(MeOOCCH=CHCOOMe)]. The Pt–N and Pt–Cl bond distances of **4**, 1.992(5) and 2.3132(19) Å, respectively, are consistent with the earlier reports for $PtCl_2\{CH_3\text{-}Se\text{-}(CH_2)_2\text{-}CH(COOMe)\text{-}NH_2\}$ (Pt–N, 2.043(5); Pt–Cl, 2.294(2)/2.322(2) Å) [36] and $PtCl\{C_6H_5\text{-}Se\text{-}(CH_2)_2\text{-}N{=}C(CH_3)\text{-}C_6H_4\text{-}2\text{-}O^-\}$ (Pt–N 1.988(12); Pt–Cl 2.306(4) Å) [23]. The Pt–O bond length of **4**, 2.005(4) Å is comparable with earlier reports [23,42] 2.034 and 1.976(10) Å. On comparing Pt–N, Pt–O, Pt–Cl and Pt–Se bond lengths with the sum of their covalent radii 2.05, 2.03, 2.29 and 2.46 Å, respectively, it appears that the observed bond distances are shorter than these values, except in the case of Pt–Cl where the observed values are marginally higher. This indicates that coordination of **L3** is quite strong with Pt also. Some more Pd/Pt–E distances from the literature reports are compiled in Table 2. These distances are sensitive to *trans* influence as well as chelate ring size. On comparing our values with these reports, it appears that our Pd–S, Pd–Se, Pd–Te and Pt–Se bond distances are some what shorter than the literature values [43–61].

It is interesting to note the effect on bond lengths/angles of sulphated Schiff base **L1** when it coordinates with metal ion Pd(II). The C(alkyl)–S–C(aryl) bond angle of 105.39(18)° in **L1** gets some what lowered to 102.81(12)° on the formation of **1**. The S–C(aryl) and S–C(alkyl) bond distances in **L1** are 1.764(4) and 1.833(4) Å, respectively, but on formation of **1**, the distances for these bonds also change (1.789(2) and 1.808(2) Å, respectively). The >C=N– bond distance in **L1** is 1.293(4) Å. However, this distance remains almost unchanged on complexation with Pd(II) [1.296(3) Å in **1**]. However, $N{-}CH_2$ bond distance of 1.481(5) Å in **L1** gets slightly increased on the formation of **1** and becomes 1.496(3) Å. The O–C distance of 1.341(4) Å for **L1** is shortened on the formation of **1** and becomes 1.314(3) Å. Generally S/Se/Te–C(alkyl) is longer than S/Se/Te–C(aryl).

2.6. Applications in Heck and Suzuki reaction

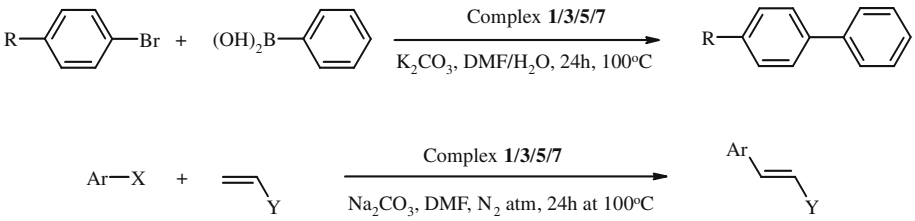
The palladium complexes are expected to be active for Heck and Suzuki reactions which were carried out using complexes **1**, **3**, **5** and **7** as summarized in Scheme 2. The percentage yields were found upto 85 (Table 3).

Heck reaction is very important in organic synthesis for carbon–carbon bond formation. The complexes used as catalysts are based on phosphorus ligands as well as involve phosphorus-free ligands. The improved catalytic activity of transition metal complexes with hemilabile ligands has been reported [62,63]. The present ligands

Table 2
M–E (E = S, Se or Te) bond lengths.

S. no.	Bond	Length (Å)	Charge on E	*Trans* group/atom	Ref.
1	Pd–S	2.3305(11)	Neutral[a]	S	[43]
2	Pd–S	2.306(5)	Neutral[b]	I	[44]
3	Pd–S	2.3204(10)–2.3430(13)	Neutral[a]	ArC	[45]
4	Pd–S	2.3208(8)–2.3225(19)	Neutral[a]	ArC	[46]
5	Pd–S	2.251(2)–2.429(2)	Neutral[b]	C, O or S	[46]
6	Pd–Se	2.401(3)–2.416(3)	Negative	Se	[47]
7	Pd–Se	2.4049(13) –2.4363(12)	Negative	Se	[48]
8	Pd–Se	2.4307(5)	Neutral[d]	PPh_3	[49]
9	Pd–Se	2.3725(3)	Neutral[d]	Cl	[50]
10	Pt–Se	2.4565(5)–2.5009(13)	Negative	PPh_3	[51]
11	Pt–Se	2.4371(6)–2.372(6)	Negative	PPh_3	[52]
12	Pt–Se	2.366(3)–2.368(2)	Neutral[e]	Cl	[53]
13	Pt–Se	2.4301(7)–2.4595(7)	Negative	PPh_3	[54]
14	Pd–Te	2.5606(8)	Neutral[c]	Cl	[55]
15	Pd–Te	2.5040(4)	Neutral[c]	Cl	[56]
16	Pd–Te	2.534(2)	Neutral[c]	SMe	[57]
17	Pd–Te	2.517(6)	Neutral[c]	SMe	[57]
18	Pd–Te	2.5007(6)/2.5101(6)	Neutral[c]	Cl	[57]
19	Pd–Te	2.4914(7)/2.5005 (7)	Neutral[c]	O^-	[58]
20	Pd–Te	2.538(2)/2.517(2)	Neutral[c]	TeRR'	[59]
21	Pd–Te	2.5301(1)/2.5313(9)	Neutral[c]	Py	[60]
22	Pd–Te	2.5951(7)/2.5872(7)	Neutral[c]	TeRR'	[61]

[a] >C=S Group.
[b] Sulphide.
[c] Telluride
[d] Selenide.
[e] Diselenide.



Scheme 2.

Table 3
Yields (%) in Suzuki and Heck reactions.

Substituents on reactants		Complex			
		1	**3**	**5**	**7**
Heck reaction					
Ar-X	Y	Yield of *trans* product (%)			
O_2N—C$_6$H$_4$—I	COOH	78	85	74	70
Cl—C$_6$H$_4$—I	COOH	70	80	65	60
O_2N—C$_6$H$_4$—Br	COOH	25	35	33	30
O_2N—C$_6$H$_4$—I	Ph	74	83	78	72
Cl—C$_6$H$_4$—I	Ph	70	78	68	70
O_2N—C$_6$H$_4$—Br	Ph	28	33	30	35
Suzuki reaction					
R		Yield (%)			
OMe		30	20	15	10
H		50	45	30	35
NO_2		80	87	84	80

L1–**L6** are also potent hemilabile ligands. However, many phosphine based catalysts are often water- and air-sensitive. Therefore, catalysis under phosphine-free conditions is a challenge of high importance, and a number of Pd-complexes of phosphine-free ligands [64–69] have been reported to exhibit promising catalytic activity for Heck reaction. Recently Pd–Se bond containing complexes [70] have found very promising for Heck reaction. This has motivated us to examine palladium(II) complexes **1**, **3**, **5** and **7** for Heck coupling. The advantage of using them is that they are air stable and moisture insensitive. Not much investigations on Pd(II) complexes of tellurated ligands for Heck reaction have been made and present results show promise of such species also. A good selectivity for *trans*-products has been observed. The catalytic activity depends on the halide, while electron-withdrawing groups on the aryl ring increase the reaction rate. The reactivity decreases drastically in the order ArI > ArBr > ArCl. For Aryl bromides (1 mmol) also, a very little amount (0.001 mmol) of a complex was found sufficient to catalyze the Heck reaction.

Suzuki–Miyaura reaction is also among the most important palladium-catalyzed cross-coupling reactions of both academic and industrial interest [20,23,71–77]. In view of air and moisture sensitivity of complexes of phosphorus ligands there is an interest in phosphine-free ligands for the Suzuki–Miyaura reaction also. Complexes **1**, **3**, **5** and **7** have been explored for Suzuki–Miyaura reaction as they offer the advantage of stability under ambient conditions. For carrying out Suzuki–Miyaura reactions of aryl bromides with phenylboronic acid the reaction conditions used were similar to those used for analogous phosphine-free systems [20,22–24,30]. Aryl bromides and phenylboronic acid were reacted under aerobic conditions at 100 °C for 24 h, using K_2CO_3 as a base, without addition of free ligand or any promoting additive and in the presence of a small amount of water (~1 equivalent with respect to the substrates). Homocoupling of phenylboronic acid to give unsubstituted biphenyl was negligible. The reaction was performed using a 1:1000 catalyst: aryl halide molar ratio. The catalytic activity was dependent on the halide, and also electron-withdrawing groups present on the aryl ring increased the reaction rate. The activity follows in the order NO_2 > H > OMe. For the activated 1-bromo-4-nitrobenzene the yields were usually about 80% or higher. Not many evaluations of palladium complexes of tellurated ligands for Suzuki–Miyaura reaction have been made so far and present results are promising. Thus palladium complexes of chalcogenated Schiff base ligands of HBP can be efficient catalysts for both Suzuki–Miyaura cross-coupling and Heck reactions. The advantage of using them is that they are air stable and also not moisture sensitive. A 1:1000 catalyst:aryl halide molar ratio was found optimum for Heck as well as Suzuki reactions. The difference in the catalytic activities of **1**, **3**, **5** and **7** is not much and can not be explained unequivocally.

3. Experimental

The recording of melting points and IR spectra (4000–250 cm^{-1}, in KBr), C and H analyses and conductivity

measurements in CH_3CN (concentration ca 1 mM) were carried out by earlier reported method [23–24]. The ^1H, $^{13}C\{^1H\}$, $^{77}Se\{^1H\}$ and $^{125}Te\{^1H\}$ NMR spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300.13, 75.47, 57.24 and 94.69 MHz, respectively. Mass spectra (ion spray) were recorded on Hybrid Quadrupole-TOF LC/MS/MS mass spectrometer (QSTAR XL System), Model 1011273/A, AB Sciex Instruments (Applied Biosystems, Canada). $PhE(CH_2)_2NH_2$, $PhE(CH_2)_3NH_2$ (E = S, Se), $ArTe(CH_2)_2NH_2$ and $ArTe(CH_2)_3NH_2$ [Ar = $-C_6H_4$–4–OCH_3] were synthesized by the literature methods [78–81].

Single crystal diffraction data for **L1**, **3**, **4**, **5** and **7** were collected on a Bruker AXS SMART Apex CCD diffractometer using Mo Kα radiations (0.71073 Å) at 298 (2) K. The software SADABS was used for absorption correction (if needed) and SHELXTL for space group, structure determination and refinements [82,83] as detailed earlier [23] The data for **1** was collected on Oxford Diffraction Gemini-R CCD diffractometer (one degree φ and ω scans were used with a 0.8 mm collimator) at 200 (2) K. CRYSALIS RED, Oxford Diffraction Ltd., Version 1.171.32.5 was used for solutions. Supplementary material consists of crystal data, structural refinements (Tables S.1 and S.2) selected bond lengths and angles (Table S.3). Proton NMR spectral details of all newly synthesized ligand (**L1**–**L6**) and their complexes **1**–**14** are given in Supplementary material.

3.1. Synthesis of *L1* and *L2*

2-(Phenylsulphanyl)ethylamine (0.765 g, 5.0 mmol)/3-(phenylsulphanyl)propylamine (0.835 g, 5.0 mmol) was stirred in dry ethanol (20 mL) at room temperature for 0.5 h. 2-hydroxybenzophenone (0.9911 g, 5.0 mmol), dissolved in dry ethanol (20 mL), was added dropwise with stirring. The mixture was stirred further at room temperature for 2 h. The solvent was evaporated off on a rotary evaporator resulting in a yellow precipitate of **L1** or dark yellow viscous oil in case of **L2**. The **L1** on recrystallization from chloroform–hexane mixture (1:1), gave yellow coloured single crystals.

L1: Yield 1.50 g (∼90%); m.p. 42 °C. Λ_M = 0.8 cm^2 mol^{-1} ohm^{-1}. *Anal.* Calc. for $C_{21}H_{19}NOS$: C, 75.64; H, 5.74; N, 4.20. Found C, 75.61; H, 5.71; N, 4.26%. $^{13}C\{^1H\}$NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 34.38 (C_5), 50.43 (C_6), 117.48 (C_{12}), 117.90 (C_{10}), 119.79 (C_8), 126.12 (C_1), 127.16 (C_{16}), 128.72 (C_{15}), 128.90 (C_2), 128.98 (C_{17}), 129.37 (C_3), 131.57 (C_{13}), 132.50 (C_{11}), 133.80 (C_{14}), 135.50 (C_4), 162.88 (C_9), 175.02 (C_7). IR (KBr, cm^{-1}): 3483, 783, 1612.

L2: Yield 1.50 g (∼85%); Λ_M = 0.6 cm^2 mol^{-1} ohm^{-1}. *Anal.* Calc. for $C_{22}H_{21}NOS$: C, 76.05; H, 6.09; N, 4.03. Found C, 76.01; H, 6.03; N, 4.09%. $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 29.89 (C_a), 31.03 (C_5), 49.75 (C_6), 117.16 (C_{12}), 117.87 (C_{10}), 119.51 (C_8), 125.83 (C_1), 127.04 (C_{16}), 128.61 (C_{15}), 128.75 (C_2), 128.90 (C_{17}), 129.07 (C_3), 131.34 (C_{13}), 132.38 (C_{11}), 133.80 (C_{14}), 135.50 (C_4), 163.32 (C_9), 174.64 (C_7). IR (KBr, cm^{-1}): 3426, 788, 1612.

3.2. Synthesis of *L3*–*L6*

2-(Phenylseleno)ethylamine (1.00 g, 5.0 mmol), 2-(phenylseleno)propylamine (1.07 g, 5.0 mmol), 2-(4-methoxyphenyltelluro)ethylamine (1.39 g, 5.0 mmol) and 3-(4-methoxyphenyl telluro)propylylamine (1.46 g, 5.0 mmol) were, respectively, reacted with 2-hydroxybenzophenone (0.991 g, 5.0 mmol) by the method given in Section 3.1, to prepare **L3**, **L4**, **L5** and **L6** as dark yellow viscous oil.

L3: Yield 1.80 g (∼94%); Λ_M = 0.8 cm^2 mol^{-1} ohm^{-1}. *Anal.* Calc. for $C_{21}H_{19}NOSe$: C, 66.33; H, 5.04; N, 3.68. Found: C, 66.39; H, 5.01; N, 3.61%. $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 27.86 (C_5), 51.07 (C_6), 117.34 (C_{12}), 117.82 (C_{10}), 119.65 (C_8), 126.83 (C_1), 127.04 (C_{16}), 128.60 (C_{15}), 128.87 (C_{17}), 128.94 (C_2), 129.31 (C_4), 131.46 (C_{13}), 132.39 (C_{11}), 132.55 (C_3), 133.66 (C_{14}), 162.86 (C_9), 174.65 (C_7); $^{77}Se\{^1H\}$NMR (57.24 MHz $CDCl_3$, 25 °C, vs Me_2Se) δ = 281.48. IR (KBr, cm^{-1}): 3436, 1612, 738, 474.

L4: Yield 1.82 g (∼92%); Λ_M = 0.6 cm^2 mol^{-1} ohm^{-1}. *Anal.* Calc. for $C_{22}H_{21}NOSe$: C, 67.01; H, 5.37; N, 3.55. Found C, 67.08; H, 5.31; N, 3.59. $^{13}C\{^1H\}$NMR (75.47, $CDCl_3$, 25 °C): δ = 24.90 (C_5), 30.86 (C_a), 50.71 (C_6), 117.10 (C_{12}), 117.78 (C_{10}), 119.50 (C_8), 126.61 (C_1), 126.98 (C_{16}), 128.55 (C_{15}), 128.81 (C_{17}), 128.86 (C_2), 129.67 (C_4), 131.26 (C_{13}), 132.26 (C_{11}), 132.31 (C_3), 133.61 (C_{14}), 163.20 (C_9), 174.46 (C_7); ($^{77}Se\{^1H\}$NMR (57.24 MHz, $CDCl_3$, 25 °C, vs Me_2Se): δ = 289.90. IR (KBr, cm^{-1}): 3438, 1612, 743, 476.

L5: Yield 2.20 g (∼95%); Λ_M = 0.6 cm^2 mol^{-1} ohm^{-1}. *Anal.* Calc. for $C_{22}H_{21}NO_2Te$: C, 57.57; H, 4.61; N, 3.05. Found C, 57.51; H, 4.57; N, 3.09%. $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 8.66 (C_5), 52.50 (C_6), 54.82 (OMe) 99.66 (C_4), 114.90 (C_2), 117.14 (C_{12}), 117.70 (C_{10}), 119.49 (C_8), 126.90 (C_{16}), 128.43 (C_{15}), 128.69 (C_{17}), 131.32 (C_{13}), 132.20 (C_{11}), 133.53 (C_{14}), 140.84 (C_3), 159.49 (C_1), 162.85 (C_9), 173.97 (C_7); $^{125}Te\{^1H\}$ NMR (94.69 MHz $CDCl_3$, 25 °C, vs Me_2Te): δ = 446.63. IR(KBr, cm^{-1}): 3440, 1612, 513.

L6: Yield 2.15 g (∼90%); Λ_M = 0.8 cm^2 mol^{-1} ohm^{-1}. *Anal.* Calc. for $C_{23}H_{23}NO_2Te$: C, 58.40; H, 4.90; N, 2.96. Found: C, 58.37; H, 4.83; N, 2.91%. $^{13}C\{^1H\}$NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 5.58 (C_5), 32.58 (C_a), 52.76 (C_6), 55.05 (OMe), 100.05 (C_4), 115.09 (C_2), 117.14 (C_{12}), 117.96 (C_{10}), 119.59 (C_8), 127.17 (C_{16}), 128.67 (C_{15}), 128.93 (C_{17}), 131.36 (C_{13}), 132.38 (C_{11}), 133.74 (C_{14}), 140.92 (C_3), 159.66 (C_1), 163.48 (C_9), 174.46 (C_7); $^{125}Te\{^1H\}$ NMR (94.69 MHz $CDCl_3$, 25 °C, vs Me_2Te) δ = 461.80. IR(KBr, cm^{-1}): 3440, 1640, 508.

3.3. Synthesis of palladium(II) complexes [PdCl(*L*-H)

$Na_2[PdCl_4]$ (0.294 g, 1 mmol) dissolved in water (5 mL) and a solution of any ligand **L1**–**L6** (1 mmol) prepared in acetone (10 mL) were stirred together vigorously. An orange precipitate of palladium(II) complex was immediately obtained, which was filtered, washed with hexane (10 mL) and dried in *vacuo*. The recrystallization of the complex from chloroform–hexane (60:40) mixture was made. Single crystals were obtained in case of [PdCl(**L1**-H)] (**1**), [PdCl(**L3**-H)](**3**), [PdCl(**L4**-H)] (**5**) and [PdCl(**L5**-H)] (**7**).

[PdCl(**L1**-H)] (**1**): Yield 0.39 g (∼82%); m.p. 162 °C. Λ_M = 6.0 cm^2 mol^{-1} ohm^{-1}. *Anal.* Calc. for $C_{21}H_{18}NOSPdCl$: C, 53.18; H, 3.83; N, 2.95. Found: C, 53.13; H, 3.89; N, 2.91%. $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 41.01 (C_5), 60.62 (C_6), 115.41 (C_{12}), 121.26 (C_8), 121.39 (C_{10}), 128.38 (C_4), 126.84, 127.08, 129.17, 129.27, 129.32 (ArC: C_{15}, C_{16} and C_{17}), 129.82 (C_2), 130.70 (C_1), 133.01 (C_3), 134.42 (C_{11}), 134.68 (C_{13}), 135.81 (C_{14}), 165.15 (C_9), 169.71 (C_7); IR (KBr, cm^{-1}): 1592, 741.

[PdCl(**L2**-H)] (**2**): Yield 0.36 g (∼73%); m.p. 158 °C. Λ_M = 8.0 cm^2 mol^{-1} ohm^{-1}. *Anal.* Calc. for $C_{22}H_{20}NOSPdCl$: C, 54.11; H, 4.13; N, 2.87. Found: C, 54.18; H, 4.11; N, 2.81%. $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 25.31 (C_a), 33.89 (C_5), 53.36 (C_6), 115.30 (C_{12}), 121.11 (C_{10}), 126.43 (C_8), 127.55, 128.80 (ArC: C_{15}, C_{16}), 129.14 (C_4), 129.62 (C_2), 129.69 (C_{17}), 129.93 (C_1), 132.23 (C_3), 134.34 (C_{13}), 134.63 (C_{11}), 136.10 (C_{14}), 165.40 (C_9), 171.04 (C_7); IR (KBr, cm^{-1}): 1588, 746.

[PdCl(**L3**-H)] (**3**): Yield ∼ 0.42 g (∼81%); m.p. 148 °C Λ_M = 8.0 cm^2 mol^{-1} ohm^{-1}. *Anal.* Calc. for $C_{21}H_{18}NOSePdCl$: C, 48.40; H, 3.48; N, 2.69. Found: C, 48.37; H, 3.41; N, 2.63%. $^{13}C\{^1H\}$NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 32.32 (C_5), 62.50 (C_6), 115.18 (C_{12}), 121.09 (C_{10}), 122.16 (C_8), 125.40 (C_4), 126.93, 127.46, 128.95, 129.13 (ArC: C_{15}, C_{16}, C_{17}), 129.91 (C_2), 130.19 (C_1) 133.66 (C_3), 134.09 (C_{11}), 135.09 (C_{13}), 136.03 (C_{14}), 165.36 (C_9), 169.77 (C_7); $^{77}Se\{^1H\}$NMR (57.24 MHz, $CDCl_3$, 25 °C, vs Me_2Se) δ = 440.0. IR (KBr, cm^{-1}): 1573, 463, 748.

[PdCl(**L4**-H)] (**5**): Yield ∼ 0.41 g (∼77%); m.p. 144 °C Λ_M = 6.0 cm^2 mol^{-1} ohm^{-1}. *Anal.* Calc. for $C_{22}H_{20}NOSePdCl$: C, 49.38; H, 3.77; N, 2.62. Found: C, 49.31; H, 3.71; N, 2.69%.

$^{13}C\{^1H\}$NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 26.61 (C_a), 29.75 (C_5), 55.45 (C_6), 115.13 (C_{12}), 121.01 (C_{10}), 126.48 (C_8), 126.59 (C_4), 127.03, 128.02, 128.54, 128.89, 129.54 (ArC: C_{15}, C_{16}, C_{17}), 129.79 (C_2, C_1), 133.28 (C_3), 134.35 (C_{13}), 134.52 (C_{11}), 136.23 (C_{14}), 165.55 (C_9), 171.04 (C_7); $^{77}Se\{^1H\}$NMR (57.24 MHz, $CDCl_3$, 25 °C, vs Me_2Se): δ = 273.7. IR(KBr, cm^{-1}): 1578, 743, 474.

[PdCl(**L5**-H)] (**7**): Yield ~ 0.53 g (~89%); m.p.171 °C. Λ_M = 8.0 cm^2 mol^{-1} ohm^{-1}. *Anal.* Calc. for $C_{22}H_{20}NO_2TePdCl$: C, 44.05; H, 3.36; N, 2.34. Found: C, 44.01; H, 3.39; N, 2.37%. $^{13}C\{^1H\}$NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 14.70 (C_5), 55.29 (OMe), 65.50 (C_6), 104.36 (C_4), 114.61 (C_{12}), 115.77 (C_2), 121.19 (C_{10}), 123.62 (C_8), 127.08, 128.01, 128.66, 128.96, 129.02 (ArC: C_{15}, C_{16}, C_{17}), 133.82 (C_{11}), 135.56 (C_{13}) 136.13 (C_{14}), 138.78 (C_3), 161.23 (C_1), 166.28 (C_9), 170.40 (C_7); $^{125}Te\{^1H\}$NMR (94.69 MHz, $CDCl_3$, 25 °C, vs Me_2Te) δ = 755.4. IR(KBr, cm^{-1}): 1589, 512, 293.

[PdCl(**L6**-H)] (**11**): Yield ~ 0.47 g (~76%); m.p. 172 °C Λ_M = 8.0 cm^2 mol^{-1} ohm^{-1}. *Anal.* Calc. for $C_{23}H_{22}NO_2TePdCl$: C, 45.00; H, 3.61; N, 2.28. Found: C, 45.07; H, 3.68; N, 2.21%. $^{13}C\{^1H\}$NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 16.72 (C_5), 27.50 (C_a), 55.25 (OMe), 60.58 (C_6), 105.13 (C_4), 114.43 (C_{12}), 115.57 (C_2), 121.06 (C_{10}), 126.05 (C_8), 127.06, 128.28, 128.72, 129.06 (ArC: C_{15}, C_{16}, C_{17}) 134.02 (C_{11}), 134.79 (C_{13}), 136.73 (C_{14}), 138.46 (C_3), 160.86 (C_1), 165.33 (C_9), 170.83 (C_7); $^{125}Te\{^1H\}$NMR (94.69 MHz, $CDCl_3$, 25 °C, vs Me_2Te): δ = 472.9. IR (KBr, cm^{-1}): 1596, 512, 293.

3.4. Synthesis of platinum(II) complex [Pt(*L*-H)Cl]

$K_2[PtCl_4]$ (0.415 g, 1 mmol) dissolved in water (5 mL) and a solution of **L3** or **L5** (1 mmol) prepared in acetone (10 mL) were stirred together vigorously. A precipitate of **4** (yellow) or **8** (orange) was immediately obtained. The precipitate was filtered, dried and recrystallized from chloroform–hexane (60:40) mixture. Single crystals were obtained in the case of **4**.

[PtCl(**L3**-H)] (**4**): Yield ~ 0.54 g (~89%); m.p. 157 °C; Λ_M = 5.0 cm^2 mol^{-1} ohm^{-1} *Anal.* Calc. for $C_{21}H_{18}NOSePtCl$: C, 41.37; H, 2.98; N, 2.30. Found: C, 41.31; H, 2.91; N, 2.33%. $^{13}C\{^1H\}$NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 33.89 (C_5), 63.75 (C_6), 116.18 (C_{12}), 121.64 (C_{10}), 122.41 (C_8), 124.44 (C_4), 126.24, 126.96, 128.83, 129.06, 129.12 (ArC: C_{15}, C_{16}, C_{17}), 129.56 (C_2), 130.30 (C_1), 133.16 (C_3), 133.50 (C_{11}), 134.43 (C_{13}), 136.89 (C_{14}), 163.30 (C_9), 165.47 (C_7); $^{77}Se\{^1H\}$NMR (57.24 MHz, $CDCl_3$, 25 °C, vs Me_2Se): δ = 389.7. IR (KBr, cm^{-1}): 1578, 462, 746.

[PtCl(**L5**-H)] (**8**): Yield ~ 0.59 g (~86%); m.p. 181 °C; Λ_M = 9.0 cm^2 mol^{-1} ohm^{-1}. *Anal.* Calc. for $C_{22}H_{20}NO_2TePtCl$: C, 38.38; H, 2.93; N, 2.03. Found: C, 38.31; H, 2.97; N, 2.09%. $^{13}C\{^1H\}$NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 13.76 (C_5), 55.32 (OCH_3), 66.53 (C_6), 101.24 (C_4), 115.32 (C_2), 115.79 (C_{12}), 121.64 (C_{10}), 123.15 (C_8), 126.69, 127.17, 128.75, 128.98, 129.14 (ArC: C_{15}, C_{16}, C_{17}), 133.56 (C_{11}), 134.76 (C_{13}), 136.95 (C_{14}), 138.35 (C_3), 161.44 (C_1), 164.37 (C_9), 166.64 (C_7); $^{125}Te\{^1H\}$NMR (94.69 MHz, $CDCl_3$, 25 °C, vs Me_2Te): δ = 631.2. IR(KBr, cm^{-1}): 1584, 512, 287.

3.5. Synthesis of platinum(II) complexes [$PtCl_2$(*L*)$_2$]

$K_2[PtCl_4]$ (0.415 g, 1 mmol) dissolved in water (5 mL) and a solution of **L4** (0.788 g, 2 mmol) or **L6** (0.946 g, 2 mmol) prepared in acetone (10 mL) were stirred together vigorously. A yellow precipitate of **6** or orange precipitate of **12** was immediately obtained, which was filtered, washed with hexane (10 mL), dried and recrystallized from chloroform–hexane (60:40) mixture.

[$PtCl_2$(**L4**)$_2$] (**6**): Yield ~ 0.92 g (~87%); m.p. 153 °C; Λ_M = 7.6 cm^2 mol^{-1} ohm^{-1}; *Anal.* Calcd. for $C_{44}H_{42}N_2O_2Se_2PtCl_2$: C, 50.12; H, 4.01; N, 2.66. Found: C, 50.16; H, 4.07; N, 2.69%. $^{13}C\{^1H\}$NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 28.34 (C_5), 31.42 (C_a), 50.83 (C_6), 117.47 (C_{12}), 117.81 (C_{10}), 119.70 (C_8), 127.07 (C_{16}), 128.86 (C_{15}), 129.07 (C_{17}), 129.54 (C_2), 130.14 (C_1), 131.56 (C_3), 132.50 (C_4), 132.96 (C_{13}), 133.02 (C_{11}), 133.70 (C_{14}), 162.86 (C_9), 175.13 (C_7); $^{77}Se\{^1H\}$NMR (57.24 MHz, $CDCl_3$, 25 °C, vs Me_2Se): δ = 339.2, 340.1. HRMS (ESI+) calcd. for $C_{44}H_{42}N_2O_2Se_2PtCl_2$ (M^+) 1055.0602, found *m*/*z* 1055.0631 (Δ 2.7862 ppm). IR(KBr, cm^{-1}): 3438, 1596, 467, 338.

[$PtCl_2$(**L6**)$_2$] (**12**): Yield ~ 0.98 g (~81%); m.p. 158 °C Λ_M = 8.0 cm^2 mol^{-1} ohm^{-1}. *Anal.* Calc. for $C_{46}H_{46}N_2O_4Te_2PtCl_2$: C, 45.59; H, 3.83; N, 2.31. found: C, 45.51; H, 3.83; N, 2.37%. $^{13}C\{^1H\}$NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 16.40, 16.88, 18.00 (C_5), 28.14, 29.08 (C_a), 51.87 (C_6) 55.17, 55.21, 55.25, 55.27 (OCH_3), 101.65, 102.38, 103.43 (C_4), 115.10, 115.15, 115.22, 115.48 (C_2), 117.30, 117.38 (C_{12}), 117.83 (C_{10}), 119.93 (C_8), 125.56, 127.09, 127.77 (C_{16}), 128.28, 128.74, 128.78 (C_{15}), 129.06, 129.15, 129.19 (C_{17}), 131.67, 132.70 (C_{13}), 133.23 (C_{14}), 133.85, 134.32 (C_{11}), 136.98, 137.82, 138.36 (C_3), 160.96, 161.24, 161.28 (C_1), 163.19, 163.76, 167.59 (C_9), 175.07 (C_7); $^{125}Te\{^1H\}$NMR (94.69 MHz, $CDCl_3$, 25 °C, vs Me_2Te): δ = 563.4, 578.5. HRMS (ESI+) calcd for $C_{46}H_{46}N_2O_4Te_2PtCl_2$ (M^+) 1215.0607, found *m*/*z* 1215.0636 (Δ 2.3811 ppm). IR (KBr, cm^{-1}): 3450, 1592, 794, 740, 695, 586, 516, 414, 306.

3.6. Synthesis of [(*p*-cymene)RuCl***L5***/***L6***]Cl (***9***/***13***)

The $[RuCl_2(p\text{-cymene})]_2$ (0.306 g, 0.5 mmol) dissolved in dichloromethane (10 mL) and a solution of **L5** (0.459 g, 1 mmol) or **L6** (0.473 g, 1 mmol) prepared in dichloromethane (20 mL) were stirred together vigorously for 3 h. The solvent was removed on a rotary evaporator which gave **9** or **13** as an orange coloured solid. It was washed with hexane and dried in *vacuo*.

9: Yield ~ 0.64 g (~83%); m.p. 163 °C Λ_M = 44 cm^2 mol^{-1} ohm^{-1}. *Anal.* Calc. for $C_{32}H_{35}NO_2TeRuCl_2$: C, 50.18; H, 4.57; N, 1.83. Found: C, 50.13; H, 4.59; N, 1.87%. $^{13}C\{^1H\}$NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 18.43 (*p*-cymene CH_3), 20.20 (C_5), 22.00, 22.34 (CH_3 of *i*-Pr of *p*-cymene), 30.73 (CH of *i*-Pr of *p*-cymene), 49.20 (C_6), 55.16 (OMe), 81.13, 81.33, 84.93 and 85.08 (ArC of *p*-cymene *m* and *o* to *i*-Pr), 97.79 (ArC of *p*-cymene attached to CH_3), 104.34 (ArC of *p*-cymene attached to *i*-Pr), 106.27 (C_4), 115.24 (C_2), 117.41(C_{12}), 117.53 (C_{10}), 119.63 (C_8), 126.81 (C_{16}), 128.56 (C_{15}), 128.83 (C_{17}), 131.54 (C_{13}), 132.30 (C_{11}), 133.50 (C_{14}), 137.70 (C_3), 161.21 (C_1), 162.40 (C_9), 174.79 (C_7); $^{125}Te\{^1H\}$NMR (94.69 MHz, $CDCl_3$, 25 °C, vs Me_2Te): δ = 505.5. HRMS (ESI+) calcd. for $C_{32}H_{35}NO_2TeRuClH$ (MH^+-Cl) 733.0540, found *m*/*z* 733.0520 (Δ 2.7746 ppm). IR (KBr, cm^{-1}): 3436, 1598, 761, 705.

13: Yield ~ 0.62 g (~79%); m.p. 145 °C. Λ_M = 52 cm^2 mol^{-1} ohm^{-1}. *Anal.* Calc. for $C_{33}H_{37}NO_2TeRuCl_2$: C, 50.82; H, 4.75; N, 1.80. Found: C, 50.87; H, 4.79; N, 1.83%. $^{13}C\{^1H\}$NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 15.62 (C_5), 18.31 (*p*-cymene CH_3), 21.83 and 22.28 (CH_3 of *i*-Pr of *p*-cymene), 29.70 (C_a), 30.64 (CH of *i*-Pr of *p*-cymene), 52.19 (C_6), 55.18 (OMe), 80.94, 81.62, 84.49 and 85.37 (ArC of *p*-cymene *m* and *o* to *i*-Pr), 97.38 (ArC of *p*-cymene attached to CH_3), 104.12 (ArC of *p*-cymene attached to *i*-Pr), 106.23 (C_4), 115.41 (C_2), 117.11 (C_{12}), 117.75 (C_{10}), 119.49 (C_8), 126.95 (C_{16}), 128.65 (C_{15}), 128.92 (C_{17}), 131.38 (C_{13}), 132.28 (C_{11}), 133.37 (C_{14}), 136.97 (C_3), 161.18 (C_1), 163.18 (C_9), 174.62 (C_7); $^{125}Te\{^1H\}$NMR (94.69 MHz, $CDCl_3$, 25 °C, vs Me_2Te): δ = 534.6. IR (KBr, cm^{-1}): 3440, 1592, 763, 712.

3.7. Synthesis of [$HgBr_2$ (***L5***/***L6***)$_2$] (***10***/***14***)

The $HgBr_2$ (0.360 g, 1.0 m mol) was dissolved in 5 mL of acetone. The solution of **L5** (0.918 g, 2.0 mmol) or **L6** (0.946 g, 2.0 mmol) made in 10 mL of chloroform was added to it with stirring. The mixture was stirred further for 3 h. The solvent was evaporated off on a rotary evaporator. The resulting residue was

washed with acetone, redissolved in minimum amount of chloroform and mixed with hexane. The resulting precipitate of **10** or **14** was filtered, washed with hexane (10 mL) and dried in *vacuo*.

10: Yield ~ 1.00 g (~78%); m.p.165 °C Λ_M = 9.0 cm^2 mol^{-1} ohm^{-1}. *Anal.* Calc. for $C_{44}H_{42}N_2O_4Te_2HgBr_2$: C, 41.30; H, 3.29; N, 2.19. Found: C, 41.38; H, 3.21; N, 2.11%. $^{13}C\{^1H\}$NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 20.30 (C_5), 49.84 (C_6), 55.35 (OMe), 101.40 (C_4), 116.17 (C_2), 117.81 (C_{12}), 117.86 (C_{10}), 119.71 (C_8), 127.04 (C_{16}), 128.93 (C_{15}), 129.23 (C_{17}), 131.95 (C_{13}), 132.87 (C_{11}), 133.57 (C_{14}), 139.52 (C_3), 161.34 (C_1), 162.56 (C_9), 175.85 (C_7); $^{125}Te\{^1H\}$NMR (94.69 MHz, $CDCl_3$, 25 °C, vs Me_2Te): δ = 361.7. HRMS (ESI+) calcd for $C_{44}H_{42}N_2O_4Te_2HgBr$ (M^+−Br) 1203.0159, found *m*/*z* 1203.0138 (Δ 1.7326 ppm). IR (KBr, cm^{-1}): 3412, 1590, 584, 513, 420, 324.

14: Yield ~ 1.10 g (~84%); m.p.172 °C Λ_M = 8.0 cm^2 mol^{-1} ohm^{-1}. *Anal.* Calc. for $C_{46}H_{46}N_2O_4Te_2HgBr_2$: C, 42.25; H, 3.52; N, 2.14. Found: C, 42.29; H, 3.58; N, 2.19%. $^{13}C\{^1H\}$NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 18.78 (C_5), 30.58 (C_a), 52.36 (C_6), 55.24 (OMe), 101.50 (C_4), 116.08 (C_2), 117.37 (C_{12}), 117.87 (C_{10}), 119.63 (C_8), 127.14 (C_{16}), 128.89 (C_{15}), 129.12 (C_{17}), 131.59 (C_{13}), 132.54 (C_{11}), 133.53 (C_{14}), 139.07 (C_3), 161.24 (C_1), 163.12 (C_9), 175.13 (C_7); $^{125}Te\{^1H\}$NMR (94.69 MHz, $CDCl_3$, 25 °C, vs Me_2Te): δ = 356.10. IR (KBr, cm^{-1}): 3424, 1594, 692, 586, 513, 416.

3.8. Procedure for catalytic Suzuki reaction

Bromobenzene or its derivative (1 mmol), benzeneboronic acid (0.183 g, 1.5 mmol), K_2CO_3 (0.276 g, 2 mmol), distilled water (0.5 mL), DMF (4 mL) and catalyst (complex **1**/**3**/**5**/**7**) (0.001 mmol) were taken in a two necked round bottom. The mixture was stirred under reflux over an oil bath for 24 h at 100 °C under ambient conditions. Thereafter, it was cooled to room temperature and mixed with 20 mL of water. The product was extracted from the mixture with hexane/diethyl ether (25−50 mL). The solvent was partly evaporated on a rotary evaporator to get white crystalline solid products, which were filtered and washed with 3−4 mL of hexane. The NMR (^1H and $^{13}C\{1H\}$) spectra of products were characteristic.

3.9. Procedure for catalytic Heck reaction

A mixture of alkene (1.5 mmol), aryl halide (1 mmol), Na_2CO_3 (0.212 g, 2.0 mmol), DMF (4.0 mL) and catalyst (complex **1**/**3**/**5**/**7**) (0.001 mmol) was stirred under reflux on oil bath for 24 h at 100 °C under nitrogen atmosphere. After cooling the reaction mixture to room temperature 20 mL of water was added to it and products were extracted into dichloromethane (40 mL) and filtered. To obtain (*E*)-1-(4-chloro/nitrophenyl)-2-phenylethene, the filtrate was washed with water (3 × 25 mL) and evaporated on rotary-evaporator. The residue was purified by silica gel column chromatography using hexane–ethylacetate mixture (9:1) to obtain the product. In case of (*E*)-3-(4-chloro/nitrophenyl)acrylic acid, the cooled reaction mixture was further mixed with $NaHCO_3$ (0.50 g) and water (30 mL) and stirred for 1 h at room temperature. It was filtered and the filtrate was washed with CH_2Cl_2 (3 × 20 mL). The aqueous phase was acidified with 5 N HCl and cooled to 0 °C. The resulting solid precipitate of pure product was filtered, washed and air dried.

4. Conclusion

Chalcogented Schiff bases of 2-hydroxybenzophenone (HBP) have been compared for the first time for their ligation properties. They behave as (E, N, O^-) type ligand (E = S, Se, Te) with Pd(II). In case of Pt(II) the coordination mode of ligand changes from (E, N, O^-) type, to E-type when there are three CH_2 groups between >C=N group and Se/Te. When these Schiff bases act as a tridentate uni-negative ligand the binding with the Pd or Pt is very strong as indicated by various M–L distances which are shorter than the sum covalent radii. Palladium complexes have potential for catalyzing Heck and Suzuki reactions (yield upto 85%). The advantage of using them is that they are not air and moisture sensitive. Optimum catalyst: aryl halide molar ratio was found be 1:1000 for Heck and Suzuki reactions both.

Acknowledgements

Authors thank Department of Science and Technology (India) for Research Project No. SR/S1/IC-23/06 and for partial financial assistance given to establish single crystal X-ray diffraction facility at IIT Delhi, New Delhi (India) under its FIST programme. A.K. thanks Council of Scientific and Industrial Research (India) for the award of Junior/Senior Research Fellowship. M.A. thanks Department of Science and Technology (India) for financial support.

Appendix A. Supplementary material

CCDC 694461, 694462, 694463, 694464, 694465 and 694466 contains the supplementary crystallographic data for **1**, **3**, **4**, **5**, **7** and **L1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.02.031.

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