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Chalcogenated Schiff bases: Complexation with palladium(II) and Suzuki coupling reactions

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Abstract. Chalcogenated Schiff bases of 5–chloroisatin (**L1**–**L3**), 2–(methythio)benzaldehyde (**L4**), 2–acetylpyridine (**L5**) and benzaldehyde (**L6**–**L7**) have been synthesized. Both the carbonyl groups of 5–chloroisatin appear to be reactive (noticed for the first time) for making >C=N bond, of course one at a time only. The ^{1}H, ^{13}C{^{1}H}, ^{77}Se{^{1}H} and ^{125}Te{^{1}H} NMR spectroscopy have been used to establish the co-existence of two products, which were found in the ratio 53:47 (E = S), 55:45 (E = Se) and 81:19 (E = Te). The larger amount is of the one in which C=O group away from NH is derivatized. The two products are not separable. Palladium complexes (**1**–**4**) of Schiff bases of other three aldehydes were synthesized. The ligands as well as complexes were characterized by multinuclear NMR spectroscopy. The crystal structures of [Pd(**L4/L5**)Cl][ClO_4] (**1/2**) have been solved. The Pd–Se bond lengths are 2.4172(17) and 2.3675(4) Å, respectively for **1** and **2**. The Pd–complexes (**3–4**) of **L6**–**L7** were explored for Suzuki–Miyaura coupling and found promising as 0.006 mol % of **3** is sufficient to obtain good conversion with TON up to 1.58×10^4.

Keywords. Chalcogenated Schiff base; palladium; Suzuki coupling; crystal structure.

1. Introduction

Schiff bases and related compounds continue to be of current interest for catalyst designing. They are extensively studied as ligands but chalcogenated Schiff bases[1] known so far, particularly those having selenium and tellurim donor sites are not many. Some tellurated Schiff bases reported include 1,6-*bis*-2-butyltellurophenyl-2,5-diazahexa-1,4-diene,[2] Schiff base derived by reacting *bis*(*o*-formylphenyl) telluride and *o*-(butyltelluro)benzaldehyde with chiral amines (R)-(+)-(1-phenylethylamine) and (1R,2S)-(-)-norephedrine, respectively[3] and macrocyclic Schiff bases.[4] Selenated Schiff bases[5–7] are known as ligands suitable for designing efficient palladium catalyst for Heck and Suzuki reactions under aerobic condition. Recently some chalcogenated Schiff bases as ligands and applications of their metal complexes have been reported by our group.[8,9] Half sandwich complexes of ruthenium(II) with chalcogenated Schiff bases and their derivatives are very efficient transfer hydrogenation catalysts for ketones as well as suitable catalysts for oxidation of alcohols.[10] The palladacycle of a Schiff base related ligand has been found efficient for Suzuki coupling of ArCl.[11] In continuation of these studies we have synthesized some new chalcogenated Schiff bases (see scheme 1) and palladium complexes of some of them. The possibilities of Suzuki coupling are explored with some representative complexes. In case of 5–chloroisatin observed Schiff base formation is not on reported lines.[12] Both carbonyl groups appear to be reactive, of course not together. Thus, mixture of two Schiff bases is formed. Their ratio varies with chalcogen. These results are presented in this paper.

2. Experimental

2.1 *Physical measurement*

Perkin–Elmer 2400 Series II C, H, N analyzer was used for elemental analyses. The ^{1}H, ^{13}C{^{1}H}, ^{77}Se{^{1}H} and ^{125}Te{^{1}H} NMR spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300.13, 75.47, 57.24 and 94.69 MHz respectively. IR spectra in the range 4000–400 cm^{-1} were recorded on a Nicolet Protége 460 FT-IR spectrometer. The diffraction data on single-crystals of **1** and **2** were collected on a Bruker AXS SMART Apex CCD diffractometer using Mo–*Ka* (0.71073 Å) radiations at 298(2) K. The software SADABS[13] was used for absorption correction (if needed) and SHELXTL for space group, structure determination and refinements.[14] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included

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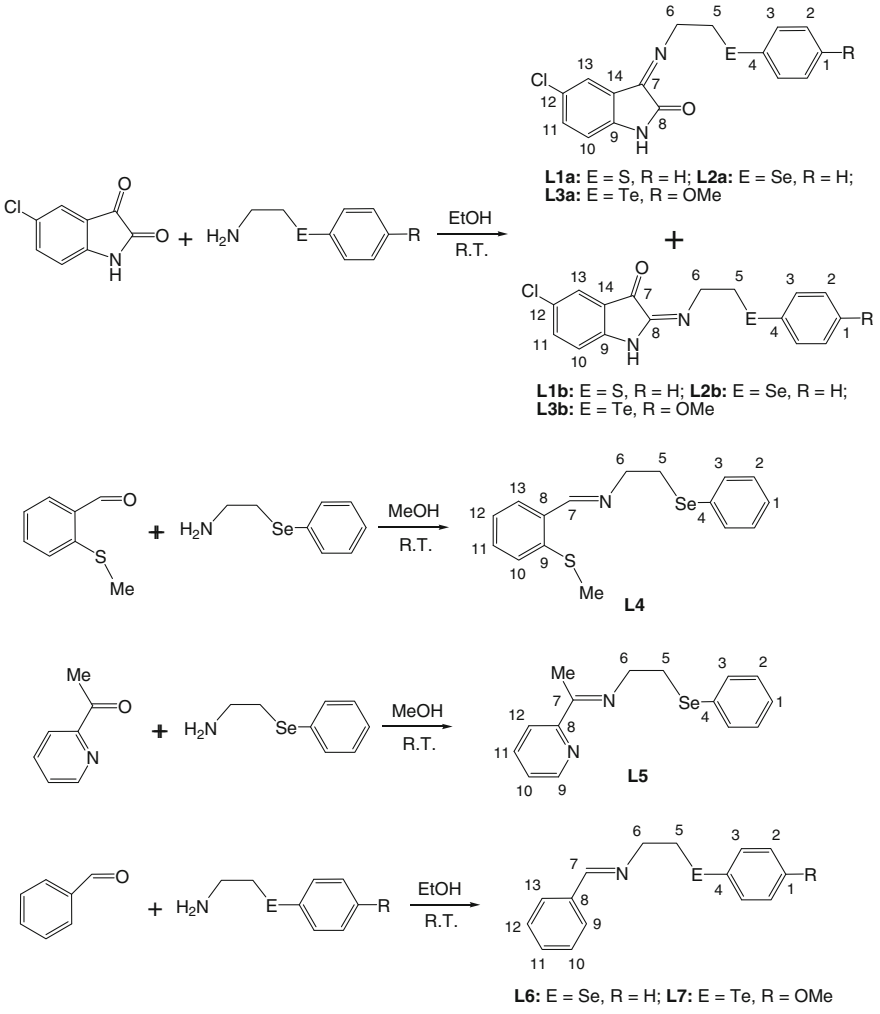


Scheme 1. Synthesis of ligands **L1–L7**.

in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they are attached. The least-square refinement cycles on F^2 were performed until the model converged. The conductivity measurements were made in CH_3CN (concentration ca. 1 mM) using ORION conductivity meter model 162. Melting points determined in open capillary are reported as such.

2.2 *Chemicals and reagents*

2–(Phenylthio)ethylamine, 2–(phenylseleno)ethylamine and 2–(4–methoxyphenyltelluro)ethylamine were synthesized by reported methods.[15–18] 2–(Methylthio)-benzaldehyde, 2–acetylpyridine, benzaldehyde, $PdCl_2$, $Na_2[PdCl_4]$, $AgClO_4$, bromobenzene or its derivatives, phenylboronic acid and Cs_2CO_3 were procured from Sigma–Aldrich (USA) and used as received. All the solvents were dried and distilled before use by well-known standard procedures.[19]

2.3 *Synthesis of **L1–L3***

2–(Phenylsulphanyl)ethylamine (0.76 g, 5.0 mmol)/2–(phenylseleno)ethylamine (1.0 g, 5.0 mmol)/2–(4–methoxyphenyltelluro)ethylamine (1.39 g, 5.0 mmol) was stirred in dry ethanol (20 mL) at room temperature for 1 h. 5–Chloroisatin (0.77 g, 5.0 mmol,) dissolved in dry ethanol (20 mL) was mixed drop-wise with stirring. The mixture was stirred further at room temperature for 2–3 h. The solvent was evaporated on rotary evaporator resulting in a yellow or orange (in case of Te) precipitate of **L1–L3**. The precipitate was filtered, washed with cold ethanol and dried *in vacuo*.

L1a–b: Yield 1.42 g, 90%. Anal. Calc. for $C_{16}H_{13}ClN_2OS$: C, 60.66; H, 4.14; N, 8.84%. Found: C, 61.06; H, 4.26; N, 8.97%. ^{1}H NMR ($CDCl_3$, 25°C, vs Me_4Si): (δ, ppm): 3.36–3.40 (t, $^3J_{H-H} = 6.9$ Hz, 2H, H_{5a}), 3.50–3.55 (t, $^3J_{H-H} = 7.5$ Hz, 2H, H_{5b}), 4.20 (t, $^3J_{H-H} = 7.5$ Hz, 2H, H_{6b}), 4.61 (t, $^3J_{H-H} = 6.9$ Hz, 2H, H_{6a}), 6.75–6.78 (d, $^3J_{H-H} = 8.4$ Hz, 1H, H_{10a}), 6.87–6.89 (d, $^3J_{H-H} = 8.4$ Hz, 1H, H_{10b}), 7.48 (s, 1H,

H_{13b}), 7.56 (s, 1H, H_{13a}), 7.15–7.43 (m 12H, H_{1a}, $H_{1b,}$ H_{2a}, $H_{2b,}$ H_{3a}, H_{3b}, H_{11a}, H_{11b}), 8.24 (s, 1H, NHa), 9.19 (s, 1H, NH_b). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C, vs Me_4Si): (δ, ppm): 34.2 (C_{5a}), 34.9 (C_{5b}), 52.1 (C_{6b}), 53.9 (C_{6a}), 111.6–164.7 (C_{Ar}).

L2a–b: Yield 1.64 g, 90%. Anal. Calc. for $C_{16}H_{13}ClN_2OSe$: C, 52.85; H, 3.60; N, 7.70%. Found: C, 53.15; H, 3.61; N, 7.90%. ^1H NMR ($CDCl_3$, 25°C, vs Me_4Si): (δ, ppm): 3.35 (t, $^3J_{H-H} = 6.9$ Hz, 2H, H_{5a}), 3.46 (t, $^3J_{H-H} = 7.5$ Hz, 2H, H_{5b}), 4.27 (t, $^3J_{H-H} = 7.5$ Hz,2H, H_{6b}), 4.71 (t, $^3J_{H-H} = 6.9$ Hz, 2H, H_{6a}), 6.75–6.78 (d, $^3J_{H-H} = 8.4$ Hz, 1H, H_{10a}), 6.87–6.90 (d, $^3J_{H-H} = 8.4$ Hz, 1H, H_{10b}), 7.22–7.57 (m 14H, H_{1a}, $H_{1b,}$ H_{2a}, $H_{2b,}$ H_{3a}, H_{3b}, H_{11a}, $H_{11b,}$ H_{13a}, H_{13b}), 8.24 (s, 1H, NH_a), 9.19 (s, 1H, NH_b). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C, vs Me_4Si): (δ, ppm): 27.49 (C_{5a}), 28.75 (C_{5b}), 52.85 (C_{6b}), 54.75 (C_{6a}), 111.49–164.57 (C_{Ar}). $^{77}Se\{^1H\}$ NMR ($CDCl_3$, 25°C, vs Me_2Se): (δ, ppm): 287.1 (a), 289.5 (b).

L3a–b: Yield 1.99 g, 90%. Anal. Calc. for $C_{17}H_{15}ClN_2O_2Te$: C, 46.16; H, 3.42; N, 6.33%. Found: C, 44.59; H, 3.40; N, 6.20%. ^1H NMR ($CDCl_3$, 25°C, vs Me_4Si): (δ, ppm): 3.25 (t, $^3J_{H-H} = 6.9$ Hz, 2H, H_{5a}), 3.33 (t, $^3J_{H-H} = 7.5$ Hz, 2H, H_{5b}), 3.78 (s, 6H, OMe-a, OMe-b), 4.36 (t, $^3J_{H-H} = 7.5$ Hz, 2H, H_{6b}), 4.83 (t, $^3J_{H-H} = 6.9$ Hz, 2H, H_{6a}), 6.75 (m, Hz, 2H, $H_{10a,}$ H_{10b}), 6.77–6.80 (d, $^3J_{H-H} = 6.9$ Hz, 2H, H_{2a}), 6.86–6.89 (d, $^3J_{H-H} = 8.4$ Hz, 2H, H_{2b}), 7.32–7.35 (d, $^3J_{H-H} = 8.4$ Hz, 1H, H_{11a}), 7.38–7.42 (d, $^3J_{H-H} = 8.1$ Hz, 1H, H_{11b}), 7.53 (s, 1H, H_{13a}), 7.58 (s, 1H, H_{13b}), 7.71–7.74 (d, $^3J_{H-H} = 8.7$ Hz, 2H, H_{3a}), 7.77 (s, 2H, H_{3b}), 8.00 (s, 1H, NH_a), 8.79 (s, 1H, NH_b). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C, vs Me_4Si): (δ, ppm): 7.6 (C_{5a}), 10.2 (C_{5b}), 54.0 (OMe-Ca, OMe-Cb), 55.1 (C_{6b}), 56.3 (C_{6a}), 99.4–164.4 (C_{Ar}). $^{125}Te\{^1H\}$ NMR ($CDCl_3$, 25°C, vs Me_2Te): (δ, ppm): 452.3 (a), 456.1 (b).

2.4 *Synthesis of **L4–L5***

2–(Methylthio)benzaldehyde (0.76 g, 5 mmol) or 2–acetylpyridine (0.61 g, 5 mmol) dissolved in 15 mL of dry CH_3OH was stirred at room temperature for 0.5 h and mixed with a solution of 2–(phenylseleno)ethylamine (1.00 g, 5 mmol) made in 10 mL of dry CH_3OH with constant stirring. The mixture was further stirred at room temperature for 24 h. The solvent was evaporated on a rotary evaporator to obtain ligands **L4** or **L5** as yellow oil.

L4: Yield 1.48 g, 90%. ^1H NMR ($CDCl_3$, 25°C, vs Me_4Si): (δ, ppm): 2.46 (s, 3H, SMe), 3.25 (t, $^3J_{H-H} = 6.9$ Hz, 2H, H_5), 3.95 (t, $^3J_{H-H} = 6.9$ Hz, 2H, H_6), 7.16–7.39 (m, 6H, H_1, H_2, H_{11}, H_{12}, H_{13}), 7.52–7.56 (m, 2H, H_3), 7.80 (d, $^3J_{H-H} = 7.8$ Hz, 1H, H_{10}), 8.72 (s, 1H, H_7). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C, vs Me_4Si): (δ, ppm): 16.9 (SMe), 28.5 (C_5), 61.5 (C_6), 125.5–132.8 (C_1, C_2, C_3, C_4, C_{10}, C_{11}, C_{12}, C_{13}), 134.1 (C_8), 139.3 (C_9), 160.3 (C_7). $^{77}Se\{^1H\}$ NMR ($CDCl_3$, 25°C, vs Me_2Se): (δ, ppm): 278.3. IR (KBr, ν_{max}/cm^{-1}): 3059 (m; $\nu_{C-H(aromatic)}$), 2921 (s; $\nu_{C-H(aliphatic)}$), 1637, 1585 (s; $\nu_{C=N}$), 1197 (m; ν_{C-N}), 746 (m; $\nu_{C-H(aromatic)}$).

L5: Yield 1.48 g, 90%. ^1H NMR ($CDCl_3$, 25°C, vs Me_4Si): (δ, ppm): 2.32 (s, 3H, Me), 3.32 (t, $^3J_{H-H} = 6.9$ Hz, 2H, H_5), 3.85 (t, $^3J_{H-H} = 6.9$ Hz, 2H, H_6), 7.20–7.29 (m, 6H, H_1, H_2, H_{10}, H_{11}, H_{12}), 7.50–7.71 (m, 2H, H_3), 8.59 (d, $^3J_{H-H} = 7.5$ Hz, 1H, H_9). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C, vs Me_4Si): (δ, ppm): 14.4 (Me), 34.6 (C_5), 52.0 (C_6), 121.0–129.2 (C_1, C_2, C_3, C_4, C_{10}, C_{11}, C_{12}), 136.3 (C_8), 148.3 (C_9), 167.7 (C_7). $^{77}Se\{^1H\}$ NMR ($CDCl_3$, 25°C, vs Me_2Se): (δ, ppm): 279.7. IR (KBr, ν_{max}/cm^{-1}): 3055 (m; $\nu_{C-H(aromatic)}$), 2924 (s; $\nu_{C-H(aliphatic)}$), 1636, 1588 (s; $\nu_{C=N}$), 1194 (m; ν_{C-N}), 746 (m; $\nu_{C-H(aromatic)}$).

2.5 *Synthesis of **L6–L7***

2-(Phenylseleno)ethylamine (1.00 g, 5 mmol) or 2-(aryltelluro)ethylylamine (1.39 g, 5 mmol) was stirred in dry ethanol (20 mL) at room temperature for 0.5 h. Benzaldehyde (0.53 g, 5.0 mmol), dissolved in dry ethanol (20 mL), was added drop-wise with stirring. The mixture was stirred further at room temperature for 2 h. The solvent was evaporated on a rotary evaporator which resulted in **L6–L7** as yellow oil.

L6: Yield 1.24 g, 86%. ^1H NMR ($CDCl_3$, 25°C, vs Me_4Si): (δ, ppm): 3.28 (t, $^3J_{H-H} = 6.9$ Hz, 2H, H_5), 3.96 (t, $^3J_{H-H} = 6.9$ Hz, 2H, H_6), 7.26–7.76 (m, 10H, H_1, H_2, H_3, H_9, H_{10}, H_{11}), 8.27 (s, 1H, H_7). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C, vs Me_4Si): (δ, ppm): 28.2 (C_5), 61.2 (C_6), 126.6 (C_{10}), 128.0 (C_1), 128.8 (C_2), 128.9 (C_4), 129.8 (C_3), 130.6 (C_9), 132.4 (C_8), 135.7 (C_{11}), 162.1 (C_7). $^{77}Se\{^1H\}$ NMR ($CDCl_3$, 25°C, vs Me_2Se): (δ, ppm): 278.5.

L7: Yield 1.66 g, 89%. ^1H NMR ($CDCl_3$, 25°C, vs Me_4Si): (δ, ppm): 3.14 (t, $^3J_{H-H} = 7.5$ Hz, 2H, H_5), 3.79 (s, 3H, OMe), 4.01 (t, $^3J_{H-H} = 7.5$ Hz, 2H, H_6), 6.74 (d, $^3J_{H-H} = 6.9$ Hz, 2H, H_3), 7.39–7.42 (m, 3H, H_{10}, H_{11}, H_{12}), 7.67–7.72 (m, 4H, H_2, H_9, H_{13}), 3.24 (s, 1H, H_7). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C, vs Me_4Si): (δ, ppm): 9.9 (C_5), 54.9 (OMe), 62.6 (C_6), 100.4 (C_4), 114.9 (C_2), 128.0–135.7 (C_8, C_9, C_{10}, C_{11}, C_{12}, C_{13}), 140.8 (C_3), 159.5 (C_1), 161.3 (C_7). $^{125}Te\{^1H\}$ NMR ($CDCl_3$, 25°C, vs Me_2Te): (δ, ppm): 437.8.

2.6 *Synthesis of Pd(II)–Complexes (**1–2**)*

The CH_3CN (20 mL) and solid $PdCl_2$ (0.18 g, 1 mmol) were mixed and the mixture was refluxed with stirring

until a clear light yellow coloured solution was obtained. The solution of a ligand **L4 / L5** (0.34 / 0.30 g, 1 mmol) made in CH_3OH (5 mL) was added to it and the mixture was refluxed for 5 h. Thereafter $AgClO_4$ (0.21 g, 1 mmol) was added and the mixture further refluxed for 3 h. It was cooled to room temperature and turbidity of AgCl was filtered off. The filtrate was concentrated to ~5 mL on a rotary evaporator and mixed with diethyl ether (10 mL) to obtain **1/2** as orange solid, which was filtered and dried *in vacuo*. The single crystals of **1/2** were grown by slow evaporation of their solutions in CH_3CN–CH_3OH mixture (3:2). *Caution: perchlorate is potentially explosive and therefore should be handled carefully*.

1: Yield 0.54 g, 85%. M.p. 150.5°C. Λ_M = 145.2 S cm^2 mol^{-1}. Anal. Calc. for $C_{16}H_{17}ClNPdSSe{\cdot}ClO_4$: C, 33.39; H, 2.98; N, 2.43%. Found: C, 33.40; H, 2.96; N, 2.40%. ^{1}H NMR (CD_3CN, 25°C, vs Me_4Si): (δ, ppm): 2.99 (s, 3H, SMe), 3.04–3.27 (m, 2H, H_5), 4.32–4.80 (m, 2H, H_6), 7.54–8.17 (m, 9H, H_1, H_2, H_3, H_{10}, H_{11}, H_{12}, H_{13}), 8.51 (s, 1H, H_7). ^{13}C{^{1}H} NMR (CD_3CN, 25°C, vs Me_4Si): (δ, ppm): 26.2 (SMe), 32.4 (C_5), 72.3 (C_6), 126.3–134.6 (C_1, C_2, C_3, C_4, C_{10}, C_{11}, C_{12}, C_{13}), 137.2 (C_8), 139.5 (C_9), 167.7 (C_7). ^{77}Se{^{1}H} NMR (CD_3CN, 25°C, vs Me_2Se): (δ, ppm): 455.1. IR (KBr, ν_{max}/cm^{-1}): 3056 (m; $\nu_{C-H(aromatic)}$), 2917 (s; $\nu_{C-H(aliphatic)}$), 1630, 1578 (s; $\nu_{C=N}$), 1190 (m; ν_{C-N}), 841 (m; ν_{P-F}), 746 (m; $\nu_{C-H(aromatic)}$).

2: Yield 0.44 g, 80%. M.p. 152.8°C. Λ_M = 143.7 S cm^2 mol^{-1}. Anal. Calc. for $C_{15}H_{16}ClN_2PdSe{\cdot}ClO_4$: C, 33.08; H, 2.96; N, 5.14%. Found: C, 33.10; H, 2.99; N, 5.10%. ^{1}H NMR ($CDCl_3$, 25°C, vs Me_4Si): (δ, ppm): 2.84 (s, 3H, Me), 3.34–3.74 (m, 2H, H_5), 4.24–4.47 (m, 2H, H_6), 7.55–8.34 (m, 8H, H_1, H_2, H_3, H_{10}, H_{11}, H_{12}), 8.86–8.89 (m, 1H, H_9). ^{13}C{^{1}H} NMR ($CDCl_3$, 25°C, vs Me_4Si): (δ, ppm): 22.1 (Me), 37.9 (C_5), 62.2 (C_6), 123.5–133.3 (C_1, C_2, C_3, C_4, C_{10}, C_{11}, C_{12}), 138.4 (C_8), 149.1 (C_9), 176.5 (C_7). ^{77}Se{^{1}H} NMR ($CDCl_3$, 25°C, vs Me_2Se): (δ, ppm): 464.9. IR (KBr, ν_{max}/cm^{-1}): 3054 (m; $\nu_{C-H(aromatic)}$), 2928 (s; $\nu_{C-H(aliphatic)}$), 1631, 1577 (s; $\nu_{C=N}$), 1188 (m; ν_{C-N}), 748 (m; $\nu_{C-H(aromatic)}$).

2.7 *Synthesis of Pd(II)-Complexes (3–4)*

The $Na_2[PdCl_4]$ (0.15 g, 0.5 mmol) was dissolved in 5 mL of water. The solution of ligand **L6** (0.14 g, 0.5 mmol) / **L7** (0.18 g, 0.5 mmol) made in 10 mL of acetone was added to it with vigorous stirring. The mixture was further stirred for 2 h. The orange red precipitate was extracted with chloroform. The chloroform layer was washed with water, dried with anhydrous Na_2SO_4 and evaporated to dryness *in vacuo* to obtain **3/4** as orange coloured solid.

3: Yield 0.18 g, 79%. M.p. 149.0°C. Λ_M = 9.2 S cm^2 mol^{-1}. Anal. Calc. for $C_{15}H_{15}Cl_2NPdSe$: C, 38.70; H, 3.25; N, 3.01%. Found: C, 38.64; H, 3.19; N, 3.11%. ^{1}H NMR (DMSO-d^6, 25°C, vs Me_4Si): (δ, ppm): 2.67–2.77 (m, 1H), 3.59–3.73 (m, 2H), 4.51–4.59 (m, 1H), 6.67 (d, $^3J_{H-H}$ = 8.7 Hz, 1H), 7.20–7.45 (m, 6H), 7.95 (s, 1H), 8.16–8.19 (m, 2H). ^{13}C{^{1}H} NMR (DMSO-d^6, 25°C, vs Me_4Si): (δ, ppm): 32.3, 64.8, 124.9, 126.6, 127.5, 129.7, 129.9, 130.4, 130.9, 133.5, 133.4, 164.2. ^{77}Se{^{1}H} NMR (DMSO-d^6, 25°C, vs Me_2Se): (δ, ppm): 439.4.

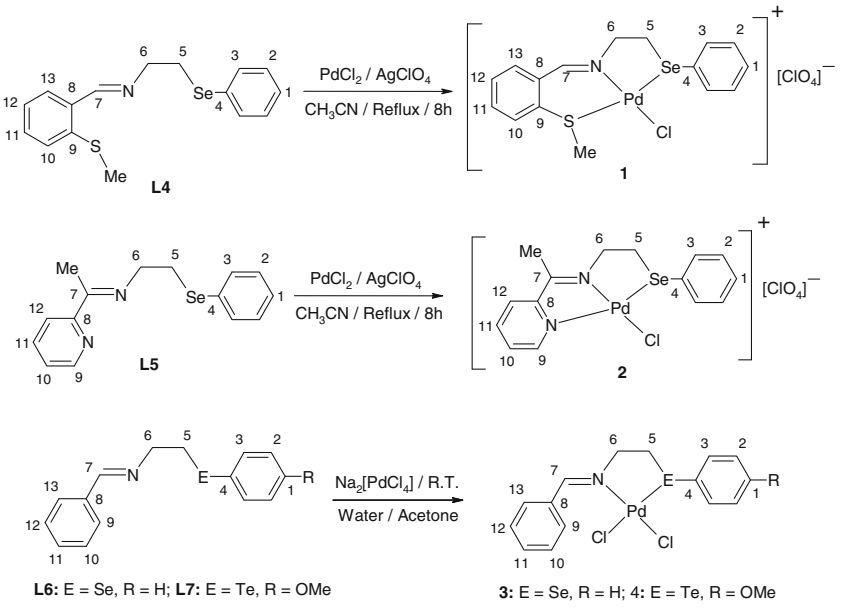
4: Yield 0.23 g, 82%. M.p. 157.0°C. Λ_M = 7.9 S cm^2 mol^{-1}. Anal. Calc. for $C_{16}H_{17}Cl_2NOPdTe$: C, 35.31; H, 3.15; N, 2.57%. Found: C, 35.29; H, 3.17; N, 2.57%. ^{1}H NMR (DMSO-d^6, 25°C, vs Me_4Si): (δ, ppm): 2.27–2.35 (m, 1H), 3.62–3.74 (m, 2H), 3.88 (s, 3H, OMe), 4.62–4.78 (m, 1H), 6.84 (d, $^3J_{H-H}$ = 8.4 Hz, 2H), 8.16–8.39 (m, 5H), 8.71 (d, $^3J_{H-H}$ = 8.1 Hz). ^{13}C{^{1}H} NMR (DMSO-d^6, 25°C, vs Me_4Si): (δ, ppm): 15.65, 57.34, 63.09, 104.36, 115.66, 128.13, 128.16, 129.71, 129.99, 138.69, 161.1, 167.9. ^{125}Te{^{1}H} NMR (DMSO-d^6, 25°C, vs Me_2Te): (δ, ppm): 679.1.

2.8 *Procedure for catalytic Suzuki reaction*

Bromobenzene or its derivative (1 mmol), phenylboronic acid (0.18 g, 1.5 mmol), Cs_2CO_3 (0.65 g, 2.0 mmol), distilled water (0.5 mL), DMF (4 mL) and catalyst were stirred together under reflux on an oil bath for 24 h under ambient conditions. The reaction mixture was cooled to room temperature and mixed with 20 mL of water. The product was extracted from the aqueous mixture with diethyl ether (25×50 mL). The solvent was evaporated on a rotary evaporator and the resulting residue was purified by column chromatography on silica gel. The ^{1}H and ^{13}C{^{1}H} NMR spectra identified the products.

3. Results and discussion

The syntheses of ligands **L1**–**L7** and Pd(II)–complexes (**1–4**) of **L4–L7** are summarized in schemes 1 and 2, respectively. **L1**–**L7** and Pd(II)-complexes (**1–4**) are stable and can be stored under ambient conditions up to six months. The molar conductance values in acetonitrile indicate 1:1 electrolyte nature of both complexes **1–2**, whereas for complexes **3–4** molar conductance values in acetonitrile indicate non-electrolytic nature. The complexes **1** and **2** show good solubility in CH_3OH, CH_3CN, CH_2Cl_2 and $CHCl_3$. On other hand, complexes **3–4** have good solubility in DMSO and DMF. Each ligand shows good solubility in all common

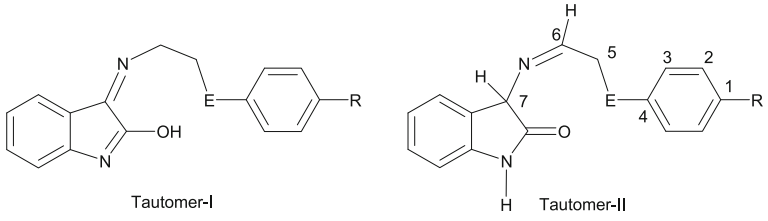


Scheme 2. Synthesis of Pd(II)-complexes (**1–4**).

organic solvents. In diethyl and petroleum ether the complexes **1–4** were found to be nearly insoluble. The solutions of complexes **1** and **2** in DMSO showed signs of decomposition within few hours.

3.1 *NMR spectra*

The ^{1}H, $^{13}C\{^{1}H\}$, $^{77}Se\{^{1}H\}$ and $^{125}Te\{^{1}H\}$ NMR spectra of ligands **L1–L7** have been found characteristic. However, in the course of reactions of 5–chloroisatin with chalcogenated amines, $H_2NCH_2CH_2E–C_6H_4–4–R$ (E = S, Se, or Te), we have observed that and probably both C=O groups react with amines as shown in scheme 1, resulting always in a mixture of Schiff bases **L1a** and **L1b** or **L2a** and **L2b** or **L3a** and **L3b**. The chromatographic separation of the pairs **L1a–L1b** or **L2a–L2b** or **L3a–L3b** did not succeed. This is an unusual reaction noticed for the first time in the context of preparation of a Schiff base by isatin or its any derivative.[12] The possibility of formation of a compound having both C=O groups derivatized in the same molecule, was ruled out by the results of elemental analyses. The ^{1}H, $^{13}C\{^{1}H\}$, $^{77}Se\{^{1}H\}$ and $^{125}Te\{^{1}H\}$ NMR spectra of the reactions products of scheme 1 were found characteristic (see figures S1–S4 in online supplementary material showing aliphatic regions of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra and relevant sections of $^{77}Se\{^{1}H\}$ and $^{125}Te\{^{1}H\}$ NMR spectra). They show signals which indicate the products as mixtures of **L1a** and **L1b** or **L2a** and **L2b** or **L3a** and **L3b**. In $^{13}C\{^{1}H\}$ NMR spectrum of **L1a**, **L2a** or **L3a** signal of C_6 is expected to be at higher frequency than that of **L1b**, **L2b** or **L3b**, as there is no possibility in the former of tautomerization, which can reduce partly double bond character of >C=N group.



The possibility that Schiff base is formed from C(7)=O and multiple signals arise from the ene-imine tautomerism of the Schiff base or tautomer-I was ruled out on the basis of following: (i) no OH peak expected from tautomer-I was observed, (ii) CH signals were not observed as expected from tautomer-II, (iii) the multiplicity of =CH-CH_2- system of tautomer-II was not observed. In fact, in ^{1}H NMR (see figures S5–S7 in supplementary material) two sets of similar signals appear. Therefore, the possibility of reaction of

both the C=O groups appears to be convincing, as $^{77}Se\{^{1}H\}$ and $^{125}Te\{^{1}H\}$ NMR spectra also have two signals. Further, the ratio of two species varies drastically with chalcogen, which does not favour tautomerization. On the basis of ^{1}H NMR (figure S1) the ratios of **L1a**:**L1b** and **L2a**:**L2b** (figure S2) has been found to be 53:47 and 55:45 for sulphur and selenium containing Schiff bases, respectively whereas **L3a**:**L3b** (figure S3) ratio was found to be 81:19. Schiff bases containing Se and Te exhibit two signals in their $^{77}Se\{^{1}H\}$ and $^{125}Te\{^{1}H\}$ NMR spectra, respectively (figure S4) supporting the reaction of both C=O groups of 5-chloroisatin with selenated or tellurated amines. The presence of tellurium in amine probably makes nitrogen electron rich, which makes the condensation reaction faster and consequently higher yield of **L3a**. As Schiff bases of isatin derivative were inseparable mixtures, their complexation was not attempted.

The NMR spectra of complexes**1–4** have been found consistent with their molecular structures shown in scheme 2 and support the presence of ligands **L4–L7** in them. The signals in $^{77}Se\{^{1}H\}$ NMR spectra of **1**, **2** and **3** appear shifted to higher frequencies by 176.8, 185.2 and 160.9 ppm with respect to those of free **L4**, **L5** and **L6**, respectively as Se is coordinated to palladium centre. Similarly, in $^{125}Te\{^{1}H\}$ NMR spectrum of **7** the signal appears at a higher frequency by 241.3 ppm relative to that of free **L7**, which is coordinated to palladium through Te. In ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **1–4** signals generally appear at higher frequencies relative to those of corresponding free ligands **L4–L7**, which coordinate with palladium (tri-dentate mode in case of **L4–L5** and bi-dentate in case of **L6–L7**). However, magnitude of shift to higher frequency is high for C_5 to C_7 (up to 10.8 ppm in $^{13}C\{^{1}H\}$ NMR) and protons attached to them (up to 0.71 ppm in ^{1}H NMR). The signals of SMe in $^{13}C\{^{1}H\}$ and ^{1}H NMR spectra of **1** also appear at higher frequency (9.3 and 0.53 ppm, respectively) relative to those **L4**. Similarly, the signals of Me in $^{13}C\{^{1}H\}$ and ^{1}H NMR spectra of **2** appear at higher frequency (7.7 and 0.52 ppm, respectively) with respect to those of corresponding free ligand **L5**.

Table 1. Crystal data and structural refinements for complexes **1**–**2**.

Compounds	**1**	**2**
Empirical formula	$C_{16}H_{17}ClNPdSSe{\cdot}ClO_4$	$C_{15}H_{16}ClN_2PdSe{\cdot}ClO_4$
Formula weight	575.64	544.56
Crystal size [mm]	0.48 × 0.23 × 0.18	0.46 × 0.22 × 0.17
Crystal system	Monoclinic	Monoclinic
Space group	$C\,2/c$	$P\,21/n$
Unit cell dimensions	$a = 18.326(14)$Å	$a = 10.2179(9)$Å
	$b = 14.414(10)$Å	$b = 16.8940(15)$Å
	$c = 15.634(10)$Å	$c = 11.3698(10)$Å
	$\alpha = 90.00°$	$\alpha = 90.00°$
	$\beta = 105.817(11)°$	$\beta = 107.776(2)°$
	$\gamma = 90.00°$	$\gamma = 90.00°$
Volume [Å^3]	3973.0(5)	1869.0(3)
Z	8	4
ρ_{calcd}[g/cm^3]	1.925	1.935
μ(Mo$K\alpha$) [mm^{-1}]	3.162	3.248
F(000)	2256.0	1064.0
θ range [°]	1.82–25.00	2.23–25.00
Index ranges	$-21 \le h \le 21$	$-12 \le h \le 12$
	$-17 \le k \le 17$	$-20 \le k \le 20$
	$-18 \le l \le 18$	$-13 \le l \le 13$
Reflections collected	45118	17308
Independent reflections (R_{int}.)	4618 (0.0409)	3287 (0.0274)
Completeness to max. θ [%]	99.4	99.7
Max./min. Transmission	0.574/0.427	0.574/0.427
Data/restraints/parameters	3496/0/236	3287/0/227
Goodness-of-fit on F^2	1.055	1.036
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0499$, $wR_2 = 0.1328$	$R_1 = 0.0287$, $wR_2 = 0.0777$
R indices (all data)	$R_1 = 0.0794$, $wR_2 = 0.1576$	$R_1 = 0.0328$, $wR_2 = 0.0800$
Largest diff. peak / hole [e.Å^{-3}]	0.867/ − 0.502	0.497/ − 0.353

3.2 *Crystal structures*

The crystal structures of **1–2** have been solved and their crystal and refinement data are given in table 1. The ORTEP diagrams of cations of **1** and **2** are given in figures 1 and 2 with selected bond lengths and angles (more values are given in supplementary material; table S1). The geometry around Pd in the cations of **1–2** is nearly square planar and the ligands are coordinated with Pd in a tri-dentate (S, N, Se) or (N, N, Se) mode forming one six- and one five-membered or two five-membered rings, respectively. The Pd–S bond length of **1**, 2.304(2) Å is consistent with normal reported range.[5,7,20,21] Pd–Se bond length of **1**, 2.4172(17) Å is greater than that of **2** (2.3675(4) Å), but both are normal.[5,7,20,21] The Pd–N and Pd–Cl bond lengths of complexes **1–2**, 1.992(3)–2.041(3) and 2.2895(9)–2.392(2) Å, respectively are also normal.[20,21] The bond angles at the coordinating S, Se and N atoms are as expected for nearly trigonal–pyramidal and tetrahedral geometries, respectively.

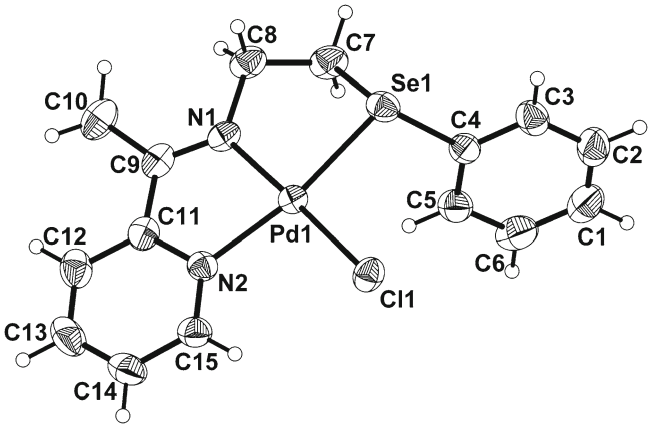


Figure 2. ORTEP diagram of the cation of **2** with ellipsoids at the 30% probability level. The ClO_4^- anion has been omitted for clarity. Selected bond lengths (Å): Pd(1)–Se(1) 2.3675(4), Pd(1)–N(1) 1.992(3), Pd(1)–N(2) 2.041(3), Pd(1)–Cl(1) 2.2895(9); bond angles (°): Se(1)–Pd(1)–N(1) 88.18(9), Se(1)–Pd(1)–N(2) 168.71(8), Se(1)–Pd(1)–Cl(1) 93.68(3), N(1)–Pd(1)–Cl(1) 177.99(9), N(2)–Pd(1)–Cl(1) 97.60(8), N(1)–Pd(1)–N(2) 80.54(11).

3.3 *Catalytic Suzuki reactions*

The Suzuki reactions between different aryl bromides and phenylboronic acid were carried out using complexes **3** and **4** as catalyst (summarized in scheme 3). The detailed results of catalysis are given in tables 2–3.

In view of air and moisture sensitivity of palladium complexes of phosphorus ligands, there is an interest in the development of phosphine-free ligands for the Suzuki–Miyaura coupling reaction. Therefore, complexes **3–4** were explored for such coupling. For carrying out Suzuki–Miyaura reactions of aryl halide with phenylboronic acid the reaction conditions used were similar to those used for analogous phosphine-free systems.[11,22] Firstly, the coupling reaction of bromobenzene with phenylboronic acid in the presence of **3** was studied to optimize the reaction conditions. The Cs_2CO_3 has been found most appropriate base as with alternatives viz. potassium carbonate, triethylamine, sodium acetate or sodium carbonate longer reaction time was necessary for reasonable conversions. Furthermore, the reaction was also influenced by the solvent. DMF and water mixture was found to be the best choice of solvent for this reaction among the several solvents investigated. The complex **3** was found to show promising activity[11] for several aryl bromides (table 2) including electron-rich ones as very low catalyst loading (up to 0.006 mol%) was found sufficient for good conversion in several cases. The highest turnover number (TON) found in case of 4-bromobenzonitrile is 1.58×10^4 with 95% yield. This value indicates that efficiency of present catalyst is of the same order as that of Pd(II)-*N*–{2–(phenylseleno)ethyl}pyrrolidine complex (Yield up to 82%, TON up to 8.2×10^4).[22] The conversions with present catalyst are comparable with those reported for other Pd(II)-selenated Schiff base (Se, N, O^-) complexes (Yield up to 95%). However, with high catalyst loading 0.5 mol% only such conversions were realized earlier.[23] The catalytic activity of tellurium analogue, **4** which differs from **3** only in type of chalcogen donor site is significantly lower (table 3) than that of **3**. This may probably be attributed to the large size and metallic character of Te. The catalytic

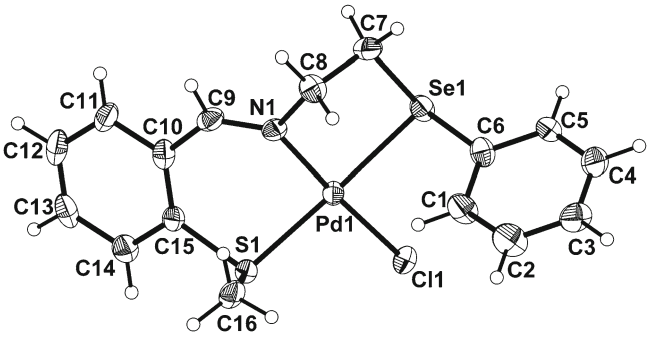
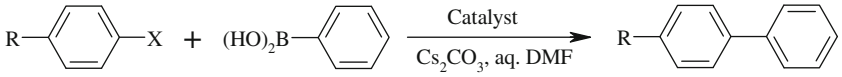


Figure 1. ORTEP diagram of the cation of **1** with ellipsoids at the 30% probability level. The ClO_4^- anion has been omitted for clarity. Selected bond lengths (Å): Pd(1)–Se(1) 2.4172(17), Pd(1)–S(1) 2.304(2), Pd(1)–N(1) 2.021(6), Pd(1)–Cl(1) 2.292(2); bond angles (°): Se(1)–Pd(1)–S(1) 176.97(6), Se(1)–Pd(1)–Cl(1) 90.08(7), Se(1)–Pd(1)–N(1) 86.76(18), S(1)–Pd(1)–Cl(1) 92.65(8), S(1)–Pd(1)–N(1) 90.51(19), N(1)–Pd(1)–Cl(1) 176.83(19).



Scheme 3. Suzuki–Miyaura coupling reaction.

Table 2. Suzuki coupling reactions catalysed by **3**[a].

Entry no.	Aryl halide	Mol%	% Yield	TON
1.	4-Bromobenzaldehyde	0.1	95	950
		0.01	70	7000
		0.006	50	8333
2.	4-Bromobenzonitrile	0.006	95	15833
3.	1-Bromo-4-nitrobenzene	0.06	95	1583
4.	Bromobenzene	1.0	58	58
5.	4-Bromotoluene	1.0	45	45
6.	4-Bromoanisol	1.0	39	39
7.	3-Bromobenzoic acid	1.0	67	67
8.	3-Bromopyridine	1.0	39	39
9.	2-Bromopyridine	1.0	35	35

[a]*Reaction conditions*: 1.0 equiv. of aryl bromide, 1.3 equiv. of phenylboronic acid and 2 equiv. of base (Cs_2CO_3), aqueous DMF as solvent and temperature of bath 100°C, reaction time 24 h, isolated yield after column chromatography

Table 3. Suzuki coupling reactions catalysed by **4**[a].

Entry no.	Aryl halide	Mol%	% Yield	TON
1.	4-Bromobenzaldehyde	1.0	55	55
2.	1-Bromo-4-nitrobenzene	1.0	57	57
3.	4-Bromobenzonitrile	1.0	62	62
4.	4-Bromotoluene	1.0	42	42
5.	4-Bromoanisol	1.0	59	59
6.	4-Bromobenzoic acid	1.0	48	48

[a]*Reaction conditions*: 1.0 equiv. of aryl bromide, 1.3 equiv. of phenylboronic acid and 2 equiv. of base (Cs_2CO_3), aqueous DMF as solvent and temperature of bath 100°C, reaction time 24 h, isolated yield after column chromatography

activity appears to be dependent on the substituent groups present on the aryl ring. The additional advantage of using these catalysts is that they are air stable and also not moisture sensitive.

4. Conclusions

The reaction of $H_2NCH_2CH_2E–C_6H_4–4–R$ (R = H; E = S or Se; R = MeO; E = Te) with 5–chloroisatin, 2–(methythio)benzaldehyde, 2–acetylpyridine and benzaldehyde results in Schiff bases (**L1–L7**). The **L1–L3** were found to be mixtures of products formed by condensation of each one of the two >C=O groups with chalcogenated amines. This kind of reactivity of >C=O groups of isatin has been observed for the first time. The ratio of two co-existing products was found to vary with chalcogen; 53:47 (E = S), 55:45 (E = Se) and 81:19 (E = Te). Pd(II)–complexes (**1–4**) were synthesized and characterized. The crystal structures of **1–2** have been solved. The Pd–Se bond lengths are 2.3675(4)–2.4172(17) Å. The Pd–complexes (**3–4**) of **L6–L7** were explored for Suzuki–Miyaura coupling and found promising as 0.006 mol% of **3** is sufficient to obtain good conversion with TON up to 1.58×10^4.

Supplementary material

CCDC numbers: **863907** and **863908** contain the supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge at www.ccdc.cam.ac.uk/data.request/cif or from The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article (figures S1–S7 and table S1) are available at http://www.ias.ac.in/chemsci.

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