

Available online at www.sciencedirect.com



POLYHEDRON

Polyhedron 27 (2008) 485-492

Selenated Schiff bases of 2-hydroxyacetophenone and their palladium(II) and platinum(II) complexes: Syntheses, crystal structures and applications in the Heck reaction

Arun Kumar, Monika Agarwal, Ajai K. Singh *

Department of Chemistry, Indian Institute of Technology, New Delhi 110 016, India

Received 20 August 2007; accepted 13 September 2007 Available online 14 November 2007

Abstract

Selenated Schiff bases 2-HO-C₆H₄C(CH₃)=N(CH₂)_nSePh (n = 2, L¹; n = 3, L²) and their complexes with Pd(II) and Pt(II), viz [Pd(L¹-H)Cl] (1), [Pt(L¹-H)Cl] (2), [Pd(L²-H)Cl] (3) and [PtL²Cl₂] (4), have been synthesized and characterized with proton, carbon-13 and ⁷⁷Se{¹H} NMR spectra. In the ⁷⁷Se{¹H} NMR spectrum of 2 the signal at δ 387.4 ppm appears as a triplet due to ¹J(¹⁹⁵Pt-Se) coupling (2043 Hz). The single-crystal structures of L¹, L², 1 and 2 were solved. The C-Se-C bond angles in L¹ and L² have been found to be around 99°. The geometry around Pd and Pt is square planar. The Pd–Se and Pt–Se bond distances are 2.3669(11) and 2.3543(16) Å, respectively. Complexes 1 and 2 are the first examples of crystal structures of Pd and Pt complexes of a (Se, N, O⁻) ligand. Complex 1 has been explored as a homogeneous catalyst for a Heck type C–C coupling reaction between methyl acrylate and *p*-iodonitrobenzene (yield ~80%; reaction time 14 h).

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Selenated Schiff base; Selenium ligand; Palladium; Platinum; Complex synthesis; Single-crystal structure; X-ray diffraction; Heck reaction; Catalysis

1. Introduction

Schiff bases constitute an important class of ligands, which have very rich and extensive chemistry, reviewed recently by Vigato and Tamburini [1]. Metal complexes of Schiff bases have found diverse applications in addition to interesting structural chemistry. Ruthenium complexes containing bidentate Schiff bases have been used [2] in catalyzing Kharasch addition, enol-ester synthesis, alkyne dimerization, olefin metathesis and atom transfer radical polymerization. Metal complexes of chiral binaphthyl Schiff bases have been used for stereoselective organic transformations [3]. Oxovanadium(III–V) complexes of tetradentate Schiff bases have the potential for multi-electron redox catalysis [4]. Metal complexes containing Schiff-base ligands have also been found to show mesomorphic behaviour [5]. Among Schiff bases, 'Salen' and related derivatives have been found to be very interesting. Their complexes with transition metals are suitable catalysts for epoxidation reactions [6-10] and a variety of other reactions like dehydrogenation plus intramolecular Diels-Alder cycloaddition [11], enantioselective conjugate addition [12] and ring opening polymerization [13]. However, selenated Schiff bases of mono ketones or aldehydes have not been studied in detail so far and recently we have reported such tellurated derivatives [14,15]. The presence of Se as a donor site in Schiff bases may modify significantly their known catalytic roles. Therefore, such systems are worth exploring. A wide range of selenated Schiff-base ligands may be designed by the reaction of a selenated amine with different aldehydes or ketones. To use this strategy we have made

^{*} Corresponding author. Tel.: +91 011 26591379; fax: +91 011 26862037.

E-mail addresses: aksingh@chemistry.iitd.ac.in, ajai57@hotmail.com (A.K. Singh).

^{0277-5387/\$ -} see front matter @ 2007 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2007.09.027

NH₂CH₂CH₂SePh and NH₂CH₂CH₂CH₂SePh [3], which have been used for designing selenated Schiff bases. Thus \mathbf{L}^1 and \mathbf{L}^2 and their complexes with Pd(II) and Pd(II), in which a metal-selenium bond is formed, have been synthesized. Selenium being a very "soft" donor in nature does not coordinate with 3-d transition metal ions in their common oxidation states. The ligands L^1 and L^2 and their complexes were characterized by NMR spectroscopy (including 77 Se{¹H}) and X-ray diffraction studies, when single crystals were obtained. The results of these investigations are reported in this paper. The catalytic activity of the selenide-Pd(II) complexes not only rivals but may outperform that of the corresponding phosphorus and sulfur analogues [16,17]. Practical advantages of the selenium-based catalysts for the Heck reaction have been reported as their straightforward synthesis and high activity in the absence of any additives as well as the enhanced stability of the selenide ligands toward air oxidation [17]. Therefore, 1 was thought to be a good candidate for exploring for the Heck reaction. Preliminary results of these explorations are also reported in this paper.



2. Experimental

The C and H analyses were carried out with a Perkin– Elmer 2400 Series II C, H, N analyzer. The ¹H, ¹³C{¹H} and ⁷⁷Se{¹H} NMR spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300.13, 75.47 and 57.24 MHz, respectively. IR spectra in the range 4000– 250 cm⁻¹ were recorded on a Nicolet Protége 460 FT-IR spectrometer as KBr pellets. The melting points determined in open capillary are reported as such. The conductivity measurements were carried out in CH₃CN (concentration ca 1 mM) using an ORION conductivity meter model 162.

Single-crystal diffraction studies were carried out with a Bruker AXS SMART Apex CCD diffractometer using Mo K α (0.71073 Å) radiation at 298(2) K. The software SADABS was used for absorption correction (if needed) and SHELXTL for space group, structure determination and refinements [18a,18b]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they are attached. The leastsquares refinement cycles on F^2 were performed until the model converged.

2-(Phenylseleno)ethylamine [19] and 3-(phenylseleno)propylamine [19] were prepared by the reported methods $[^{77}\text{Se}\{^{1}\text{H}\}$ NMR (vs Me₂Se, 25 °C) δ , ppm: 256.6 and 257.5, respectively].

2.1. Synthesis of L^1

2-(Phenylseleno)ethylamine (1.00 g, 5.0 mmol) was stirred in dry ethanol (20 mL) at room temperature for 0.5 h. o-Hydroxyacetophenone (0.68 g, 5.0 mmol), dissolved in dry ethanol (20 mL), was mixed dropwise with stirring. The mixture was stirred further at room temperature for 2 h. The solvent was evaporated on a rotary evaporator which resulted in a yellow precipitate. The precipitate on recrystallization from chloroform-hexane (1:1) gave yellow coloured single-crystals of L^1 . Yield 1.43 g (~90%); m.p. 84–85 °C. $\Lambda_{\rm M} = 0.88 \text{ cm}^2 \text{ mol}^{-1} \Omega^{-1}$. Anal. Calc. for C₁₆H₁₇NOSe: C, 60.33; H, 5.34; N, 4.39. Found: C, 60.46; H, 5.28; N, 4.46%. NMR (¹H, CDCl₃, 25 °C, vs SiMe₄) δ , ppm: 2.25 (s, 3H, CH₃), 3.22 (t, $J = 6.9 \text{ Hz}, 2\text{H}, \text{ SeCH}_2), 3.81 (t, J = 6.9 \text{ Hz}, 2\text{H}, \text{H}_6),$ 6.78 (t, J = 7.2 Hz, 1H, H₁₂), 6.94 (d, J = 8.4 Hz, 1H, H₁₃), 7.25–7.30, (m, 4H, H₂, H₁ and H₁₁), 7.49 (d, J = 8.4 Hz, 1H, H₁₀), 7.52–7.55 (m, 2H, H₃), 15.93 (bs, 1H, OH) ($^{13}C{^{1}H}$, CDCl₃, 25 °C vs SiMe₄) δ , ppm: 14.6 (CH₃), 27.8 (SeCH₂), 49.4 (C₆), 117.2 (C₁₀), 118.5 (C₁₂), 119.3 (C₈), 127.2 (C₁), 128.0 (C₁₃), 129.1 (C₂), 129.2 (C₄), 132.4 (C₁₁), 133.0 (C₃), 163.2 (C₉), 171.8 (C₇) (77 Se{¹H}, CDCl₃, 25 °C vs Me₂Se) δ , ppm: 282.3. IR (KBr, cm⁻¹): 3484, 1607, 470, 734.

2.2. Synthesis of L^2

3-(Phenylseleno)propylamine (1.07 g, 5.0 mmol) was stirred in dry ethanol (20 mL) at room temperature for 0.5 h. o-Hydroxyacetophenone (0.68 g, 5.0 mmol), also dissolved in dry ethanol (20 mL), was added to it dropwise with stirring. The mixture was stirred further at room temperature for 2 h. On evaporating the solvent on a rotary evaporator a yellow precipitate of L^2 was obtained, which on recrystallization from a chloroform-hexane mixture (1:1) afforded yellow single-crystals of L². Yield 1.49 g (~90%); m.p. 82–83 °C. Anal. Calc. for C₁₇H₁₉NOSe: C, 61.40; H, 5.71; N, 4.21. Found: C, 61.45; H, 5.73; N, 4.28%. NMR (¹H CDCl₃, 25 °C, vs SiMe₄) δ , ppm: 2.15 (quintet, J = 6.6 Hz, 2H, H₆), 2.29 (s, 3H, CH₃), $3.06 (t, J = 6.9 Hz, 2H, SeCH_2), 3.66 (t, J = 6.6 Hz, 2H, H_7),$ 6.77 (t, J = 7.5 Hz, 1H, H₁₃), 6.92 (d, J = 8.1 Hz, 1H, H₁₄), 7.23-7.31 (m, 4H, H₂, H₁ and H₁₂), 7.48-7.50 (m, 2H, H₁₁ and H₃), 16.40 (bs, 1H, OH) (${}^{13}C{}^{1}H{}$ CDCl₃, 25 °C, vs SiMe₄) *δ*, ppm: 14.3 (CH₃), 25.2 (SeCH₂), 30.46 (C6), 48.4 (C7), 116.9 (C11), 118.7 (C13), 119.1 (C9), 126.8 (C1), 127.9 (C14), 129.0 (C2), 129.7 (C4), 132.4 (C12), 132.5 (C3), 164.0 (C₁₀), 172.0 (C₈) (⁷⁷Se {¹H}, CDCl₃, 25 °C, vs Me₂Se) δ , ppm: 286.6. IR (KBr, cm⁻¹): 1612, 461, 734.

2.3. Synthesis of $[PdCl(L^{1}-H)]$ (1)

An aqueous solution (5 mL) of Na₂[PdCl₄] (0.294 g, 1 mmol) was mixed with a solution of L^1 (0.3182 g,

1 mmol) prepared in acetone (10 mL) with vigorous stirring. An orange precipitate of 1, obtained instantaneously, was filtered and dried. It was recrystallized from chloroform-hexane (2:1) mixture. Single-crystals of 1 were obtained from the same solvent system (a few drops of MeOH were added additionally). Yield ca. 0.3626 g (~79%); m.p. 159 °C. $\Lambda_{\rm M} = 7.0 \text{ cm}^2 \text{ mol}^{-1} \Omega^{-1}$. Anal. Calc. for C₁₆H₁₆ClNOPdSe (powder form): C, 41.83; H, 3.49; N, 3.05. Found: C, 41.68; H, 3.41; N, 3.10%. NMR (¹H, CDCl₃, 25 °C, vs SiMe₄) δ, ppm: 2.22 (s, 3H, CH₃), 2.69– 2.72 (m, 1H, H₅), 3.56-3.71 (m, 2H, H₅ + H₆), 4.48-4.53(m, 1H, H₆), 6.62 (t, J = 7.8 Hz, 1H, H₁₂), 7.12 (d, J = 8.7 Hz, 1H, H₁₃), 7.23–7.38 (m, 2H, H₁₁ and H₁₀), 7.41–7.43 (m, 3H, H_2 and H_1), 8.16–8.19 (m, 2H, H_3) $(^{13}C\{^{1}H\}, CDCl_{3}, 25 \circ C, vs SiMe_{4}) \delta$, ppm: 19.7 (CH₃), 32.4 (SeCH₂), 60.7 (=NCH₂), 115.4 (C₁₀), 121.6 (C₁₂), 123.4 (C₄), 125.7 (C₈), 129.9 (C₂), 130.1 (C₁₁), 131.1 (C₁), 133.4 (C₁₃), 133.6 (C₃), 164.2 (C₉), 168.1 (C₇). (77 Se{¹H} CDCl₃, 25 °C vs Me₂Se) δ , ppm: 440.4. IR (KBr, cm⁻¹): 1572, 463, 747.

2.4. Synthesis $[PtCl(L^{1}-H)]$ (2)

K₂[PtCl₄] (0.415 g, 1 mmol) was dissolved in water (5 mL). A solution of L^1 (0.3182 g, 1 mmol) prepared in acetone (10 mL) was added to it with vigorous stirring. An orange precipitate of 2 was obtained, which was filtered and dried. The orange solid was recrystallized from chloroform-hexane (2:1). Single-crystals of 2 were obtained from the same solvent system. Yield ca. 0.3626 g (~79%); m.p. 162 °C $\Lambda_{\rm M} = 5.0 \text{ cm}^2 \text{ mol}^{-1} \Omega^{-1}$. Anal. Calc. for C₁₆H₁₆ClNOPtSe: C, 35.10; H, 2.92; N 2.56. Found: C, 35.50; H, 2.96; N, 2.51%. NMR (¹H, $CDCl_3$, 25 °C, vs SiMe₄) δ , ppm: 2.14 (s, 3H, CH₃), 2.55 (t of d, J = 2.7 Hz, J = 12.3 Hz, 1H, H₅), 3.38 (d of t, J = 4.2 Hz, J = 12 Hz, 1H, H₅), 3.56 (d of t, J = 3.9 Hz, 12.3 Hz, 1H, H₆) 4.37 (t of d, J = 2.4 Hz, J = 13.5 Hz, 1H, H₆), 6.66 (t, J = 7.2 Hz, 1H, H₁₂), 7.20 (d, J =8.4 Hz, 1H, H_{13}), 7.34 (t, J = 8.4 Hz, 1H, H_{11}), 7.39– 7.42 (m, 3H, H₂, H₁), 7.47 (d, J = 8.4 Hz, H₁₀), 8.10-8.13 (m, 2H, H₃) ($^{13}C{^{1}H}$, CDCl₃, 25 °C, vs SiMe₄) δ , ppm: 20.6 (CH₃), 34.2 (SeCH₂), 61.9 (=NCH₂), 116.4 $(C_{10}), 122.0 (C_{12}), 123.1 (C_4), 124.7 (C_8), 129.5 (C_2),$ 130.2 (C_{11}), 130.5 (C_1), 132.9 (C_{13}), 133.1 (C_3), 162.5 (C₉), 163.7 (C₇) (⁷⁷Se{¹H}, 25 °C, vs Me₂Se) δ , ppm: 387.36. IR (KBr, cm^{-1}): 1572, 465, 747.

2.5. Synthesis of $[PdCl(L^2-H)]$ (3)

Na₂[PdCl₄] (0.294 g, 1 mmol) dissolved in water (5 mL) and a solution of L² (0.332 g, 1 mmol) prepared in acetone (10 mL) were stirred together vigorously. An orange precipitate of **3** was immediately obtained, which was filtered and dried. It was recrystallized from a chloroform–hexane (60:40) mixture. Yield ~0.42 g (~90%); m.p. 170 °C. $\Lambda_{\rm M} = 6.0 \text{ cm}^2 \text{ mol}^{-1} \Omega^{-1}$ Anal. Calc. for C₁₇H₁₈NOSePdCl: C, 43.12; H, 3.80; N, 2.95. Found:

C, 42.82; H, 3.99; N, 3.15%. NMR (¹H, CDCl₃, 25 °C, vs SiMe₄) δ , ppm: 2.02–2.07 (m, 2H, H₆), 2.34 (s, 3H, CH₃), 2.88 (d of t, J = 4.2 Hz, 1H, H₅), 3.10 (d of t, J = 4.2 Hz, J = 11.1 Hz, 1H, H₅), 3.65–3.69 (m, 2H, H₇), 6.65 (t, J = 7.8 Hz, 1H, H₁₃), 7.10 (d, J = 8.7 Hz, 1H, H₁₄), 7.22 (t, J = 7.5 Hz, 1H, H₁₂), 7.33–7.44 (m, 4H, H₁₁, H₂, H₁), 8.05–8.07 (m, 2H, H₃) (¹³C{¹H} CDCl₃, 25 °C, vs SiMe₄) δ , ppm: 19.6 (CH₃), 26.3 (SeCH₂), 29.7 (C6), 53.4 (NCH₂), 116.0 (C₁₁), 121.8 (C₁₃), 126.6 (C₉), 129.7 (C₄), 129.8 (C₂), 129.8 (C₁₂), 130.3 (C₁), 133.3 (C₃), 134.1 (C₁₄), 164.6 (C₁₀), 169.1 (C₈) (⁷⁷Se{¹H}, 25 °C, vs Me₂Se) δ , ppm: 293.6. IR (KBr, cm⁻¹): 1592, 468, 748.

2.6. Synthesis $[PtCl(L^2)]$ (4)

K₂[PtCl₄] (0.415 g, 1 mmol) was dissolved in water (5 mL). A solution of L^2 (0.332 g, 1 mmol) in acetone (10 mL) was added with vigorous stirring. An orange coloured precipitate of 4 was immediately obtained, which was filtered and dried. It was recrystallized from a chloroform-hexane (60:40) mixture. Yield ~ 0.415 g (~50%); m.p. 147 °C. $\Lambda_{\rm M} = 6.8 \text{ cm}^2 \text{ mol}^{-1} \Omega^{-1}$. Anal. Calc. for C₁₇H₁₉NOSePtCl₂: C, 34.11; H, 3.18; N, 2.34. Found: C, 33.67; H, 3.58; N, 2.43%. NMR (¹H, CDCl3, 25 °C, vs SiMe₄) δ , ppm: 2.21–2.41 (m, 5H, H₆ + CH₃), 3.10 (t of d, J = 3.6 Hz, J = 8.1 Hz, 1H, H₅), 3.54– 3.58(m, 1H, H₅), 3.65–3.66 (m, 2H, NCH₂), 6.78 (t, J = 7.2 Hz, 1H, H₁₃), 6.91 (d, J = 8.4 Hz, 1H, H₁₄), 7.28 (t, J = 8.1 Hz, 1H, H₁₂), 7.34–7.42 (m, 3H, H₂), H_1), 7.49 (d, J = 7.8 Hz, H_{11}), 7.86–7.89 (m, 2H, H_3), 16.28 (bs, 1H, OH); (¹³C{¹H} CDCl₃, 25 °C, vs SiMe₄) δ , ppm: 14.6 (CH₃), 28.2 (SeCH₂), 31.6 (C₆) 48.7 (NCH₂), 117.3 (C₁₁), 118.5 (C₁₃), 119.3 (C₉), 128.1 (C₁₄), 129.6 (C₂), 130.2 (C₁), 132.5 (C₁₂), 132.9 (C₄), 133.0 (C₃), 163.4 (C₁₀), 172.5 (C₈); (⁷⁷Se{¹H}, 25 °C, vs Me₂Se) δ , ppm: 337.4, 338.5. IR (KBr, cm⁻¹): 3395, 1582, 465, 739, 685.

2.7. Procedure for the homogeneous catalytic Heck reaction with 1

A mixture of methyl acrylate (0.172 g, 2 mmol), *p*-iodonitrobenzene (0.62 g, 2.5 mmol), Et_3N (0.54 g, 3.0 mmol), *p*-xylene (2.0 mL) and **1** (22.95 mg) was stirred for 14 h at 140 °C and cooled thereafter to room temperature. It was treated with chloroform (40 mL) and filtered. The filtrate was evaporated on a rotary-evaporator to obtain the product.

It was purified through a silica gel column using hexane:ethylacetate mixture (9:1); yield 0. 33 g (~80%); NMR (¹H, CDCl₃, 25 °C, vs TMS) δ , ppm: 3.84 (s, 3H, OCH₃), 6.58 (d, J = 15.9 Hz, 1H, =CH-COOMe), 7.69 (d, 2H, J = 9 Hz, ArH, *o* to NO₂), 7.74 (d, J = 15.9 Hz, 1H, =CH-Ar), 8.27 (d, 2H, J = 9 Hz, Ar H, *m* to NO₂).

3. Results and discussion

The ligands L^1 and L^2 and their complexes have been synthesized by the reactions given in Scheme 1. The ligands are stable and can be stored under ambient conditions up to 6 months. They have good solubility in CHCl₃, CH₂Cl₂, CH₃CN, MeOH, EtOH and acetone. In hexane both ligands are sparingly soluble. Both ligands are non-electrolytes. Complexes 1–4 are stable under ambient conditions and are soluble in CHCl₃, CH₂Cl₂, CH₃CN, EtOH, MeOH and acetone, but insoluble in hexane. All of them are nonionic in nature. In the IR spectra of complexes 1–4 the C=N- stretching frequency has been observed to be red shifted by 20–35 cm⁻¹ with respect to those of L¹ and L², indicating the involvement of its nitrogen in coordination. Elemental analyses of 1 and 2 were carried out using their non-crystalline samples.

3.1. NMR spectra

The ¹H NMR spectra of both L^1 and L^2 have been found characteristic. On complexation of L^1 with Pd(II) the -CH₂ groups in the -Se-CH₂-CH₂-N system show a group of three signals, two correspond to a single proton and one to two protons (one from each $NCH_2 + SeCH_2$). Their assignments are based on the HMQC NMR spectrum of 1. However in the case of complex 2, the -Se-CH₂-CH₂-N system shows a group of four signals, each one corresponding to one proton. These assignments are also in agreement with the HMOC NMR spectrum of 1. On complexation of L^1 with Pd(II)/Pt(II) one signal for the H₆ protons is deshielded by $\sim 0.60-0.70$ ppm and the other one is shielded by $\sim 0.14-0.25$ ppm. Similarly, of the two signals of H_5 , one shows shielding of 0.52-0.67 ppm and the other deshielding of 0.16–0.38 ppm. The CH₃ signal shifts to upfield marginally (up to 0.1 ppm) on complexation. The H_{13} signal shows deshielding of the order of 0.18–0.26 ppm on the formation of 1 and 2. The deshielding of the H_3 signal was found to be between 0.58 and 0.64 ppm on complexation. In complex 3 the signal of H_6 was observed as a multiplet (upfield ~ 0.1 ppm). The NCH₂ signal was also found to be a mul-



tiplet and deshielded by an amount <0.02 ppm. The pattern of the -SeCH₂ signals were found to be similar to those of **1**, but deshielded by up to 0.2 ppm only. The lower deshielding appears to be the effect of one six membered ring formed in the case of **3**. In the proton spectrum of **4**, the OH signal was observed but shielded insignificantly (~0.1 ppm). The signals of H₆ and CH₃ were found to be overlapping but not much shifted with respect to those of the free ligand L². The signal of H₇ was found as a multiplet, but unshifted with respect to that of free L². The protons of the SeCH₂ group give a multiplet deshielded by 0.5 ppm with respect to those of free L² and a triplet of doublets at a position similar to that of L².

The ${}^{13}C{}^{1}H$ NMR spectra of both L^1 and L^2 are also characteristic. On formation of 1 and 2 signals of carbon atoms C₂, C₃, C₉, C₁₀ and C₁₁ exhibit deshielding of up to 12.5 ppm. The signal of C₆ shows maximum deshielding (11.3–12.5 ppm) on complexation. The deshielding of the C_1 , C_5 , C_8 and C_{13} signals is of the order of 3–6 ppm. The signals of C_4 , C_7 and C_{11} have been observed to be shielded by 2-8 ppm with respect to those signals of free L^1 . On formation of **3** signals of carbon atoms C₁, C₇, C₉, C₁₃, C₁₄ and CH₃ exhibit deshielding between 3.0 and 7.5 ppm. Of them, the signal of C₉ shows maximum deshielding (7.5 ppm) on complexation. The deshielding of signals C_2 , C_3 , C_5 and C_{10} is of the order of 0.8 –1.0 ppm. The signals of C₄, C₆, C₈, C₁₁ and C₁₂ have been observed to be shielded (by up to 2.8 ppm) with respect to those of free L^2 . On complexation of L^2 with Pt(II), the signals of most of the carbon atoms are shifted marginally (0.1–0.6 ppm), except those of C_1 , C_4 and C_5 which are deshielded by 3.3, 3.2 and 3.0 ppm, respectively. These observations suggest that in 1–3 the ligands L^1 and L^2 coordinate in a tridentate mono-anionic mode. The bonding of L^2 with Pt(II) appears to be through N and Se only.

In the ⁷⁷Se{¹H} NMR spectra, ligands L¹ and L² exhibit singlets at 282.3 and 286.6 ppm, respectively, which are deshielded (~25–29 ppm) with respect to those of the precursor selenated amines. On complexation of L¹ with Pd(II) and Pt(II), the signals in the ⁷⁷Se{¹H} NMR spectra were found to be shifted downfield by 158 and 105 ppm respectively. In the case of 2, the signal at 387.4 appears as a triplet because of ¹J(¹⁹⁵Pt–Se) coupling (2043 Hz). On formation of 3 and 4, the deshielding of the signals in the ⁷⁷Se NMR spectra was found only to be 6.9 and 51.3 ppm. This is probably due to formation of one six membered ring in these cases (see Table 1).

3.2. Crystal structures

The crystal structures of L^1 , L^2 , 1 and 2 were solved. The structures of 1 and 2 are isomorphous. The molecular structure of L^1 is shown in Fig. 1 and its selected bond lengths and angles are given in Table 2. The C–Se bond lengths of 1.916(4) and 1.953(4) Å are consistent with the earlier reports (1.939 Å) [20]. The Se–C(Ar) bond distance is somewhat shorter than the Se–C(alkyl) distance, as

Table 1 Crystal data and structural refinements for L^1 , L^2 , 1 and 2

| Compound | \mathbf{L}^1 | \mathbf{L}^2 | 1 | 2 |
|---|--------------------------------------|--------------------------------------|-----------------------------------|---|
| Empirical formula | C ₁₆ H ₁₇ NOSe | C ₁₇ H ₁₉ NOSe | C17H17Cl4NOPdSe | C ₁₇ H ₁₇ Cl ₄ NOPt Se |
| Formula weight | 318.27 | 332.29 | 578.50 | 667.16 |
| Crystal size (mm) | $0.363 \times 0.217 \times 0.156$ | $0.480 \times 0.190 \times 0.160$ | $0.463 \times 0.215 \times 0.167$ | $0.363 \times 0.217 \times 0.156$ |
| Crystal system | monoclinic | monoclinic | monoclinic | monoclinic |
| Space group | P2(1)/n | P2(1)/c | P2(1)/c | P2(1)/c |
| Unit cell dimensions | | | | |
| a (Å) | 6.8629(16) | 16.474(3) | 14.854(2) | 14.814(3) |
| b (Å) | 29.966(7) | 6.7098(11) | 17.861(3) | 17.863(3) |
| <i>c</i> (Å) | 7.3948(18) | 14.689(2) | 15.917(2) | 15.998(3) |
| β (°) | 107.114(0) | 108.084(2) | 102.150(3) | 101.672(4) |
| Volume (Å ³) | 1453.4(60) | 1543.5(40) | 4128.3(10) | 4145.9(13) |
| Z | 4 | 4 | 8 | 8 |
| $D_{\rm calc}$ (Mg m ⁻³) | 1.454 | 1.430 | 1.862 | 2.138 |
| Absorption coefficient (mm ⁻¹) | 2.575 | 2.428 | 3.186 | 9.046 |
| F(000) | 648 | 680 | 2256 | 2512 |
| θ Range (°) | 1.36-25.50 | 1.30-25.00 | 1.40-25.50 | 1.40-25.50 |
| Index ranges | $-8 \leqslant h \leqslant 8$, | $-19 \leq h \leq 19$, | $-17 \leq h \leq 17$, | $-17 \leq h \leq 17$, |
| e | $-36 \leq k \leq 36$, | $-7 \leqslant k \leqslant 7$, | $-21 \leq k \leq 21,$ | $-21 \leq k \leq 21,$ |
| | $-8 \leqslant l \leqslant 8$ | $-17 \leq l \leq 17$ | $-19 \leqslant l \leqslant 19$ | $-19 \leqslant l \leqslant 19$ |
| Reflections collected | 14406 | 13862 | 40756 | 40899 |
| Independent reflections (R_{int}) | 2701(0.1000) | 2706 (0.367) | 7669(0.0765) | 7698(0.0946) |
| Maximum/minimum transmission | 0.671/0.515 | 0.678/0.529 | 0.580/0.442 | 0.246/0.104 |
| Data/restraints/parameters | 2701/1/174 | 2706/0/186 | 7668/0/457 | 7690/0/453 |
| Final R indices $[I > 2\sigma(I)]$ | $R_1 = 0.0490,$ | $R_1 = 0.0412,$ | $R_1 = 0.0712,$ | $R_1 = 0.0801,$ |
| | $wR_2 = 0.1259$ | $wR_2 = 0.1183$ | $wR_2 = 0.1357$ | $wR_2 = 0.1407$ |
| R indices (all data) | $R_1 = 0.0626,$ | $R_1 = 0.0490,$ | $R_1 = 0.0960,$ | $R_1 = 0.1028,$ |
| . / | $wR_2 = 0.1411$ | $wR_2 = 0.1260$ | $wR_2 = 0.1490$ | $wR_2 = 0.1521$ |
| Largest difference peak/hole $(e \text{ \AA}^{-3})$ | 0.761/-0.458 | 0.749/-0.687 | 0.824/-0.606 | 1.235/-2.728 |



Fig. 1. ORTEP diagram of L^1 with 50% probability ellipsoids.

| Table 2 | | | | | | | | |
|----------|------|---------|-----|-----|--------|-----|------|----|
| Selected | bond | lengths | (Å) | and | angles | (°) | of L | ,1 |

| Bond length | | Bond angle | Bond angle | | |
|-------------------------------|----------|--------------------|------------|--|--|
| Se(1)–C(11) | 1.916(4) | C(11)-Se(1)-C(10) | 99.1(2) | | |
| Se(1) - C(10) | 1.953(4) | C(7) - N(1) - C(9) | 121.3(3) | | |
| N(1)–C(7) | 1.284(4) | N(1)-C(7)-C(8) | 122.4(3) | | |
| N(1)–C(9) | 1.455(4) | N(1)-C(9)-C(10) | 109.5(3) | | |
| C(9)–C(10) | 1.518(5) | N(1)-C(7)-C(1) | 117.6(3) | | |
| O(1)–C(6) | 1.343(4) | C(12)-C(11)-Se(1) | 120.9(3) | | |
| $H(1) \cdot \cdot \cdot N(1)$ | 1.786(3) | C(16)-C(11)-Se(1) | 120.2(3) | | |

expected. Similarly the C–Se–C bond angle of 99.1(2)° was found as expected. Intramolecular hydrogen bonding, O– $H \cdots N$, exists in the structure of L^1 . A perspective view of the structure of L^2 is shown in Fig. 2. It also has intramolecular hydrogen bonding, O– $H \cdots N$. The Se–C bond



Fig. 2. ORTEP diagram of L^2 with 50% probability ellipsoids.

distances, 1.914(3) and 1.956(3) Å and the C–Se–C bond angle are consistent with those of L^1 and earlier reports [20]. In this case it is also found that the Se–C(Ar) bond distance is shorter than the Se–C(alkyl) bond distance (see Table 3).

The molecular structure of 1 is shown in Fig. 3 and its selected bond distances and angles are given in Table 4. In the asymmetric unit there are two chemically similar but crystallographically independent molecules and two molecules of chloroform solvent. The 1 is the first example of a crystal structure of a Pd complex of a (Se, N, O⁻) ligand. The geometry around Pd is square planar. The Pd–Se

Table 3 Selected bond lengths (Å) and angles (°) of L^2

| Bond length | | Bond angle | Bond angle | | |
|-------------------------------|----------|-------------------|------------|--|--|
| Se(1)–C(12) | 1.914(3) | C(12)-Se(1)-C(11) | 99.5(1) | | |
| Se(1) - C(11) | 1.956(3) | C(7)-N(1)-C(9) | 122.0(2) | | |
| N(1)–C(7) | 1.284(4) | N(1)-C(7)-C(6) | 117.6(2) | | |
| N(1)–C(9) | 1.458(4) | N(1)-C(7)-C(8) | 123.0(3) | | |
| C(9)–C(10) | 1.513(4) | N(1)-C(9)-C(10) | 110.7(2) | | |
| O(1)–C(1) | 1.330(3) | C(17)-C(12)-Se(1) | 119.1(3) | | |
| $H(1) \cdot \cdot \cdot N(1)$ | 1.53(6) | C(13)-C(12)-Se(1) | 121.8(3) | | |



Fig. 3. ORTEP diagram of 1 with 50% probability ellipsoids.

Table 4 Selected bond lengths (Å) and angles (°) of 1 and 2

| $\begin{array}{llllllllllllllllllllllllllllllllllll$ | (1) | | (2) | |
|---|-------------------|------------|----------------------|------------|
| $\begin{array}{llllllllllllllllllllllllllllllllllll$ | Bond lengths (Å) | | | |
| $\begin{array}{llllllllllllllllllllllllllllllllllll$ | Pd(1)-Se(1) | 2.3669(11) | Pt(1)-Se(1) | 2.3543(16) |
| $\begin{array}{llllllllllllllllllllllllllllllllllll$ | Pd(1)-Cl(1) | 2.305(2) | Pt(1)-Cl(1) | 2.306(4) |
| $\begin{array}{llllllllllllllllllllllllllllllllllll$ | Pd(1) - N(1) | 2.003(7) | Pt(1) - N(1) | 1.988(12) |
| $\begin{array}{llllllllllllllllllllllllllllllllllll$ | Pd(1)–O(1) | 1.977(6) | Pt(1)–O(1) | 1.976(10) |
| $\begin{array}{llllllllllllllllllllllllllllllllllll$ | Se(1)-C(1) | 1.929(8) | O(1)–C(6) | 1.314(15) |
| $\begin{array}{llllllllllllllllllllllllllllllllllll$ | Se(1)-C(7) | 1.947(9) | N(1)-C(7) | 1.316(18) |
| $\begin{array}{llllllllllllllllllllllllllllllllllll$ | N(1)-C(8) | 1.493(10) | N(1)-C(9) | 1.512(18) |
| $\begin{array}{llllllllllllllllllllllllllllllllllll$ | N(1)-C(9) | 1.309(11) | Se(1)-C(10) | 1.95 (2) |
| $\begin{array}{llllllllllllllllllllllllllllllllllll$ | O(1)-C(11) | 1.312(10) | Se(1)-C(11) | 1.938(14) |
| $\begin{array}{llllllllllllllllllllllllllllllllllll$ | Bond angles (°) | | | |
| $\begin{array}{llllllllllllllllllllllllllllllllllll$ | O(1)-Pd(1)-N(1) | 93.0(3) | O(1) - Pt(1) - N(1) | 93.1(5) |
| $\begin{array}{llllllllllllllllllllllllllllllllllll$ | O(1)–Pd(1)–Cl(1) | 88.3(2) | O(1) - Pt(1) - Cl(1) | 86.7(3) |
| $\begin{array}{llllllllllllllllllllllllllllllllllll$ | N(1)-Pd(1)-Cl(1) | 173.4(2) | N(1)-Pt(1)-Cl(1) | 174.5(3) |
| $\begin{array}{llllllllllllllllllllllllllllllllllll$ | O(1)-Pd(1)-Se(1) | 176.0(2) | O(1) - Pt(1) - Se(1) | 175.4(3) |
| $\begin{array}{llllllllllllllllllllllllllllllllllll$ | N(1)-Pd(1)-Se(1) | 90.5(2) | N(1)-Pt(1)-Se(1) | 90.9(4) |
| $\begin{array}{llllllllllllllllllllllllllllllllllll$ | Cl(1)-Pd(1)-Se(1) | 88.40(7) | Cl(1)-Pt(1)-Se(1) | 89.6(1) |
| $\begin{array}{llllllllllllllllllllllllllllllllllll$ | C(1)-Se(1)-C(7) | 98.8(4) | C(11)-Se(1)-C(10) | 98.8(7) |
| $\begin{array}{llllllllllllllllllllllllllllllllllll$ | C(1)-Se(1)-Pd(1) | 104.3(2) | C(11)-Se(1)-Pt(1) | 107.0(5) |
| $\begin{array}{llllllllllllllllllllllllllllllllllll$ | C(7)-Se(1)-Pd(1) | 91.5(3) | C(10)-Se(1)-Pt(1) | 91.7(5) |
| $\begin{array}{llllllllllllllllllllllllllllllllllll$ | C(9)–N(1)–Pd(1) | 125.3(6) | C(7)-N(1)-Pt(1) | 127.2(5) |
| $\begin{array}{llllllllllllllllllllllllllllllllllll$ | C(8)-N(1)-Pd(1) | 114.4(6) | C(9)-N(1)-Pt(1) | 114.7(5) |
| $\begin{array}{llllllllllllllllllllllllllllllllllll$ | C(9)-N(1)-C(8) | 119.3(7) | C(7)-N(1)-C(9) | 117.7(1) |
| $\begin{array}{cccc} O(1)-C(11)-C(12) & 125.8(8) & O(1)-C(6)-C(5) & 115.7(1) \\ O(1)-C(11)-C(16) & 115.9(8) & O(1)-C(6)-C(1) & 126.5(1) \\ \end{array}$ | C(11)-O(1)-Pd(1) | 123.8(5) | C(6)-O(1)-Pt(1) | 123.2(9) |
| O(1)-C(11)-C(16) 115.9(8) O(1)-C(6)-C(1) 126.5(1) | O(1)-C(11)-C(12) | 125.8(8) | O(1)-C(6)-C(5) | 115.7(1) |
| | O(1)-C(11)-C(16) | 115.9(8) | O(1)-C(6)-C(1) | 126.5(1) |

bond length, 2.3669(11) Å, is shorter than those reported for $[Pd(PEt_3)_2(SePh)(PO(OPh)_2)]$ (2.518(9) Å) [21] and $[Pd(Me_2PCH_2CH_2PMe_2)(Me)(SeC_6H_4-4-Cl)]$ (2.4483(8)

Å) [22]. The shorter Pd–Se bond in 1 may be attributed to the tridentate nature of ligand L^1 , which makes two chelate rings and forces Se to bind with Pd(II) somewhat strongly in comparison to those complexes in which the selenium ligand is a monodentate one. The Pd-N. Pd-O and Pd-Cl bond distances, 2.003(7), 1.977(6) and 2.305(2) Å, respectively, are consistent with earlier reports [Pd-N = 2.01(1) Å, Pd-O = 2.03(1) Å and Pd-Cl = 2.290(4) Å] on a Pd(II) complex of a tridentate ligand of the (Te, N, O⁻) type [14]. In Fig. 4 the molecular structure of 2 is shown. In Table 4 selected bond lengths and angles are given. In the unit cell of the crystal of 2 also there are two almost similar molecules. One molecule of chloroform per molecule of 2 is also present in the lattice. The structure of 2 is also the first example of a crystal structure of a Pt-complex of a (Se, N, O⁻) ligand. The geometry around Pt is nearly square planar. The Pt-Se bond length, 2.3543(16) Å, is consistent with the earlier reported value in the case of [CH₃SeCH₂CH₂CH₂CH(COO-Me)NH₂ · PtCl₂] (2.3697(8) Å) [23], but is shorter than those reported for $cis-[Pt(SePh)_2(PPh_3)_2]$ (2.4970(9), 2.4604(10) Å) [24] and *trans*-[Pt(SePh)₂(2,9-dimethyl-1, 10-phenanthroline)(MeOOCCH=CHCOOMe)] (2.5197, 2.5142 Å) [25]. The shorter Pt-Se bond in 2 may again be attributed to the tridentate nature of the ligand L^1 , as in the case of the Pd(II) complex mentioned above. The absence of the *trans* influence may also contribute, particularly in comparison with *trans*-[Pt(SePh)₂(2,9-dimethyl-1,10-phenanthroline)(MeOOCCH=CHCOOMe)]. The Pt-N and Pt-Cl bond distances, 1.988(12) and 2.306(4) Å, respectively, are consistent with the earlier reports [23], 2.043(5) and 2.294(2), 2.322(2) Å, respectively. The Pt-O bond length of 1.976(10) Å is comparable with earlier reports (2.034 Å) [26]. On comparing Pd/Pt-N, Pd/Pt-O, Pd/Pt-Cl and Pd/Pt-Se bond lengths with the sum of their covalent radii 2.03/2.05, 2.01/2.03. 2.27/2.29 and 2.44/2.46 Å. respectively, it appears that the observed bond distances are shorter than this sum, except in the case of Pd/Pt-Cl where the observed values are marginally higher. This indicates that coordination of \mathbf{L}^1 is quite strong with Pd as well as with Pt.



Fig. 4. ORTEP diagram of 2 with 50% probability ellipsoids.



Fig. 5. Kinetic profile of the Heck reaction.

3.3. Application as a homogeneous catalyst for the Heck reaction

1 was found to be suitable to catalyze the Heck coupling reaction, as shown below with ${\sim}80\%$ yield.



Using 1, the time for completion of the reaction is only 14 h, less than that of a recently reported palladium(II) complex of a bidenate Se-ligand (20–90 h at a similar reaction temperature) [17]. The kinetic profile of the above reaction followed by proton NMR is shown in Fig. 5. The temperature cannot be much increased beyond 140 °C as the yield decreases. However at a lower temperature, around 100 °C, the yield goes down to 40–45%. The reaction was carried out in the presence of Na₂CO₃ at 140 °C and the yield was found to be only 20–25%. The trialkylamines (alkyl group = Me, Et, *n*-Bu or *t*-Bu) give the maximum yield.

4. Conclusion

Selenated Schiff bases 2-OH-C₆H₄C(CH₃)=N(CH₂)_n SePh (n = 2, L¹; n = 3, L²) have been designed as such species are scantly known and explored for complexation with Pd(II)/Pt(II). Proton, carbon-13 and selenium-77 NMR spectra of the complexes support the coordination of L¹ and L² through Se. In the case of **2**, satellites due to coupling with ¹⁹⁵Pt were observed (¹J (¹⁹⁵Pt–Se) = 2043 Hz). **1** and **2** are the first examples of crystal structures of Pd and Pt complexes of a (Se, N, O⁻) ligand. Its explored for the homogeneous catalysis of the Heck reaction between methyl acrylate and *p*-iodonitrobenzene. The yield is ~80% and the reaction time is only 14 h.

Acknowledgements

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

Appendix A. Supplementary material

CCDC 651260, 651261, 651259 and 655400 contain the supplementary crystallographic data for L^1 , L^2 , 1 and 2. These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, fax: (+44) 1223-336-033, or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.09.027.

References

- [1] P.A. Vigato, S. Tamburini, Coord. Chem. Rev. 248 (2004) 1717.
- [2] R. Drozdzak, B. Allaert, N. Ledoux, I. Dragutan, V. Dragutan, F. Verpoort, Coord. Chem. Rev. 249 (2005) 3055.

- [3] C.-M. Che, J.-S. Huang, Coord. Chem. Rev. 242 (2003) 97.
- [4] E. Tsuchida, K. Oyaizu, Coord. Chem. Rev. 237 (2003) 213.
- [5] R. Ziessel, Coord. Chem. Rev. 216–217 (2001) 195.
- [6] E.M. McGarrigle, D.G. Gilheany, Chem. Rev. 105 (2005) 1563.
- [7] D. Wang, M. Wang, X. Wang, Y. Chen, A. Gao, L. Sun, J. Catal. 237 (2006) 248.
- [8] R. Ferreira, H. Garcia, B. de Castro, C. Freire, Eur. J. Inorg. Chem. (2005) 4272.
- [9] A. Martinez, C. Hemmert, C. Loup, G. Barre, B. Meunier, J. Org. Chem. 71 (2006) 1449.
- [10] H. Zhang, S. Xiang, C. Li, Chem. Commun. (2005) 1209.
- [11] C.P. Chow, K.J. Shea, J. Am. Chem. Soc. 127 (2005) 3678.
- [12] M.S. Taylor, D.N. Zalatan, A.M. Lerchner, E.N. Jacobsen, J. Am. Chem. Soc. 127 (2005) 1313.
- [13] D.J. Darensbourg, P. Ganguly, D. Billodeaux, Macromolecules 39 (2006) 2722.
- [14] R. Kumar P., A.K. Singh, P. Sharma, J.E. Drake, M.B. Hursthouse, M.E. Light, Inorg. Chem. Commun. 7 (2004) 502.
- [15] R. Kumar P., A.K. Singh, R.J. Butcher, P. Sharma, R.A. Toscano, Eur. J. Inorg. Chem. (2004) 1107.

- [16] J. Kjellgren, J. Audin, O.A. Wallner, I.V. Saltaova, K.J. Szabo, Chem. Eur. J. 11 (2005) 5260.
- [17] Q. Yao, E.P. Kinney, C. Zheng, Org. Lett. 6 (2004) 2997.
- [18] (a) G.M. Sheldrick, Acta Crystallogr., Sect. A 46 (1990) 467;
 (b) G.M. Sheldrick, SHELXL-NT Version 6.12, University of Gottingen, Germany, 2000.
- [19] A. Khanna, A. Bala, B.L. Khandelwal, J. Organomet. Chem. 494 (1995) 199.
- [20] B. Umezawa, O. Hoshino, S. Sawaki, H. Sashida, K. Mori, Y. Hamada, K. Kotera, Y. Iitaka, Tetrahedron 40 (1984) 1783.
- [21] L.-B. Han, N. Choi, M. Tanaka, J. Am. Chem. Soc. 118 (1996) 7000.
- [22] A.J. Canty, M.C. Denney, J. Patel, H. Sun, B.W. Skelton, A.H. White, J. Organomet. Chem. 689 (2004) 672.
- [23] M. Carland, B.F. Abrahams, T. Rede, J. Stephenson, V. Murray, W.A. Denny, W.D. McFadyen, Inorg. Chim. Acta 359 (2006) 3252.
- [24] V.P. Ananikov, I.P. Beletskaya, G.G. Aleksandrov, I.L. Eremenko, Organometallics 22 (2003) 1414.
- [25] V.G. Albano, M. Monari, I. Orabona, A. Panunzi, F. Ruffo, J. Am. Chem. Soc. 123 (2001) 4352.
- [26] K. Sakai, S. Takahashi, Acta Crystrallogr., Sect. E 59 (2003) m532.