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2-(Dimethylamino)ethaneselenolates of palladium(II): synthesis, structure, spectroscopy and transformation into palladium selenide

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Bis[2-(dimethylamino)ethyl] diselenide was prepared by the reaction of Na_2Se_2 with $ClCH_2CH_2NMe_2$. 2-(Dimethylamino)ethaneselenolate complexes of palladium(II) of the type $[PdCl(SeCH_2CH_2NMe_2)]_3$ **1**, $[PdCl(SeCH_2CH_2NMe_2)(PR_3)]$ **2**, $[Pd_2Cl_3(SeCH_2CH_2NMe_2)(PR_3)_2]$ **3** and $[Pd(SeCH_2CH_2NMe_2)_2(PPh_3)_2]$ **4** have been synthesized and characterized by elemental analysis, IR and NMR (^1H, ^{31}P, ^{77}Se) spectroscopy. The structures of orange **1** and of violet (λ_{max} = 514 nm) **2c** have been established by single crystal X-ray diffraction analyses. The trimer **1** contains a six-membered Pd_3Se_3 ring in twist conformation. The thermal behaviour of three complexes, yielding $Pd_{17}Se_{15}$ has been investigated.

Introduction

The continuing drive to scale down dimensions of electronic devices has necessitated the introduction of new classes of growth techniques (*cf.* MOCVD, plasma CVD, *etc.*) which employ molecular precursors rather than the elements for the synthesis of solid state inorganic materials.[1] Accordingly, research in the design and development of molecular precursor chemistry has accelerated in recent years.[2]

Platinum group metal chalcogenides (M_xE_y; M = Pd or Pt; E = S, Se or Te) find several applications in catalysis[3] and in the electronic industry.[4–6] Platinum group metal chalcogenolates have an attractive potential to serve as precursors for the synthesis of such chalcogenides.[7,8] Their chemistry is dominated by thiolate complexes[9] which in most cases have been isolated as polymeric, non-volatile, insoluble or sparingly soluble complexes. To suppress polymerization, sterically demanding chalcogenolate ligands[10] or strongly coordinating neutral ligands such as tertiary phosphines[11,12] have been employed. In an alternative approach, internally functionalized ligands, which not only yield low nuclearity complexes but also enhance complex stability, have been used as demonstrated for compounds with 3-dimethylamino-1-propanethiolate,[13] 2-selenopyridinates[14,15] and phosphorus–sulfur donor ligands.[16] With the current interest in selenium containing inorganic materials[17] and in pursuance of our program on the molecular design of platinum group precursors, we have now synthesized $(Me_2NCH_2CH_2Se)_2$ and investigated the chemistry of its palladium complexes.

Experimental

All reactions were carried out under nitrogen using conventional Schlenk techniques. Solvents were dried by standard methods with subsequent distillation under nitrogen. Grey selenium (NFC, Hyderabad, India), tertiary phosphines (Strem Chemicals, USA) and $Me_2NCH_2CH_2Cl{\cdot}HCl$ were obtained from commercial sources. The complexes Na_2PdCl_4, $[PdCl_2(PPh_3)_2]$, $[Pd_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ ($PR_3 = PMe_2Ph$, $PMePh_2$ or PPh_3) were prepared according to literature methods.[18–20]

Melting points were determined in capillary tubes and are uncorrected. Elemental analyses were carried out by the Analytical Chemistry Division of B.A.R.C. ^1H, $^{13}C\text{-}\{^1H\}$, $^{31}P\text{-}\{^1H\}$ and $^{77}Se\text{-}\{^1H\}$ NMR spectra were recorded on a Bruker DPX-300 NMR spectrometer operating at 300, 75.47, 121.49 and 57.24 MHz, respectively. Chemical shifts are relative to the internal chloroform peak at δ 7.26 for ^1H and δ 77.0 for ^{13}C, external 85% H_3PO_4 for ^{31}P, and Me_2Se for ^{77}Se. A 90° pulse was used in each case. The IR spectra were recorded as Nujol mulls between CsI plates on a Bomen MB-102 FT-IR spectrometer, UV/Vis absorption spectra on a Bruins Instruments Omega 10 spectrophotometer. Cyclic voltammetry was carried out at 100 mV s^{-1} scan rate in dichloromethane–0.1 M Bu_4NPF_6 using a three-electrode configuration (glassy carbon electrode, platinum counter electrode, Ag–AgCl reference) and a PAR 273 potentiostat and function generator. The ferrocene–ferrocenium couple served as internal reference. FAB mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer at CDRI, Lucknow, India. Thermogravimetric analysis (TGA) was carried out on a Setaram 92-16-18 instrument calibrated with $CaC_2O_4{\cdot}H_2O$. The TG curves were recorded at a heating rate of 3 °C min^{-1} under a flow of argon. X-Ray powder diffraction was measured using Cu-Kα radiation. SEM photographs were taken on a JEOL JSM-T330A instrument.

Preparations

Bis[2-(dimethylamino)ethyl] diselenide $(Me_2NCH_2CH_2Se)_2$. Finely powdered grey selenium (14.2 g, 179.8 mmol) and sodium metal (4.2 g, 182.6 mmol) were charged in liquid ammonia (250 cm^3) at −78 °C. The brownish red solution of sodium diselenide was stirred for 2 h and ammonia evaporated at room temperature. The brown mass of Na_2Se_2 was dried under vacuum and dissolved in DMF (250 cm^3), then stirred for 4 h. Freshly dried and distilled $Me_2NCH_2CH_2Cl$ (19.4 g, 180.3 mmol) [from $Me_2NCH_2CH_2Cl{\cdot}HCl$ by neutralising with aq. NaOH, extracting with diethyl ether, drying over $CaCl_2$ and distilling at 107–108 °C] was added dropwise. The mixture was stirred for 1 h at 70 °C. After cooling to room temperature the reaction was quenched with water (250 cm^3), followed by

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hexane (250 cm^3). The organic layer was separated and the aqueous layer extracted with hexane (3 × 100 cm^3). The combined extracts were dried over $CaCl_2$. After evaporation of the solvent the red liquid was distilled *in vacuo* (118–124 °C, 0.1 mmHg) to give an orange-red liquid (19.6 g, 72%). ^{1}H NMR ($CDCl_3$): δ 2.26 (s, 6H, NMe_2); 2.63 (t, *J* 7.1, 2H, $SeCH_2$) and 3.05 (t, *J* 7.1 Hz, 2H, NCH_2). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 28.3 (s, $^1J(^{77}Se–^{31}C)$ 73 Hz, $SeCH_2$); 45.0 (s, NMe_2) and 60.3 (s, NCH_2). ^{77}Se-{^{1}H} NMR ($CDCl_3$): δ 293.3.

$[PdCl(SeCH_2CH_2NMe_2)]_3$ 1. To a methanolic solution (25 cm^3) of $(Me_2NCH_2CH_2Se)_2$ (917 mg, 3.03 mmol) was added a methanolic solution (25 cm^3) of $Na_2[PdCl_4]$ (891 mg, 3.03 mmol) at room temperature whereupon a yellow precipitate formed. The mixture was stirred for 3 h. The precipitate was washed thoroughly with water, ethanol, diethyl ether and hexane and dried *in vacuo* (yield: 718 mg, 81%). It was recrystallized from dichloromethane as orange microcrystals (682 mg, 95%). mp 216 °C (decomp.). Calc. for $C_4H_{10}ClNPdSe$: C, 16.4; H, 3.4; N, 4.8. Found: C, 15.9; H, 3.4; N, 4.7%. ^{1}H NMR ($CDCl_3$): δ 2.82 (br, s, NMe_2 + $SeCH_2$) and 3.06 (br, s, NCH_2). IR (Nujol): 303 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} 274, 293 and 385 (sh) nm. FAB-MS: *m*/*z* 879, 845 and 736.

$[PdCl(SeCH_2CH_2NMe_2)(PMe_2Ph)]$ 2a. A dichloromethane solution (20 cm^3) of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ (184 mg, 0.29 mmol) was added to a freshly prepared methanolic solution of $NaSeCH_2CH_2NMe_2$ (prepared from $(Me_2NCH_2CH_2Se)_2$ (90 mg, 0.29 mmol) and $NaBH_4$ (23 mg, 0.60 mmol)) with stirring at room temperature. After 3 h the solvents were evaporated *in vacuo*. The brown residue was extracted with dichloromethane (3 × 8 cm^3), the solution passed through a Florisil column and the solvent removed *in vacuo*. The residue was recrystallized from dichloromethane–acetone. Yield 113 mg (45%). mp 175 °C. Calc. for $C_{12}H_{21}ClNPdSeP$: C, 33.4; H, 4.9; N, 3.2. Found: C, 32.0; H, 4.8; N, 2.7%. ^{1}H NMR ($CDCl_3$): δ 1.85 (d, ^2J(P–H) 11.5, PMe_2), 2.55 (t, *J* 6.2, $SeCH_2$); 2.63, 2.64 (each s, NMe_2); 3.04 (t, *J* 5.8 Hz, NCH_2) and 7.40 (m), 7.64–7.71 (m) [Ph]. ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 2.6.

$[PdCl(SeCH_2CH_2NMe_2)(PMePh_2)]$ 2b. Prepared analogously to complex **2a** by using $[Pd_2Cl_2(\mu\text{-}Cl)_2(PMePh_2)_2]$ (202 mg, 0.27 mmol) and $NaSeCH_2CH_2NMe_2$ (prepared from $(Me_2NCH_2CH_2Se)_2$ (80 mg, 0.27 mmol) and $NaBH_4$ (21 mg, 0.55 mmol)) as starting materials. The compound was recrystallized from a dichloromethane–acetone mixture. Yield 148 mg (40%). mp 194 °C. Calc. for $C_{17}H_{23}ClNPdSeP$: C, 41.4; H, 4.7; N, 2.8. Found: C, 40.9; H, 4.7; N, 2.6%. ^{1}H NMR ($CDCl_3$): δ 2.22 (d, ^2J(P–H) 11.4, PMe); 2.52 (t, 6.2 Hz, $SeCH_2$); 2.71, 2.72 (each s, NMe_2); 3.13 (t, *J* 5.9 Hz, NCH_2) and 7.36–7.46 (m), 7.62–7.69 (m) [Ph]. ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 16.7.

$[PdCl(SeCH_2CH_2NMe_2)(PPh_3)]$ 2c. *Method (a)*. To a dichloromethane suspension (30 cm^3) of $[PdCl(SeCH_2CH_2NMe_2)]_3$ (412 mg, 1.40 mmol) solid PPh_3 (372 mg, 1.41 mmol) was added and the mixture stirred for 1 h under nitrogen. The pinkish solution was dried *in vacuo*, the solid washed with hexane and recrystallized from dichloromethane–acetone to yield violet crystals (710 mg, 91%). mp 212 °C. Calc. for $C_{22}H_{25}ClNPdSeP$: C, 47.6; H, 4.5; N, 2.5. Found: C, 46.8; H, 4.7; N, 2.4%. ^{1}H NMR ($CDCl_3$): δ 2.52 (t, *J* 6.1, $SeCH_2$); 2.76, 2.77 (each s, NMe_2); 3.21 (t, *J* 5.7 Hz, NCH_2) and 7.36–7.47 (m), 7.72–7.79 (m) [Ph]. ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 29.5. ^{77}Se-{^{1}H} NMR ($CDCl_3$): δ 364.6. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ 344 (1980) and 514 nm (80) (M^{-1} cm^{-1}). FAB-MS: *m*/*z* 555, 520 and 447.

Method (b). As described for complex **2a** by using $[Pd_2Cl_2(\mu\text{-}Cl)_2(PPh_3)_2]$ (230 mg, 0.26 mmol), $NaSeCH_2CH_2NMe_2$ (prepared from $(Me_2NCH_2CH_2Se)_2$ (79 mg, 0.26 mmol) and $NaBH_4$ (19.9 mg, 0.53 mmol)) as starting materials. Melting point, analyses and other data were consistent with the product obtained in method (a).

$[PdCl(SeCH_2CH_2NMe_2)(P(C_6H_4Me\text{-}p)_3)]$ 2d. As described for complex **2c** in method (a). The pink product was recrystallized from dichloromethane–acetone. Yield 75%. mp 222 °C. Calc. for $C_{25}H_{31}ClNPdSeP$: C, 50.3; H, 5.2; N, 2.3. Found: C, 50.1; H, 5.6; N, 2.1%. ^{1}H NMR ($CDCl_3$): δ 2.35 (s, C_6H_4*Me*); 2.51 (br, s, $SeCH_2$); 2.74 (br, s, NMe_2); 3.18 (br, s, NCH_2) and 7.18 (br), 7.61 (br) (C_6H_4). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 27.5. ^{77}Se-{^{1}H} NMR ($CDCl_3$): δ 354.4.

$[PdCl(SeCH_2CH_2NMe_2)(PPh_2C_5H_4N\text{-}2)]$ 2e. As described for complex **2c** in method (a). The violet-brown product was recrystallized from dichloromethane–acetone. Yield 72%. mp 217 °C. Calc. for $C_{21}H_{24}ClN_2PdSeP$: C, 45.3; H, 4.3; N, 5.0. Found: C, 45.1; H, 4.4; N, 5.2%. ^{1}H NMR ($CDCl_3$): δ 2.53 (t, *J* 6.1, $SeCH_2$); 2.78, 2.79 (each s, NMe_2); 3.22 (t, *J* 5.7, NCH_2); 7.28–7.46 (m), 7.71–7.85 (m) (Ph + 2H py); 8.41 (t, *J* 7, 1 H py) and 8.73 (dd, *J* 0.8, 1.7 Hz, 1 H, py). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 28.2.

$[Pd_2Cl_3(SeCH_2CH_2NMe_2)(PMePh_2)_2]$ 3a. To a dichloromethane solution (20 cm^3) of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PMePh_2)_2]$ (30 mg, 0.04 mmol) solid $[PdCl(SeCH_2CH_2NMe_2)(PMePh_2)]$ (55 mg, 0.08 mmol) was added and the mixture stirred for 4 h. The solvent was evaporated *in vacuo*. The residue was recrystallized from dichloromethane–hexane. Yield 74%. mp 123 °C. Calc. for $C_{30}H_{36}Cl_3NPd_2SeP_2$: C, 41.4; H, 4.2; N, 1.6. Found: C, 41.2; H, 4.2; N, 1.3%. ^{1}H NMR ($CDCl_3$): δ 1.94–3.59 (complex pattern, NMe_2, PMe, NCH_2/$SeCH_2$) and 6.83–7.72 (br m, Ph). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 7.7, 16.4 and 17.6.

$[Pd_2Cl_3(SeCH_2CH_2NMe_2)(PPh_3)_2]$ 3b. *Method (a)*. As described for complex **3a**. The yellow solid was recrystallized from acetone. Yield 75%. mp 168 °C. Calc. for $C_{40}H_{40}Cl_3NPd_2SeP_2$: C, 48.3; H, 4.1; N, 1.4. Found: C, 46.8; H, 3.7; N, 0.9%. ^{1}H NMR ($CDCl_3$): δ 2.16 (s, NMe_2); 2.83 (br, NCH_2/$SeCH_2$) and 7.35–7.89 (m, Ph). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 21.7, 23.7 and 27.6.

Method (b). As described for complex **2a** by using $[Pd_2Cl_2(\mu\text{-}Cl)_2(PPh_3)_2]$ (204 mg, 0.23 mmol), $NaSeCH_2CH_2NMe_2$ (prepared from $(Me_2NCH_2CH_2Se)_2$ (36 mg, 0.12 mmol) and $NaBH_4$ (9.1 mg, 0.24 mmol)) as starting materials. The NMR spectra and other data of the product were consistent with those of the sample obtained in method (a).

$[Pd(SeCH_2CH_2NMe_2)_2(PPh_3)_2]$ 4. To a methanolic solution (8 cm^3) of $NaSeCH_2CH_2NMe_2$ (prepared from $(Me_2NCH_2CH_2Se)_2$ (144 mg, 0.48 mmol) and $NaBH_4$ (35.8 mg, 0.96 mmol)) was added a suspension of $[PdCl_2(PPh_3)_2]$ (334 mg, 0.48 mmol) in 25 cm^3 toluene and the reactants were stirred for 3 h. The solvents were evaporated *in vacuo* and the residue was extracted with acetone. The extracts were concentrated and the solid recrystallized from acetone–hexane (267 mg, 60%). Owing to PPh_3 dissociation, analyses varied from sample to sample. Typical analysis: Calc. for $C_{44}H_{50}N_2PdSe_2P_2$: C, 56.7; H, 5.4; N, 3.0; found C, 53.3; H, 4.9; N, 4.4%. mp 145 °C. ^{1}H NMR complicated due to mixture of products. ^{31}P-{^{1}H} NMR (acetone-d$_6$): δ −4.9 (PPh_3); 26.8, 32.0 and 35.8. When treated with CCl_4–$CHCl_3$ $[PdCl(SeCH_2CH_2NMe_2)(PPh_3)]$ was formed exclusively. This also formed in some preparations but is insoluble in acetone and can be separated easily.

Crystallography

X-Ray data of an orange single crystal of $[PdCl(SeCH_2CH_2NMe_2)]_3$ **1** were collected on a Stoe IPDS diffractometer (at room temperature) using graphite monochromated Mo-Kα radiation. Unit cell parameters were determined from 5000 reflections. The intensity data were corrected for Lorentz polarization and absorption effects.[21] X-Ray data of a violet crystal of $[PdCl(SeCH_2CH_2NMe_2)(PPh_3)]$ **2c** were collected at 173(2) K on a Siemens P3 diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å), employing the ω–2θ scan technique. The unit cell parameters (Table 1) were determined from 25 reflections measured by a random search routine. The intensity data were corrected for Lorentz polarization and absorption effects. The structure was solved using direct methods. The non-hydrogen atoms were refined anisotropically.

CCDC reference number 186/2302.

See http://www.rsc.org/suppdata/dt/b0/b008310k/ for crystallographic files in .cif format.

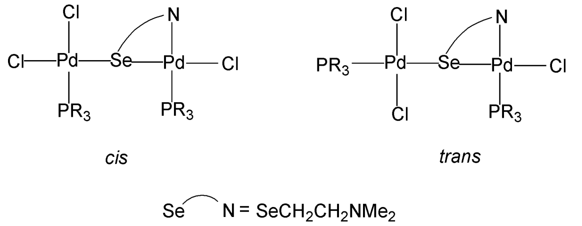
Results and discussion

Synthesis and spectroscopic data

When a methanolic solution of $Na_2[PdCl_4]$ was treated with $(Me_2NCH_2CH_2Se)_2$, a yellow, insoluble product formed initially which on recrystallization from dichloromethane afforded orange microcrystals of empirical composition $[PdCl(SeCH_2CH_2NMe_2)]_n$ **1** (eqn. 1). The IR spectrum of **1** exhibits a ν(Pd–Cl) band at 303 cm^{-1}. The ^1H NMR spectrum in $CDCl_3$ shows broad resonances due to NMe_2, $SeCH_2$ and NCH_2 protons, indicative of fluxional behaviour. The analogous palladium complex with 3-dimethylamino-1-propanethiolate is dimeric ($[PdCl(SCH_2CH_2NMe_2)]_2$[22]) while 2-sulfanylnicotinic acid forms a trimer.[23] A trinuclear structure containing a Pt_3S_3 ring has been reported for $[PtBr(SCH_2CH_2NMe_2)]_3$.[24] The FAB mass spectrum of **1** displayed a peak at *m*/*z* 879 suggesting that this complex is trimeric. No signal attributable to either the monomer (*m*/*z* 293) or the dimer (*m*/*z* 586) is observed. Other prominent peaks were due to $[M - Cl]$ (*m*/*z* 845) and $[M - (Cl_2 + CH_2CH_2NMe_2)]$ (*m*/*z* 736). The trimeric structure of **1** is confirmed by X-ray diffraction analysis (*cf.* below).

Reaction of complex **1** with tertiary phosphines readily afforded violet complexes $[PdCl(SeCH_2CH_2NMe_2)(PR_3)]$ **2**. The latter have also been synthesized by treatment of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PPh_3)_2]$ with $NaSeCH_2CH_2NMe_2$ (eqn. 1). The ^1H NMR spectra of compounds **2** display characteristic peaks and integration for various groups. The NMe_2 protons are anisochronous, two separate methyl signals being observed. The NMe_2 and NCH_2 protons showed phosphine dependence while the $SeCH_2$ protons were little affected. This suggests that the phosphine ligand is in *trans* position to the nitrogen atom of the chelating selenolate ligand. This is further supported by vanishingly small ^2J(Se–P) coupling in the ^{77}Se NMR spectra of these complexes. The magnitudes of the ^2J(Se–P) *cis* and *trans* couplings have been reported to be ≈10 and 80 Hz, respectively.[12] The ^{31}P NMR spectra of compounds **2** show single resonances. The FAB mass spectrum of **2c** exhibits a peak at *m*/*z* 555, indicating the monomeric nature of the product which is confirmed by structural analysis. Other peaks are at *m*/*z* 520 $[M - Cl]$ and 447 $[M - (Cl + CH_2CH_2NMe_2)]$. The distinct violet colour of **2c** is due to a weak absorption at 514 nm (in CH_2Cl_2 solution). The low molar absorption coefficient of only 80 M^{-1} cm^{-1} points to a symmetry-forbidden transition which we tentatively identify as occurring from the highest occupied molecular orbital (HOMO) at the selenolate center to the lowest unoccupied (LUMO) situated at the PPh_3 ligand. Cyclic voltammetry in CH_2Cl_2 confirmed that there is a high-lying HOMO (oxidation at +0.55 V) and a rather low-lying LUMO (−2.04 V; all peak potentials for irreversible processes *vs.* the ferrocene–ferrocenium couple).

When compounds **2** are treated with $[Pd_2Cl_2(\mu\text{-}Cl)_2(PPh_3)_2]$ a new series of dinuclear complexes with the composition $[(R_3P)Cl_2Pd(SeCH_2CH_2NMe_2)PdCl(PR_3)]$ **3** ($PR_3 = PMePh_2$ (**3a**) or PPh_3 (**3b**)) is isolated. Complex **3b** can also be prepared by reaction of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PPh_3)_2]$ with one equivalent of $NaSeCH_2CH_2NMe_2$. The ^{31}P NMR spectra of complexes **3** display three resonances. The most deshielded signal may be attributed to the phosphine bound to the palladium atom which connects with the chelating selenolate group. The other two resonances, lower in intensities, can be assigned to the phosphine attached to the $PdCl_2$ fragment. Recently we have reported similar dinuclear palladium/platinum complexes containing 2-selenopyridine.[15]



Reaction of $[PdCl_2(PPh_3)_2]$ with 2 equivalents of $NaSeCH_2CH_2NMe_2$ yielded $[Pd(SeCH_2CH_2NMe_2)_2(PPh_3)_2]$ **4** which dissociated into $[Pd(SeCH_2CH_2NMe_2)_2(PPh_3)]$ and PPh_3. Similar behaviour is observed for analogous $[M(EC_5H_4N)_2(PPh_3)_2]$ (M = Pd or Pt; E = S or Se) complexes.[15,25] When **4** is treated with CCl_4–$CHCl_3$ **2c** forms readily.

Structure of $[PdCl(SeCH_2CH_2NMe_2)]_3$ 1

The structure of complex **1**, established by single crystal X-ray diffraction analysis (Table 1), is shown in Fig. 1, selected bond lengths and angles are given in Table 2. The molecule contains three distorted square planar palladium centers held together by three bridging selenium atoms of the chelating dimethylaminoethaneselenolate ligand. The resulting six-membered Pd_3Se_3 ring adopts a twist conformation (Fig. 2). The coordination around each palladium atom is defined by two mutually *cis* positioned selenium atoms, a nitrogen donor atom and a terminally bonded chloride ligand. The dimethylaminoethane selenolate ligands form "exocyclic" five-membered $PdSeC_2N$ chelate rings, with envelope conformations.

Although the Pd–Se distances (2.367–2.419 Å) are well within the expected range[12,15] there are clearly two different types of bonds. The one in the chelate ring is typically shorter (≈ 2.37 Å) than the other kind (≈ 2.40 Å). The angles around the selenium atoms show considerable deviation from the ideal tetrahedral value (109.5 °C) and lie in the range 92.6(2)–110.18(19)°. The strong *trans* influence of the selenolate ligand is reflected in the Pd–Cl distances which are marginally longer (av. 2.356 Å) than those reported in other complexes (≈ 2.30 Å).[15] The Pd–Cl, Pd–N (av. 2.136 Å), Se–C (av 1.965 Å) distances in the three

$$3Na_2[PdCl_4] + \tfrac{3}{2}(Me_2NCH_2CH_2Se)_2 \longrightarrow [PdCl(SeCH_2CH_2NMe_2)]_3\ \mathbf{1} \qquad (1)$$

$$\big\downarrow 3PR_3$$

$$[Pd_2Cl_2(\mu\text{-}Cl)_2(PPh_3)_2] + 2NaSeCH_2CH_2NMe_2 \longrightarrow [PdCl(SeCH_2CH_2NMe_2)(PR_3)]$$

$PR_3 = PMe_2Ph$ (**2a**)
$PMePh_2$ (**2b**)
PPh_3 (**2c**)
$P(C_6H_4Me\text{-}p)_3$ (**2d**)
$PPh_2C_5H_4N\text{-}2$ (**2e**)

Table 1 Crystal data and structure refinement for [PdCl(SeCH$_2$CH$_2$NMe$_2$)]$_3$ **1** and [PdCl(SeCH$_2$CH$_2$NMe$_2$)(PPh$_3$)] **2c**

	1	**2c**
Chemical formula	$C_{12}H_{30}Cl_3N_3Pd_3Se_3$	$C_{22}H_{25}ClNPPdSe$
Formula weight	878.82	555.21
Crystal system, space group	Monoclinic, $P2_1/a$	Monoclinic, $P2_1/n$
a/Å	10.7805(5)	9.527(2)
b/Å	13.1187(9)	19.827(4)
c/Å	16.6749(8)	11.661(2)
β/°	95.899(5)	95.77(3)
V/Å^3	2345.8(2)	2191.4(8)
Z	4	4
μ/mm^{-1}	7.274	2.710
Refinement method	Full matrix least squares on $F^2 > 0$	Full matrix least squares on $F^2 > 0$
Reflections collected/unique	22492/5593	7291/5997
Data/restraints/parameters	5593/0/218	5997/0/245
Final $R1$, $wR2$ indices	0.0357, 0.0938	0.0478, 0.1354
(all data)	0.0520, 0.0883	0.0597, 0.1469

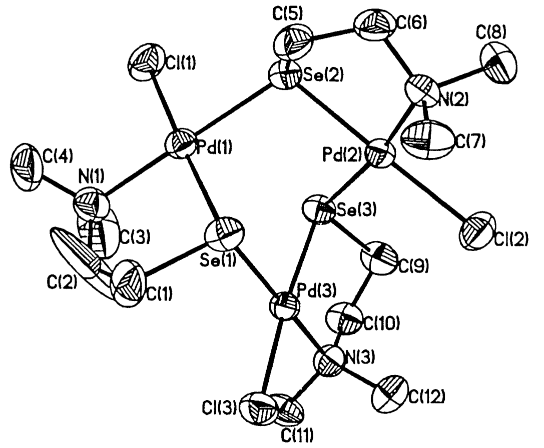


Fig. 1 Molecular structure of [PdCl(SeCH$_2$CH$_2$NMe$_2$)]$_3$ **1** with atomic numbering scheme.

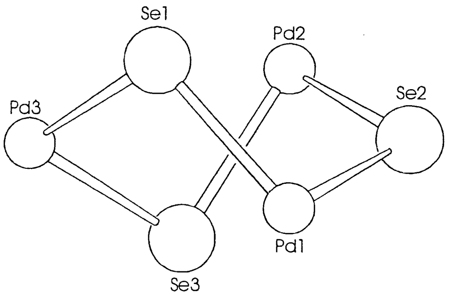


Fig. 2 Conformation of the six-membered Pd$_3$Se$_3$ ring of [PdCl(SeCH$_2$CH$_2$NMe$_2$)]$_3$ **1**.

Table 2 Selected bond lengths (Å) and angles (°) for [PdCl(SeCH$_2$CH$_2$NMe$_2$)]$_3$ **1**

Pd(1)–Se(1)	2.3783(7)	Se(1)–C(1)	1.978(7)
Pd(1)–Se(2)	2.3982(7)	Se(2)–C(5)	1.942(7)
Pd(2)–Se(2)	2.3672(7)	Se(3)–C(9)	1.975(6)
Pd(2)–Se(3)	2.4115(6)	N(1)–C(2)	1.444(11)
Pd(3)–Se(3)	2.3709(6)	N(2)–C(6)	1.496(7)
Pd(3)–Se(1)	2.4199(7)	N(3)–C(10)	1.476(7)
Pd(1)–Cl(1)	2.3455(16)	C(1)–C(2)	1.250(13)
Pd(2)–Cl(2)	2.3673(16)	C(5)–C(6)	1.507(9)
Pd(3)–Cl(3)	2.3540(14)	C(9)–C(10)	1.520(8)
Pd(1)–N(1)	2.133(5)		
Pd(2)–N(2)	2.135(4)		
Pd(3)–N(3)	2.141(5)		
Se(1)–Pd(1)–Se(2)	91.45(2)	N(1)–Pd(1)–Se(2)	178.94(15)
Se(1)–Pd(1)–Cl(1)	177.41(5)	Pd(3)–Se(1)–C(1)	99.8(2)
Se(1)–Pd(1)–N(1)	88.19(15)	Pd(1)–Se(1)–C(1)	92.6(2)
Pd(1)–Se(1)–Pd(3)	102.41(2)	Pd(1)–N(1)–C(2)	110.0(5)
Pd(1)–Se(2)–Pd(2)	107.00(2)	Se(1)–C(1)–C(2)	115.8(6)
Cl(1)–Pd(1)–Se(2)	86.86(5)	N(1)–C(2)–C(1)	130.2(8)
Cl(1)–Pd(1)–N(1)	93.46(16)		
Se(2)–Pd(2)–Se(3)	84.16(2)	N(2)–Pd(2)–Se(3)	169.91(13)
Se(2)–Pd(2)–Cl(2)	178.98(5)	Pd(2)–Se(2)–C(5)	92.9(2)
Se(2)–Pd(2)–N(2)	86.88(13)	Pd(1)–Se(2)–C(5)	107.0(2)
Pd(2)–Se(3)–Pd(3)	94.89(2)	Pd(2)–N(2)–C(6)	112.6(3)
Cl(2)–Pd(2)–Se(3)	96.23(4)	Se(2)–C(5)–C(6)	105.8(5)
Cl(2)–Pd(2)–N(2)	92.81(13)	N(2)–C(6)–C(5)	112.3(4)
Se(3)–Pd(3)–Se(1)	90.92(2)	Pd(3)–Se(3)–C(9)	94.45(17)
Se(3)–Pd(3)–Cl(3)	174.15(4)	Pd(2)–Se(3)–C(9)	110.18(19)
Se(3)–Pd(3)–N(3)	87.28(12)	Pd(3)–N(3)–C(10)	111.6(4)
Cl(3)–Pd(3)–Se(1)	89.39(5)	Se(3)–C(9)–C(10)	104.8(4)
Cl(3)–Pd(3)–N(3)	92.66(13)	N(3)–C(10)–C(9)	112.6(5)
N(3)–Pd(3)–Se(1)	176.85(13)		

"PdCl(SeCH$_2$CH$_2$NMe$_2$)" fragments are comparable, however various angles in each fragment differ slightly.

Structure of [PdCl(SeCH$_2$CH$_2$NMe$_2$)(PPh$_3$)] 2c

An ORTEP plot[26] with the atomic numbering scheme of [PdCl(SeCH$_2$CH$_2$NMe$_2$)(PPh$_3$)] **2c** is shown in Fig. 3; selected bond lengths and angles are summarized in Table 3. The geometry around the palladium center is essentially square planar with the atoms P, Cl, Se, N, defining the coordination sphere. The phosphine ligand is *trans* to the nitrogen atom while the chloride is *trans* to the Se atom of the chelating ligand. The *trans* influence of various ligands is reflected in the Pd–X distances. Thus, Pd–N [2.160(3) Å] and Pd–Cl [2.382(1) Å] are slightly longer owing to the strong *trans* influence of PPh$_3$ and Se when compared to those in [Pd$_2$Cl$_2$(μ-Me$_2$pz)$_2$(PMe$_2$Ph)$_2$] (Pd–Cl$_{av}$ 2.30, Pd–N 2.03–2.08 Å)[27] and [(PPr$_3$)Cl$_2$Pd(μ-SeC$_5$H$_4$N)PdCl(PPr$_3$)] (Pd–Cl$_{av}$ 2.30, Pd–N 2.10 Å).[15] Consequently, the Pd–Se distance (2.371 Å) is slightly shorter than the values reported for [Pd(SePh)$_2$(dppe)] (Pd–Se 2.444(1), 2.480(1) Å)[12] and [(PPr$_3$)Cl$_2$Pd(μ-SeC$_5$H$_4$N)PdCl(PPr$_3$)] (Pd–Se 2.508, 2.421 Å).[15] The five-membered chelate ring (Pd–Se–C–C–N) exists in a puckered conformation with the carbon atoms [C(19) and C(20)] lying on opposite sides of the mean plane. The geometry around the nitrogen atom is distorted tetrahedral (106.6–114.8°).

Thermal studies

Thermogravimetric analyses of [Pd(SeCH$_2$CH$_2$NMe$_2$)Cl]$_3$ **1** (Fig. 4) and [PdCl(SeCH$_2$CH$_2$NMe$_2$)(PPh$_3$)] **2c** were carried out under a flowing argon atmosphere. The TG curve of **1** showed two closely spaced steps of decomposition (284 °C), leading to formation of Pd$_{17}$Se$_{15}$ as inferred from the calculated mass loss. The XRD pattern of the product and the elemental analyses [Found: C 3.9, Pd 59.0, Se 41.0 (±2%), H and N not detected

Table 3 Selected bond distances (Å) and bond angles (°) for [PdCl(SeCH$_2$CH$_2$NMe$_2$)(PPh$_3$)] **2c**

Pd–N	2.160(3)	N–C(20)	1.500(5)
Pd–P	2.2554(11)	N–C(21)	1.484(5)
Pd–Se	2.3710(6)	N–C(22)	1.489(6)
Pd–Cl	2.3823(10)	C(19)–C(20)	1.514(6)
Se–C(19)	1.963(4)	P–C(av.)	1.826
N–Pd–P	173.13(10)	C(21)–N–C(22)	107.9(4)
N–Pd–Se	87.33(9)	C(21)–N–C(20)	106.6(3)
P–Pd–Se	88.95(3)	C(22)–N–C(20)	109.6(3)
N–Pd–Cl	91.82(9)	C(21)–N–Pd	114.8(3)
P–Pd–Cl	91.31(4)	C(22)–N–Pd	106.6(3)
Se–Pd–Cl	174.29(3)	C(20)–N–Pd	111.3(2)
Pd–Se–C(19)	95.71(13)	N–C(20)–C(19)	111.1(3)
		Se–C(19)–C(20)	109.1(3)

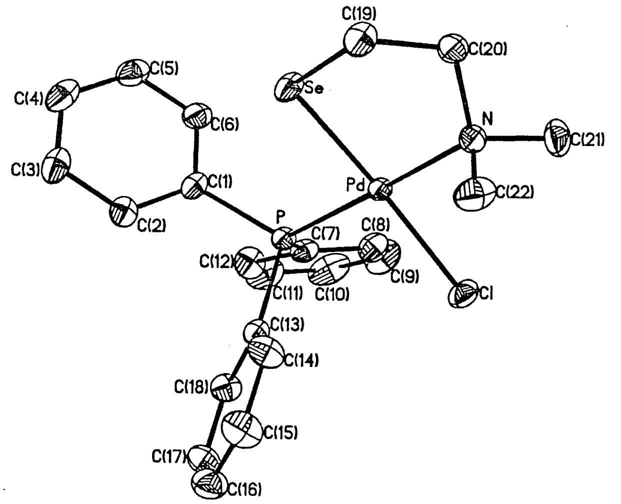


Fig. 3 Molecular structure of [PdCl(SeCH$_2$CH$_2$NMe$_2$)(PPh$_3$)] **2c** with atomic numbering scheme.

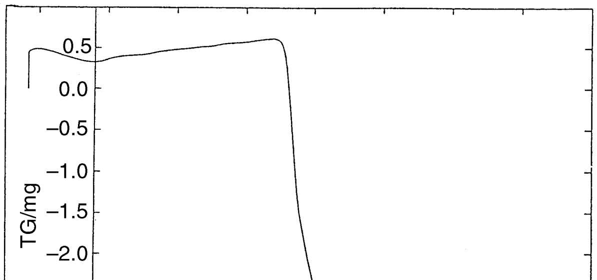


Fig. 4 TG curve of [PdCl(SeCH$_2$CH$_2$NMe$_2$)]$_3$ **1**.

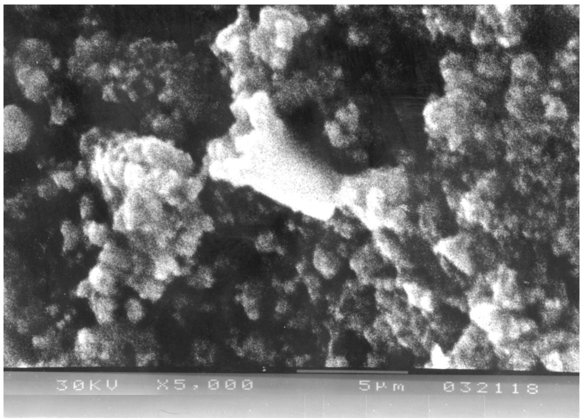


Fig. 5 SEM picture of Pd$_{17}$Se$_{15}$ obtained from [PdCl(SeCH$_2$CH$_2$NMe$_2$)]$_3$ **1**.

(detection limit 0.2%). Calc. for Pd$_{17}$Se$_{15}$: Pd, 60.9; Se, 39.6%] are consistent with the Pd$_{17}$Se$_{15}$ formulation. The complex [PdCl(SeCH$_2$CH$_2$NMe$_2$)(PPh$_3$)] **2c** also decomposes *via* two steps resulting in Pd$_{17}$Se$_{15}$ at 350 °C (from calculated mass loss), as confirmed by the XRD pattern. The intermediate steps could not be identified because of superimposition.

To prepare large quantities of palladium selenide, a substantial amount of precursors (**1**, **2c**, **2d**) (100–500 mg) was heated in a furnace under a dry flowing argon atmosphere and then annealed at 400 (**1**), 450 (**2c**) and 400 °C (**2d**). The Pd$_{17}$Se$_{15}$ thus obtained showed a similar XRD pattern to that of samples obtained from TG, indicating formation of the same product in each case. The XRD pattern of these products has been interpreted in terms of a cubic structure with the lattice parameter 10.584(1) Å. The X-ray diffraction patterns are in compliance with patterns reported for the standard compound.[28] The surface morphology of these products was studied by the SEM technique. The scanning electron micrographs (Fig. 5) of Pd$_{17}$Se$_{15}$ taken at different resolutions showed large aggregates of microcrystals.

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