Cyclohexanone selenosemicarbazone: A convenient starting material for the preparation of functionalised selenosemicarbazones and their Pt and Pd complexes

Patrick Bippus, Anja Molter, David Müller, Fabian Mohr*

Fachbereich C – Anorganische Chemie, Bergische Universität Wuppertal, 42119 Wuppertal, Germany

A B S T R A C T

The reaction of hydrazine hydrate with KSeCN in acidic aqueous ethanol in the presence of cyclohexanone affords cyclohexanone selenosemicarbazone in good yields. Cyclohexanone selenosemicarbazone was converted into various functionalised selenosemicarbazones by treatment with aldehydes. Salicylaldehyde selenosemicarbazone and its 1,2-naphthyl-derivative were prepared and reacted with some Pd (II) and Pt(II) phosphine complexes to give compounds of the type $[M(L^{Se})(P)]$ where M = Pt and Pd, L^{Se} is the doubly deprotonated selenosemicarbazone and P a monodentate phosphine. In these complexes the ligands act as tridentate, dianionic $[Se-N-O]^{2-}$ ligands, which was confirmed by single-crystal X-ray diffraction of the Pd derivative.

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1. Introduction

Selenosemicarbazide, $H_2NC(Se)NHNH_2$, has been used as convenient commercially available starting material for the synthesis of a variety of N-functionalised selenosemicarbazones. These have been shown to act as monoanionic $[Se-N-N]^-$ ligands in metal complexes containing Pt, Pd, Zn and Cd (Chart 1) [1–3]. However, selenosemicarbazide has recently been discontinued by chemical suppliers (in Europe at least) and is no longer available commercially, thus the need arose to find an alternative material that could easily be prepared and conveniently handled and stored. In the literature from the 1950s there are various descriptions for the preparation of acetone selenosemicarbazone and cyclohexanone selenosemicarbazone as well as their conversion into other substituted selenosemicarbazones [4,5]. Given the higher yield and better storage stability of the cyclohexanone derivative, we optimised the synthetic procedure from the patent literature [6] and spectroscopically and structurally characterised the product for the first time. We have recently begun a systematic investigation of the coordination chemistry of organoselenium compounds containing the −NHC (Se)− unit with gold [7–9] and other transition- and main-

group-metals [10]. We now wished to extend this chemistry to include tridentate, dianionic $[Se-N-O]^{2-}$ ligands, derived from the reaction of cyclohexanone selenosemicarbazone with hydroxyl-functionalised aldehydes. Such ligands should be able to form complexes with square planar transition metals in the oxidation state +2 such as Pd and Pt (Chart 1). Indeed, the Ni(II)-phosphine complex containing the dianion derived from salicylaldehyde selenosemicarbazone (Chart 1) was reported and structurally characterised in 1974 [11]. Since then however, no one appears to have worked with this ligand system.

2. Results and discussion

The reaction of hydrazine hydrate with KSeCN in aqueous ethanol under acidic conditions in the presence of cyclohexanone affords cyclohexanone selenosemicarbazone in yields greater than 60%. The material can be stored without apparent decomposition at room temperature in amber glass bottles for several months. During the preparation significant amounts of black selenium metal are formed which can be recovered and reused in the synthesis of KSeCN, thus making the overall reaction quite atom efficient with respect to selenium metal. Cyclohexanone selenosemicarbazone was characterised by NMR spectroscopy and also by single-crystal X-ray diffraction. The proton NMR spectrum shows the expected multiplets for the cyclohexane ring as well as two broad signals for

* Corresponding author.
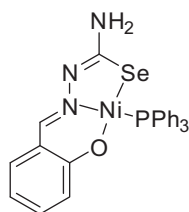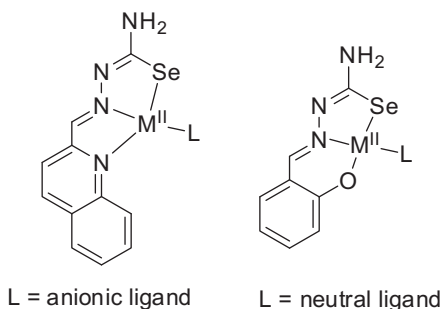 *E-mail address:* fmohr@uni-wuppertal.de (F. Mohr).

L = anionic ligand   L = neutral ligand

Chart 1.

the NH$_2$ group and a singulet at 10.41 ppm due to the NH proton. In the ^{13}C NMR spectrum the carbon atom of the C=Se group is observed at *ca.* 174 ppm with ^{77}Se satellites ($^1J_{Se-C} = 209$ Hz). The signals due to the other carbon atoms in the molecule appear at their expected chemical shifts. Slow evaporation of an ethanolic solution gave large, colourless crystals which were subjected to an X-ray diffraction study. The molecular structure of cyclohexanone selenosemicarbazone (**1**) is shown in Fig. 1, important bond distances and angles are collected in the figure caption.

The molecule consists of a planar H$_2$NC(Se)NHN=C unit to which the cyclohexane ring is attached in chair conformation. In the crystal two molecules of **1** form a dimer through a pair of Se–H bonds of *ca.* 2.7 Å as shown in Fig. 2. In addition, there is an intramolecular N–H bond between the C=N and NH$_2$ units. Furthermore, the second H atom of the NH$_2$ group forms a slightly longer (*ca.* 2.9 Å) Se–H bond to an adjacent dimeric unit with an angle of *ca.* 45°. Overall, an infinite network of dimeric units (Fig. 3) is formed *via* Se–H bonds.
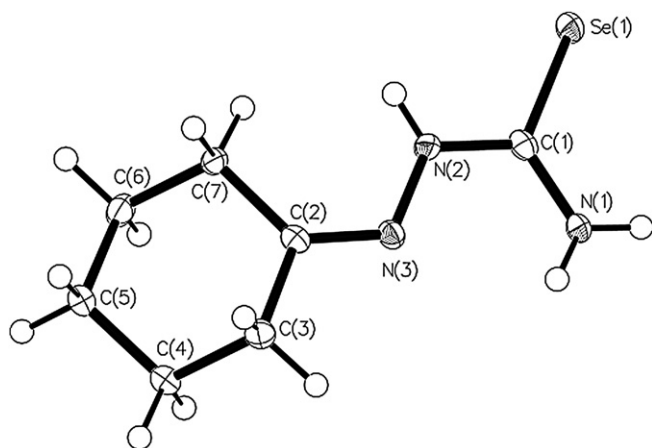

Fig. 1. Molecular structure of **1**. Ellipsoids show 50% probability levels. Hydrogen atoms are shown as spheres with arbitrary radii. Selected bond distances [Å]: C(1)-Se(1) 1.8565(19), C(1)-N(1) 1.315(3), C(1)-N(2) 1.336(2), N(2)-N(3) 1.386(2), N(3)-C(2) 1.285(2). Selected angles [°]: N(2)-C(1)-Se(1) 118.72(15), N(1)-C(1)-Se(1) 123.54(16), N(1)-C(1)-N(2) 117.70(18), C(1)-N(2)-N(3) 119.22(17), N(2)-N(3)-C(2) 117.89(16).

Cyclohexanone selenosemicarbazone reacts with various functionalised aldehydes in water or water–ethanol mixtures in the presence of acetic acid to give good yields of the mono- and bis-selenosemicarbazones **2-5** as shown in Scheme 1.

The four compounds were fully characterised by spectroscopic techniques, the data (see Experimental) being fully consistent with the proposed structures. The ^{77}Se-NMR chemical shifts of compounds **2-4** are all around 200 ppm, typical for compounds containing the C=Se unit. The hydroxyl-functionalised selenosemicarbazones H$_2$L1^{Se} (**2**) and H$_2$L2^{Se} (**3**) react with the palladium(II) and platinum(II) phosphine complexes *cis* or *trans*-[MCl$_2$(P)$_2$] where M = Pt, Pd and P = Ph$_3$P or PTA (PTA = 1,3,5-triaza-7-phosphaadamantane) in the presence of a base to afford the yellow or orange complexes [M(L^{Se})(P)] **6-9** as air-stable solids in good yields as shown in Scheme 2.

Although the compounds are air-stable in the solid state, in solution precipitation of a dark solid occurs after *ca.* 24 h. Nevertheless, complexes **6-9** were fully characterised by spectroscopic methods and, in the case of **6**, by X-ray crystallography. The ^{31}P{^{1}H} NMR spectra of complexes **6-9** show singulet resonances at chemical shifts typical for the coordinated phosphines. In addition, the Pt-derivative **7** displays Pt-satellites with $^1J_{Pt-P} = 3562$ Hz. Unfortunately, for the structurally related sulfur complex [Pt(L2^S)(PPh$_3$)] no ^{31}P NMR spectroscopic data has been reported for comparison [12]. Due to the instability and also poor solubility of the complexes, we were unable to measure ^{77}Se NMR spectra of any of the metal complexes. The deprotonation of both the hydroxyl and the NH functionalities of the selenosemicarbazone is apparent from the disappearance of the NH and OH proton signals in the ^{1}H NMR spectra of compounds **6-9**. This data supports the proposed structure, in which the selenosemicarbazone acts as a dianionic [Se–N–O]$^{2-}$ ligand towards the metal. This was indeed confirmed by an X-ray diffraction experiment of complex **6**, the molecular structure of which is shown in Fig. 4.

The dianionic selenosemicarbazone binds to the metal through Se, the imine N and O; the Ph$_3$P ligand, located *trans* to the imine nitrogen atom, completes the square planar coordination geometry about the Pd atom. Thus, the planar, tridentate Se, N, O-ligand forms one five- and one six-membered ring incorporating the palladium atom. The overall geometry is similar to that of the related sulfur complex [Pd(L2^S)(PPh$_3$)] [13], except that some bond distances and angles are different, as expected when sulfur is exchanged for the larger selenium. The Pd–P, Pd–N and Pd–O bond distances in complex **6** are very similar to those in [Pd(L2^S)(PPh$_3$)], whilst the Pd–Se distance of 2.3414(3) Å is similar to that observed in the selenourea Pd-complexes [Pd{κ^{2}C,N-4-MeC$_6$H$_3$N(Me)NO}{κ^{2}Se,O-C$_6$H$_5$C(O)NC(Se)NMePh}] and [Pd{κ^{2}Se,O-C$_6$H$_5$C(O)NC(Se)N^{n}Bu$_2$}$_2$] in which the Pd–Se distances are 2.3470(4) and 2.3411(3) Å, respectively [14,15]. In contrast to the sulfur analogue [Pd(L2^S)(PPh$_3$)], which forms a dimeric unit *via* a pair of intermolecular H-bonds between N(3)H$_2$ and N(2) of the adjacent molecule [13], there are no H-bonding interactions in complex **6**. There are however aromatic π-stacking interactions between the naphthyl ring and one of the phenyl rings of the Ph$_3$P ligand in the range of *ca.* 3.2–3.8 Å.

We also attempted to prepare Pd complexes using HL3^{Se} (**4**) and H$_2$L4^{Se} (**5**). However, in the case of HL3^{Se}, we obtained complex product mixtures which we were unable to separate. Ligand H$_2$L4^{Se} gave dark, insoluble materials which we could not characterise. We are currently investigating reactivity of these two ligands in more detail.

In summary, we have shown here that cyclohexanone selenosemicarbazone is readily accessible from simple precursors and can be further functionalised by the reaction with various aldehydes including salicylaldehyde. Doubly deprotonated salicylaldehyde selenosemicarbazone forms metals complexes with Pt and Pd
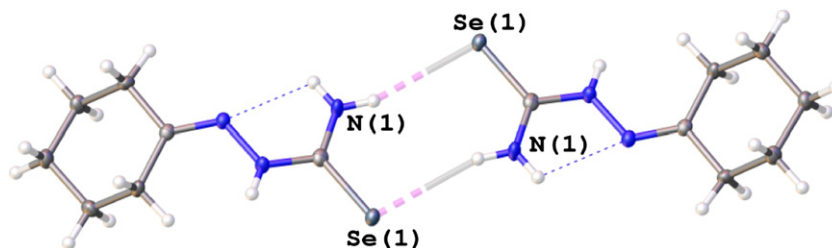
Fig. 2. Packing diagram of compound **1** showing the formation of dimeric units through Se-H bonds as well as intramolecular N-H bonds.

phosphine complexes, which were spectroscopically and structurally characterised.

3. Experimental

3.1. General

^{1}H, ^{13}C, ^{77}Se and ^{31}P{^{1}H} NMR spectra were recorded on a 400 MHz Bruker Avance or 600 MHz Bruker Avance II spectrometer. Chemical shifts are quoted relative to external SiMe$_4$ (^{1}H, ^{13}C), Me$_2$Se (^{77}Se) and 85% H$_3$PO$_4$ (^{31}P). Elemental analyses were performed by staff of the microanalytical laboratory of the University of Wuppertal. All reactions were carried out under aerobic conditions unless stated otherwise. KSeCN as well as the Pt and Pd phosphine complexes [MCl$_2$(P)$_2$] [M = Pt, Pd; P = PPh$_3$, PTA] were prepared as described in the literature [16–18]. All other chemicals and solvents (HPLC grade) were sourced commercially and used as received.

3.2. Cyclohexanone selenosemicarbazone (1)

To a mixture of EtOH (200 mL) and water (25 ml) was added hydrazine hydrate (7.5 mL), concentrated HCl (10 mL) and a solution of KSeCN (7.2 g, 0.05 mol) in water (25 mL). Subsequently, cyclohexanone (16 mL) was added and the mixture was heated to reflux for 2 h. After this time the solution was filtered while hot to remove some gray selenium. The filtrate was concentrated in vacuum to *ca.* 20 mL to give a pale yellow oil which solidified on cooling. The solid was isolated by filtration, was washed with water and left to dry in air. The dry solid was then dissolved in CHCl$_3$ filtered through celite and the filtrate was evaporated to dryness to afford 7.6 g (71 %) of the product as a colourless solid. ^{1}H NMR

(400 MHz, CDCl$_3$, 25°C): δ = 10.41 (s, 1 H, NH), 8.34 (br. s, 1 H, NH$_2$), 7.95 (br. s, 1 H, NH$_2$), 2.39 (m, 2 H, Cy ring), 2.20 (t, J = 5.8 Hz, 2 H, Cy ring), 1.58-1.65 (m, 2 H, Cy ring), 1.50−1.57 (m, 4 H, Cy ring). ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ = 173.77 ($^{1}J_{C-Se}$ = 209 Hz, C=Se), 159.23 (C=N), 34.84, 27.54, 26.82, 25.70, 24.94 (Cy ring). ^{77}Se NMR (76 MHz, CDCl$_3$, 25 °C): δ = 172. Anal. calc. for C$_7$H$_{13}$N$_3$Se (218.16): C, 38.54; H, 6.01; N, 19.26. Found: C, 38.34; H, 5.99; N, 19.54 %. X-ray quality crystals were obtained by slow evaporation of an ethanolic solution of the compound.

3.3. H$_2$L1^{Se} (2)

A mixture of cyclohexanone selenosemicarbazone (0.474 g, 2.17 mmol) and 2-hydroxynaphthaldehyde (0.375 g, 2.18 mmol) in EtOH (20 mL) containing 1 mL glacial acetic acid was refluxed for *ca.* 1 h. The resulting yellow solid was isolated by filtration and was dried in air to give 0.366 g (58%) of the product. ^{1}H NMR (400 MHz, dmso-d_6, 25 °C): δ = 11.65 (br. s, 1 H, NH), 10.50 (br. s, 1 H, OH), 9.15 (s, 1 H, HC=N), 8.64 (br. s, 1 H, NH$_2$), 8.52 (d, J = 8.7 Hz, 1 H, H8), 8.33 (br. s, 1 H, NH$_2$), 7.89 (d, J = 8.9 Hz, 1 H, H4), 7.85 (d, J = 8.3 Hz, 1 H, H5), 7.56 (dt, J = 8.3, 1.3 Hz, 1 H, H7), 7.37 (dt, J = 7.8, 0.9 Hz, 1 H, H6), 7.19 (d, J = 9.2 Hz, 1 H, H3). ^{13}C NMR (100 MHz, dmso-d_6, 25 °C): δ = 172.60 (C=Se), 156.93 (C2), 144.66 (C=N), 132.95 (C4), 131.59 (C9), 128.76 (C5), 128.16 (C10), 128.08 (C7), 123.61(C6), 123.05 (C8), 118.41 (C3), 109.68 (C1). ^{77}Se NMR (76 MHz, dmso-d_6, 25 °C): δ = 202. Anal. calc. for C$_{12}$H$_{11}$N$_3$OSe (292.20): C, 49.33; H, 3.79; N, 14.38. Found: C, 49.34; H, 3.73; N, 14.45 %.

3.4. H$_2$L2^{Se} (3)

This was prepared as described above using cyclohexanone selenosemicarbazone (0.362 g, 1.66 mmol) and salicylaldehyde
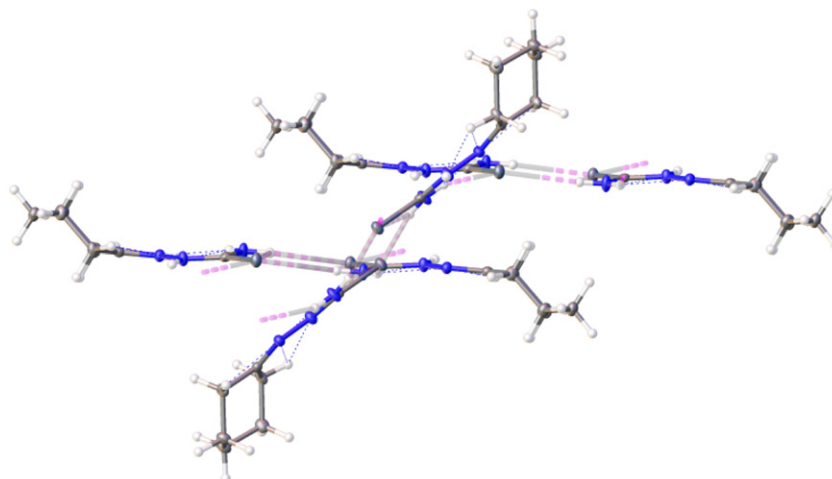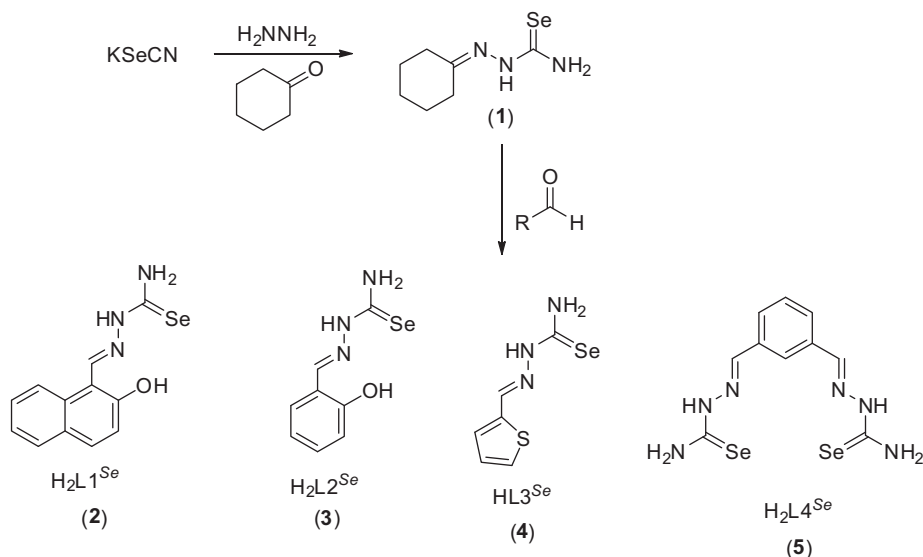

Fig. 3. . Packing diagram of compound **1** showing the network structure formed through Se−H bonds between dimeric units.

Scheme 1.

(0.175 mL, 1.66 mmol). 0.313 g (89%) of a yellow solid was obtained. ^{1}H NMR (400 MHz, dmso-d_6, 25 °C): δ = 11.63 (s, 1 H, NH), 9.87 (br. s, 1 H, OH), 8.51 (br. s, 1 H, NH$_2$), 8.48 (s, 1 H, HC=N), 8.39 (br. s, 1 H, NH$_2$), 7.92 (dd, J = 7.5, 1.4 Hz, 1 H, H6), 7.22 (dt, J = 7.4, 1.8 Hz, 1 H, H4), 6.86 (d, J = 8.2 Hz, 1 H, H3), 6.81 (t, J = 7.5 Hz, 1 H, H5). ^{13}C NMR (100 MHz, dmso-d_6, 25 °C): δ = 173.13 (C=Se), 156.59 (C2), 141.18 (C=N), 131.41 (C4), 126.93 (C6), 120.14 (C1), 119.32 (C5), 116.10 (C3). ^{77}Se NMR (114 MHz, dmso-d_6, 25 °C): δ = 197. Anal. calc. for C$_8$H$_9$N$_3$OSe (242.14): C, 39.68; H, 3.75; N, 17.35. Found: C, 39.76; H, 3.69; N, 17.12 %.

3.5. HL3^{Se} (4)

This was prepared as described above using cyclohexanone selenosemicarbazone (0.355 g, 1.63 mmol) and 2-thio-phenecarboxaldehyde (0.15 mL, 1.63 mmol). 0.269 g (80%) of a pale yellow solid was obtained. ^{1}H NMR (400 MHz, dmso-d_6, 25 °C): δ = 11.68 (s, 1 H, NH), 8.59 (br. s, 1 H, NH$_2$), 8.34 (s, 1 H, HC=N), 8.04 (br. s, 1 H, NH$_2$), 7.68 (dd, J = 5.0, 0.5 Hz, 1 H, H5), 7.49 (dd, J = 3.6, 0.5 Hz, 1 H, H3), 7.12 (dd, J = 5.0, 3.7 Hz, 1 H, H4). ^{13}C NMR (100 MHz, dmso-d_6, 25 °C): δ = 173.19 (C=Se), 138.94 (C=N), 131.08 (C3), 129.29 (C5), 127.99 (C4). ^{77}Se NMR (114 MHz, dmso-d_6, 25 °C): δ = 201. Anal. calc. for C$_6$H$_7$N$_3$SSe (232.16): C, 31.04; H, 3.04; N, 18.10. Found: C, 30.97; H, 3.18; N, 18.28%.

3.6. H$_2$L4^{Se} (5)

This was prepared as described above using cyclohexanone selenosemicarbazone (0.505 g, 2.31 mmol) and *iso*-

phthaloyldicarboxaldehyde (0.164 g, 1.22 mmol). 0.332 g (78%) of a colourless solid was obtained. ^{1}H NMR (400 MHz, dmso-d_6, 25 °C): δ = 11.79 (s, 2 H NH), 8.68 (br. s, 2 H, NH$_2$), 8.56 (br. s, 2 H, NH$_2$), 8.23 (s, 1 H, H2), 8.18 (s, 2 H, HC=N), 7.85 (dd, J = 7.8, 1.5 Hz, 2 H, H4, H6), 7.44 (t, J = 7.7 Hz, 1 H, H5). ^{13}C NMR (100 MHz, dmso-d_6, 25 °C): δ = 173.87 (C=Se), 143.03 (C=N), 134.63 (C1, C3), 129.10 (C4, C5, C6), 126.01 (C2). Anal. calc. for C$_{10}$H$_{12}$N$_6$Se$_2$ (374.16): C, 32.10; H, 3.23; N, 22.46. Found: C, 32.46; H, 3.28; N, 22.66 %.

3.7. Preparation of the metal complexes

To a suspension of the metal precursor (0.100 g) in toluene (10 mL) was added the appropriate functionalised selenosemi-carbazone (1 eq.) and Et$_3$N (1 ml). The mixture was stirred at room temperature for *ca.* 8 h. The orange or yellow solution was passed through a short column of celite and the filtrate was evaporated to dryness. The resulting solids were crystallised from CH$_2$Cl$_2$/hexane or CH$_2$Cl$_2$/Et$_2$O.

3.8. [Pd(L1^{Se})(PPh$_3$)] (6)

This was prepared as described above from *trans*-[PdCl$_2$(PPh$_3$)$_2$] (0.100 g, 0.142 mmol) and H$_2$L1^{Se} (0.042 g, 0.144 mmol). 0.061 g (65%) of an orange solid was obtained. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 9.26 (d, J_{P-H} = 13.3 Hz, 1 H, HC=N), 8.09 (d, J = 8.6 Hz, 1 H, H8), 7.72–7.79 (m, 6 H, o-Ph$_3$P), 7.64 (dd, J = 7.9, 1.2 Hz, 1 H, H5), 7.59 (d, J = 9.1 Hz, 1 H, H4), 7.42–7.54 (m, 10 H, m-Ph$_3$P, p-Ph$_3$P, H7), 7.22 (dt, J = 7.9, 0.9 Hz, 1 H, H6), 6.82 (d, J = 9.0 Hz, 1 H, H3), 4.76 (br. s, 2 H, NH$_2$). ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ = 163.21 (C2),
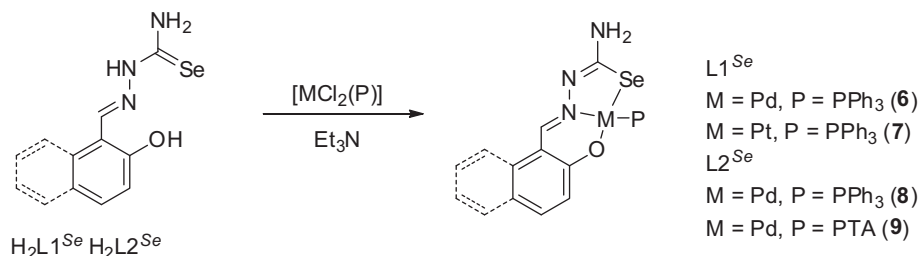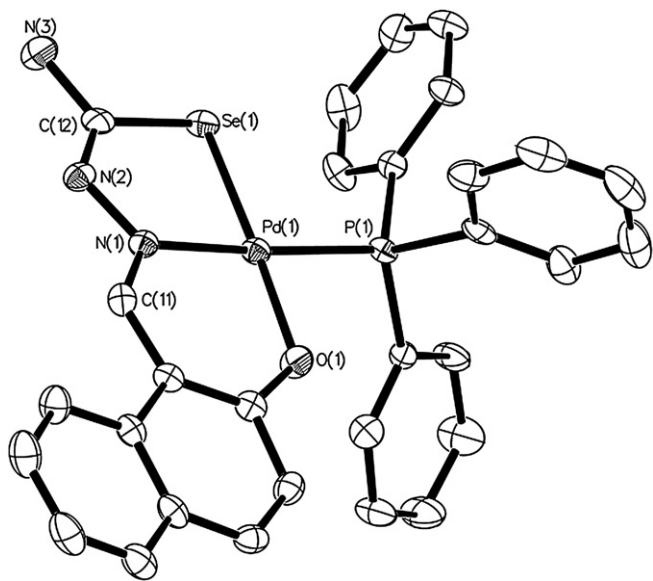

Scheme 2.

Fig. 4. Molecular structure of complex **6**. Ellipsoids show 50% probability levels. Hydrogen atoms have been omitted for clarity. Selected bond distances [Å]: Pd(1)-Se (1) 2.3414(3), Pd(1)-O(1) 2.0388(17), Pd(1)-N(1) 2.0256(19), Pd(1)-P(1) 2.2679(6), Se (1)-C(12) 1.911(3), C(12)-N(3) 1.369(3), C(12)-N(2) 1.285(3), N(2)-N(1) 1.403(3), N(1)-C (11) 1.291(3). Selected angles [°]: P(1)-Pd(1)-N(1) 176.77(6), Se(1)-Pd(1)-O(1) 177.03 (5), Se(1)-Pd(1)-P(1) 91.878(19), O(1)-Pd(1)-P(1) 91.08(5), Pd(1)-Se(1)-C(12) 91.75(8), N(2)-C(12)-Se(1) 125.31(19).

159.71 (d, J_{P-C} = 10.8 Hz, CSe), 148.12 (d, J_{P-C} = 3.2 Hz, C=N), 134.57 (d, J_{P-C} = 11.7 Hz, o-Ph$_3$P), 133.76 (C4), 131.06 (d, J_{P-C} = 2.7 Hz, p-Ph$_3$P), 129.66 (d, J_{P-C} = 50.5 Hz, ipso-Ph$_3$P), 128.73 (C5), 128.38 (d, J_{P-C} = 10.9 Hz, m-Ph$_3$P), 127.11 (C7), 126.93 (C10), 124.12 (d, J_{P-C} = 2.3 Hz, C3), 121. 79 (C6), 119.83 (C8), 106.76 (C1). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 25 °C): δ = 22.4. Anal. calc. for C$_{30}$H$_{24}$N$_3$OPSePd (658.88): C, 54.69; H, 3.67; N, 6.38. Found: C, 54.76; H, 3.88; N, 6.18 %. X-ray quality crystals were obtained by slow diffusion of Et$_2$O into a CH$_2$Cl$_2$ solution of the compound.

3.9. [Pt(L1^{Se})(PPh$_3$)] (7)

This was prepared as described above from trans-[PtCl$_2$(PPh$_3$)$_2$] (0.100 g, 0.126 mmol) and H$_2$L1^{Se} (0.037 g, 0.126 mmol). 0.061 g (64%) of a yellow solid was obtained. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 9.59 (d, J_{P-H} = 11.4 Hz, 1 H, HC=N), 8.16 (d, J = 8.7 Hz, 1 H, H8), 7.74–7.81 (m, 6 H, o-Ph$_3$P), 7.67 (dd, J = 8.0, 0.8 Hz, 1 H, H5), 7.63 (d, J = 9.2 Hz, 1 H, H4), 7.41-7.53 (m, 10 H, m-Ph$_3$P, p-Ph$_3$P, H7), 7.26 (dt, J = 7.3, 0.8 Hz, 1 H, H6), 6.85 (d, J = 9.2 Hz, 1 H, H3), 4.91 (br. s, 2 H, NH$_2$). ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ = 161.60 (d, J_{P-C} = 9.8 Hz, ipso-Ph$_3$P), 160.95 (C2), 145.86 (d, J_{P-C} = 2.6 Hz, C=N), 134.62 (d, J_{P-C} = 11.2 Hz, o-Ph$_3$P), 133.40 (C4), 131.03 (d, J_{P-C} = 2.5 Hz, p-Ph$_3$P), 130.36 (CSe), 129.76 (C9), 128.74 (C5), 128.20 (d, J_{P-C} = 11.1 Hz, m-Ph$_3$P), 127.39 (C10), 127.17 (C7), 124.31 (C3), 122.30 (C6), 119.81 (C8), 107.50 (C1). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 25 °C): δ = 7.14 (J_{Pt-P} = 3562 Hz). Anal. calc. for C$_{30}$H$_{24}$N$_3$OPSePt (747.55): C, 48.20; H, 3.24; N, 5.62. Found: C, 47.98; H, 3.16; N, 5.69 %.

3.10. [Pd(L2^{Se})(PPh$_3$)] (8)

This was prepared as described above from trans-[PdCl$_2$(PPh$_3$)$_2$] (0.100 g, 0.142 mmol) and H$_2$L2^{Se} (0.035 g, 0.144 mmol). 0.055 g (63%) of an orange solid was obtained. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 8.28 (d, J = 13.2 Hz, 1 H, HC=N), 7.73-7.80 (m, 6 H, o-Ph$_3$P), 7.50-7.55 (m, 3 H, p-Ph$_3$P), 7.43-7.49 (m, 6 H, m-Ph$_3$P), 7.30 (dd, J = 7.9, 1.8 Hz, 1 H, H6), 7.24 (dt, J = 8.6, 1.9 Hz, 1 H, H5), 6.69 (d,

J = 8.6 Hz, 1 H, H3), 6.62 (dt, J = 8.0, 1.2 Hz, 1 H, H4), 4.80 (br. s, 1 H, NH$_2$). ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ = 163.06 (C2), 161.35 (d, J_{P-C} = 10.6 Hz, CSe), 155.30 (d, J_{P-C} = 2.9 Hz, C=N), 134.57 (d, J_{P-C} = 11.4 Hz, o-Ph$_3$P), 134.38 (C6), 133.51 (C5), 131.04 (d, J_{P-C} = 2.7 Hz, p-Ph$_3$P), 129.91 (d, J_{P-C} = 50.8 Hz, ipso-Ph$_3$P), 128.34 (d, J_{P-C} = 10.9 Hz, m-Ph$_3$P), 120.55 (d, J_{P-C} = 2.2 Hz, C3), 117.34 (C1), 114.58 (C4). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 25 °C): δ = 22.09. Anal. calc. for C$_{26}$H$_{22}$N$_3$OPSePd (608.83): C, 51.29; H, 3.64; N, 6.90. Found: C, 51.04; H, 3.90; N, 6.59 %.

3.11. [Pd(L2^{Se})(PTA)] (9)

This was prepared as described above from cis-[PdCl$_2$(PTA)$_2$] (0.100 g, 0.202 mmol) and H$_2$L2^{Se} (0.049 g, 0.202 mmol). 0.056 g (55%) of a yellow solid was obtained. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 8.22 (d, J_{P-H} = 12.8 Hz, 1 H, HC=N), 7.30 (dt, J = 8.7, 1.7 Hz, 1 H, H5), 7.25 (d, J = 8.5 Hz, 1 H, H6), 6.99 (d, J = 8.4 Hz, 1 H, H3), 6.63 (t, J = 7.6 Hz, 1 H, H4), 5.17 (br. s, 2 H, NH$_2$), 4.56 (AB quart., J = 13.7 Hz, 6 H, NCH$_2$N), 4.36 (s, 6 H, PCH$_2$N). ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ = 162.79 (C2), 160.43 (d, J_{P-C} = 12.7 Hz, CSe), 152.57 (d, J_{P-C} = 2.5 Hz, C=N), 134.65 (C6), 133.71 (C5), 120.54 (d, J_{P-C} = 1.4 Hz, C3), 117.27 (C1), 115.01 (C4), 73.15 (d, J_{P-C} = 7.7 Hz, NCH$_2$N), 51.66 (d, J_{P-C} = 16.8 Hz, PCH$_2$N). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 25 °C): δ = −44.21. Anal. calc. for C$_{14}$H$_{19}$N$_6$OPSePd (503.69): C, 33.38; H, 3.80; N, 16.68. Found: C, 33.49; H, 4.02; N, 16.52 %.

3.12. X-ray crystallography

Diffraction data were collected at 150 K using an Oxford Diffraction Gemini E Ultra diffractometer, equipped with an EOS CCD area detector and a four-circle kappa goniometer. For the data collection the Mo source emitting graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) was used. Data integration, scaling and empirical absorption correction was carried out using the CrysAlis Pro program package [19]. The structure was solved using Direct Methods (**1**) or Patterson Methods (**6**) and refined by Full-Matrix-Least-Squares against F^2. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed at idealised positions and refined using the riding model. All calculations were

Table 1
Crystal data and refinement details of compounds **1** and **6**.

	1	**6**
Empirical formula	C$_7$H$_{13}$SeN$_3$	C$_{30}$H$_{24}$N$_3$OPdSeP
Colour	Colourless	Orange
M_r, g mol^{-1}	218.16	658.85
Crystal system	Monoclinic	Monoclinic
Space group	P2$_1$/n	P2$_1$/n
a, Å	10.1698(6)	14.2882(8)
b, Å	8.4215(4)	10.7668(7)
c, Å	11.0316(7)	17.9064(10)
β,°	111.079(7)	110.268(6)
V, Å^3	881.58(9)	2584.1(3)
Z	4	4
$D_{calc.}$, g cm^{-3}	1.644	1.693
μ, mm^{-1}	4.200	2.218
F(000)	440	1312
Crystal size, mm^3	0.13 × 0.15 × 0.16	0.04 × 0.19v0.27
θ range for data collection	3.13−29.47°	2.94−29.16°
Refl. collected	3943	12151
Independent refl.	2058	5879
Abs. corr.	Multi-scan	Multi-scan
Max. / min. trans.	1.00000/0.80997	1.00000/0.47936
Parameters	109	342
R_1 (all data)	0.0336	0.0432
wR^2 (all data)	0.0477	0.0534
Largest diff. peak / hole, e Å^{-3}	0.323/−0.390	0.487/-0.366

carried out using the program Olex2 [20]. Important crystallographic data and refinement details are summarised in Table 1.

Acknowledgements

Appendix. Supplementary data

Full crystallographic details of compounds **1** and **6** (CIF file format) are available from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK by quoting the deposition codes CCDC 765520 and 765521.

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