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Palladium(II) and platinum(II) 2-(methoxycarbonyl)ethylselenolates: Synthesis, spectroscopy, structures and their conversion into metal selenide

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Abstract

A diselenide, $(MeOOCCH_2CH_2Se)_2$ (**1**) has been prepared by esterification of $(HOOCCH_2CH_2Se)_2$ in methanol. The reductive cleavage of Se–Se bond in **1** by $NaBH_4$ in methanol generates $MeOOCCH_2CH_2SeNa$. The latter in different stoichiometries reacts with $[M_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ to give a variety of products of compositions $[M_2Cl_2(\mu\text{-}SeCH_2CH_2COOMe)_2(PR_3)_2]$ (**2**); $[M_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeCH_2CH_2COOMe)(PR_3)_2]$ (**3**); $[Pd_2(SeCH_2CH_2COOMe)_2(\mu\text{-}SeCH_2CH_2COOMe)_2(PR_3)_2]$ (**4**); $[Pd_3Cl_2(\mu\text{-}SeCH_2CH_2COOMe)_4(PR_3)_2]$ (**5**). Treatment of complexes **2** with $[M_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ affords complexes **3** in nearly quantitative yield. The formation of various products in these reactions is sensitive to stoichiometric ratio of reactants employed. This enables interconversion of various complexes by manipulating mole ratios of appropriate starting materials. A homoleptic palladium complex, $[Pd(SeCH_2CH_2COOMe)_2]_6$ (**6**) was isolated from a reaction between Na_2PdCl_4 and $MeOOCCH_2CH_2SeNa$. All these complexes have been characterized by elemental analysis, IR, UV–Vis and NMR (^{1}H, ^{13}C, ^{31}P, ^{77}Se, ^{195}Pt) spectroscopy. Structures of *trans*-$[Pd_2Cl_2(\mu\text{-}SeCH_2CH_2COOMe)_2(PPh_3)_2]$ (**2d**), $[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeCH_2CH_2COOMe)(P^{n}Pr_3)_2]$ (**3e**), $[Pd_3Cl_2(\mu\text{-}SeCH_2CH_2COOMe)_4(P^{n}Pr_3)_2]$ (**5**) and $[Pd(SeCH_2CH_2COOMe)_2]_6$ (**6**) have been established unambiguously by X-ray crystallography. In these complexes, there are bridging selenolate ligands with their uncoordinated ester groups. Compound **6** has a centrosymmetric Pd_6Se_{12} hexagon in which every two palladium atoms are bridged by selenolate ligands. Thermal behaviour of some complexes has been investigated. Pyrolysis of compound **2b** in tributylphosphate at 195 °C gave $Pd_{17}Se_{15}$ nanoparticles which were characterized by XRD and EDAX.

Keywords: Palladium; Platinum; Selenolates; NMR; Palladium selenide; X-ray

1. Introduction

The chemistry of platinum group metals with chalcogenolate ligands has been a subject area of considerable research for more than two decades [1]. There are several obvious reasons for the sustained interest in this area as these complexes show a rich structural diversity [1] and have relevance in catalysis [2]. More recently, their role as molecular precursors for the synthesis of metal chalcogenides (M_xE_y; M = Pd or Pt; E = S, Se, Te) for electronic devices has been demonstrated [3,4]. The area of metal chalcogenolates is dominated by molecules containing M–SR linkage. In most cases these molecules are isolated as nonvolatile, insoluble (or sparingly soluble) polymeric species, limiting their utility as precursors for the synthesis of metal chalcogenides. Several strategies have been developed to suppress polymerization, the use of hybrid ligands has been quite successful. Recently we have employed internally functionalized hemi-labile ligands like pyridine-2-chalcogenolates [5,6] and dimethylaminoalkyl chalcogenolates, $Me_2N(CH_2)_nE^-$ [7–12]. These ligands have not only shown versatile coordination chemistry but their complexes

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have also served as precursors for the synthesis of metal chalcogenides [5–7] as well as for the study of metal mediated donor–acceptor interactions [8,9]. The continued interest in selenium/tellurium containing inorganic materials [13–15] and in pursuance of our work on design and development of precursors for chalcogenide materials, we have now synthesized $(MeOOCCH_2CH_2Se)_2$ and explored the chemistry of its palladium and platinum complexes. Results of this work are reported herein.

2. Results and discussion

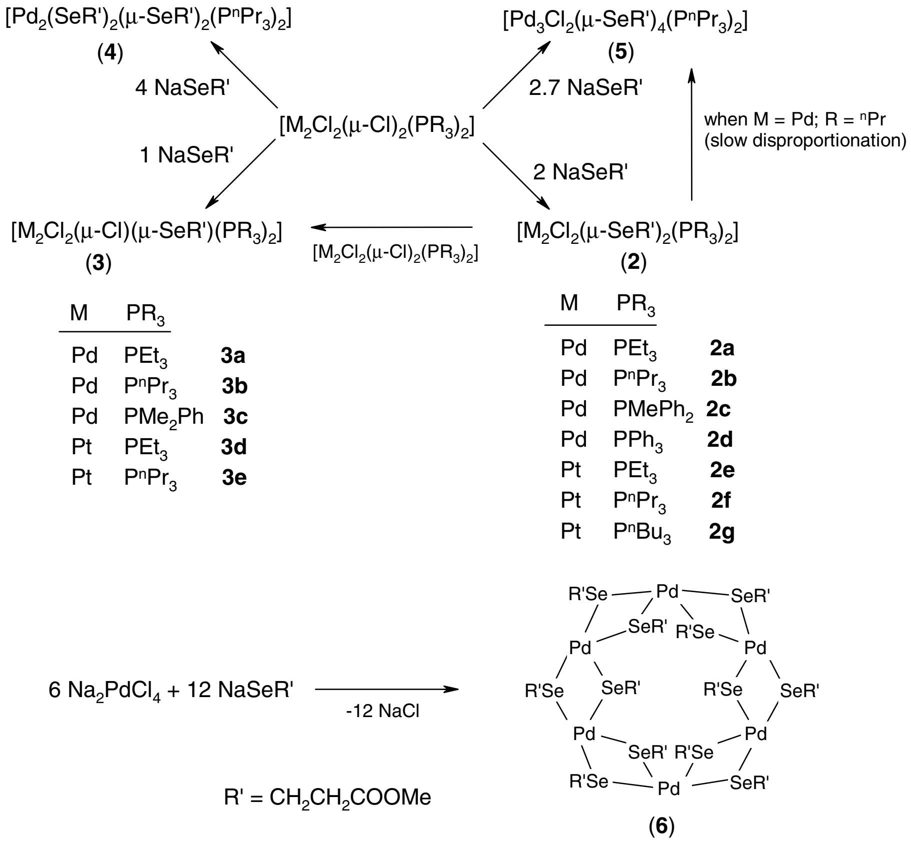
2.1. Synthesis

Esterification of $(HOOCCH_2CH_2Se)_2$ in methanol in the presence of concentrated sulfuric acid gave the corresponding methyl ester, $(MeOOCCH_2CH_2Se)_2$ (**1**), as a yellow orange oil which can be purified by distillation under vacuum. Reductive cleavage of the Se–Se bond in **1** with sodium borohydride in methanol gave $NaSeCH_2CH_2COOMe$ which was used *in situ* for the reactions with palladium and platinum complexes. Reaction of $[M_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ with 2 equiv. of $NaSeCH_2CH_2COOMe$ gave binuclear selenolate-bridged complexes of composition, $[M_2Cl_2(\mu\text{-}SeCH_2CH_2COOMe)_2(PR_3)_2]$ (**2**) which were isolated as a mixture of *syn-cis* and *trans* isomers. The reaction in 1:1 stoichiometry, however, afforded mixed chloro/selenolato bridged *cis* complexes; $[M_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeCH_2CH_2COOMe)(PR_3)_2]$ (**3**) (Scheme 1). The latter were isolated in quantitative yields on treatment of $[M_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ with the complexes **2**.

Reaction of $[Pd_2Cl_2(\mu\text{-}Cl)_2(P^nPr_3)_2]$ with 2.7 and 4 equiv. of $NaSeCH_2CH_2COOMe$ gave $[Pd_3Cl_2(\mu\text{-}SeCH_2CH_2COOMe)_4(P^nPr_3)_2]$ (**5**) (red solid) and $[Pd_2(SeCH_2CH_2COOMe)_4(P^nPr_3)_2]$ (**4**) (red oil), respectively. Compound **5** was also isolated in poor yields as disproportionation product when **2b** was left for recrystallization. Reaction of Na_2PdCl_4 with 2 equiv. of $NaSeCH_2CH_2COOMe$ in methanol afforded a homoleptic hexanuclear palladium complex, $[Pd(SeCH_2CH_2COOMe)_2]_6$ (**6**).

2.2. Spectroscopy

The IR spectra of compound **1** and palladium/platinum complexes exhibited an absorption band at ~1730 cm^{-1} due to the carbonyl group. The corresponding complexes **2** and **3** showed a band in the region 302–322 cm^{-1} assignable to ν_{M-Cl} stretchings [16]. The electronic spectra of compound **1** as well as complexes displayed absorptions in the region 235–439 nm. The absorptions with $\lambda_{max} <$ 308 nm can be attributed to the transitions in the electron rich selenolate group while bands having $\lambda_{max} >$ 308 nm may be assigned to a ligand(Se)-to-ligand(PR_3) charge transfer (LL′CT) transition [8,9]. This transition has lower energy for complexes **3** than the corresponding complexes **2**. Aggregation in complexes **5** and **6** further shifts these



Scheme 1.

transition to lower energies due to increased orbital interaction. The palladium complexes showed absorptions at lower energies than the corresponding platinum analogues.

The ^{1}H NMR spectra of complexes **2** showed expected resonances and peak multiplicities. The ^{31}P{^{1}H} NMR spectra displayed two signals assignable to *cis* and *trans* isomers. Resonances for platinum complexes were flanked by the satellites of ^{195}Pt isotope with $^{1}J(^{195}\text{Pt}–^{31}\text{P})$ values of ~3100 Hz which can be compared with the couplings reported for $[\text{Pt}_2\text{Cl}_2(\mu\text{-ER})_2(\text{PR}_3)_2]$ (E = S, Se, Te) [17–20]. The signal with larger $^{1}J(\text{Pt–P})$ value is assigned to the *cis* isomer [21]. The ^{195}Pt{^{1}H} NMR spectra (Fig. 1) showed two doublets due to coupling with phosphorus nucleus. The doublet at higher field (shielding by ~100 ppm) with larger $^{1}J(^{195}\text{Pt}–^{31}\text{P})$ has been assigned to the *cis* isomer. The ^{77}Se{^{1}H} NMR spectra of complexes **2** exhibited three signals (Fig. 2) in the region −47 to −243 ppm. Shielding is higher in platinum complexes than the analogous palladium derivative which reflects weaker bonding of the selenolate in the latter, as a consequence disproportionation is notable (e.g. isolation of complex **5** from **2b**). The signal at ~−240 ppm in platinum complexes is attributed to the *trans* isomer while the remaining two resonances at lower field have been assigned to the *cis* isomer. These signals were flanked by platinum satellites with $^{1}J(^{195}\text{Pt}–^{77}\text{Se})$ of 132–245 Hz. The $^{1}J(^{195}\text{Pt}–^{77}\text{Se})$ in platinum(II) selenolate complexes has been reported in the range 100–472 Hz [8,20].

The ^{1}H, ^{31}P{^{1}H} and ^{77}Se{^{1}H} NMR spectra of complexes **3** showed one set of resonances indicative of the formation of only one isomer exclusively, although three isomeric forms, viz. a *trans* and two *cis*, are possible. The former would give two ^{31}P signals while for the latter only one resonance is expected. The magnitude of $^{1}J(^{195}\text{Pt}–^{77}\text{Se})$ (~3900 Hz) is in conformity with the phosphine *trans* to the bridging chloride. The *cis* configuration with phosphine *trans* to bridging chloride is reported for $[\text{M}_2\text{Cl}_2(\mu\text{-Cl})(\mu\text{-ER})(\text{PR}_3)_2]$ (E = S, Se, Te) [16]. The ^{195}Pt{^{1}H} NMR spectra displayed a doublet at ~−4000 ppm with $^{1}J(^{195}\text{Pt}–^{31}\text{P})$ of ~3900 Hz.

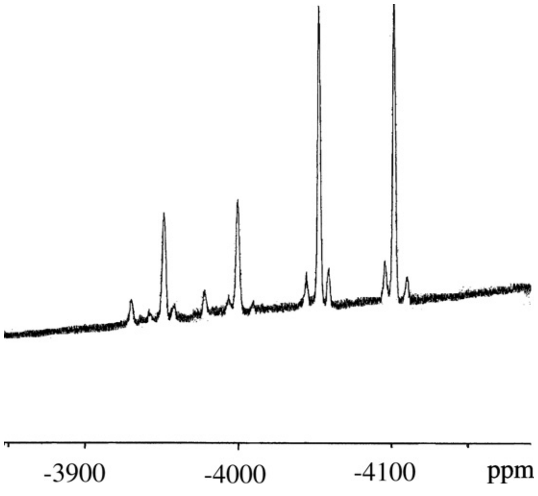


Fig. 1. ^{195}Pt{^{1}H} NMR spectrum of $[\text{Pt}_2\text{Cl}_2(\mu\text{-SeCH}_2\text{CH}_2\text{COOMe})_2(\text{PEt}_3)_2]$ (**2e**) in CDCl_3.

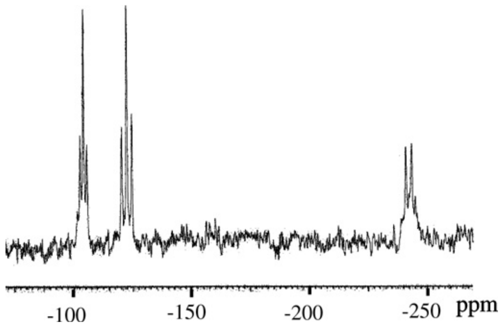


Fig. 2. ^{77}Se{^{1}H} NMR spectrum of $[\text{Pt}_2\text{Cl}_2(\mu\text{-SeCH}_2\text{CH}_2\text{COOMe})_2(\text{PEt}_3)_2]$ (**2e**) in CDCl_3.

The ^{31}P{^{1}H} NMR spectrum of **4** exhibited two peaks which can be assigned to *cis* and *trans* isomers. In the ^{77}Se{^{1}H} NMR spectrum four signals at −271.1, 93.7, 97.7 and 141.5 ppm were observed. The signal at −271.1 ppm may be originated from terminal selenolate group of both the isomers, while the remaining three can be assignated to bridging selenolate groups (93.7 ppm for *trans* and 97.7 and 141.5 ppm for *cis* isomer). This can be supported with the fact that the terminal selenolates are more electron rich than the bridging ones and hence show greater shielding. Similar pattern has been reported for ^{125}Te NMR chemical shifts of $[\text{Cd}\{\text{TeSi(SiMe}_3)_3\}_2]_2$ [1b]. In the ^{31}P{^{1}H} NMR spectra of **5** only a single resonance is observed suggesting the formation of one isomeric species. Except the carbonyl carbon resonance, the ^{13}C{^{1}H} and ^{77}Se{^{1}H} NMR spectra of **6** displayed two sets of resonances. The existence of other oligomeric species in solution may not be ruled out, although in the solid state complex **6** has a symmetrical hexameric structure with bridging selenolate groups (Table 1).

2.3. Crystallography

An ORTEP diagram with atomic number scheme for *trans*-$[\text{Pd}_2\text{Cl}_2(\mu\text{-SeCH}_2\text{CH}_2\text{COOMe})_2(\text{PPh}_3)_2]$ (**2d**) is shown in Fig. 3 and selected bond lengths and angles are given in Table 2. The complex is a centrosymmetric dimer with *syn-trans* configuration. Two square planar palladium atoms are held together by two selenolate groups which adopt an *anti* configuration. The four-membered Pd_2Se_2 ring is planar. In $[\text{Pt}_2\text{Cl}_2(\mu\text{-SeEt})_2(\text{PEt}_3)_2]$ the Pt_2Se_2 ring is planar [17], but in alkyl thiolate derivatives the M_2S_2 ring adopts a non-planar configuration [16]. The Pd–Se distances *trans* to phosphine ligands are longer than those *trans* to terminal chloride due to strong *trans* influence of the PPh_3 ligand. The Pd–Se [4,12], Pd–Cl [22,23] and Pd–P [22,23] distances are in agreement with the reported values. Owing to the strain in the four membered Pd_2Se_2 ring, the Se–Pd–Se angles [82.21(3)°] are reduced significantly from the ideal value of 90°.

Table 1
Crystal data and structure refinement details of *trans*-$[Pd_2Cl_2(\mu\text{-}SeR')_2(PPh_3)_2]\cdot 2H_2O$ (**2d**), $[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeR')(P^nPr_3)_2]$ (**3e**), $[Pd_3Cl_2(\mu\text{-}SeR')_4(P^nPr_3)_2]$ (**5**), $[Pd(\mu\text{-}SeR')_2]_6$ (**6**) ($R' = CH_2CH_2COOMe$)

	2d	**3e**	**5**	**6**
Chemical formula	$C_{44}H_{48}Cl_2O_6P_2Pd_2Se_2$	$C_{22}H_{49}Cl_3O_2P_2Pt_2Se$	$C_{34}H_{70}Cl_2O_8P_2Pd_3Se_4$	$C_{48}H_{84}O_{24}Pd_6Se_{12}$
Formula weight	1176.38	983.04	1374.78	2631.08
Crystal size (mm)	0.15 × 0.12 × 0.10	0.32 × 0.27 × 0.22	0.34 × 0.28 × 0.22	0.44 × 0.33 × 0.31
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Wavelength, Mo Kα (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Tetragonal	Triclinic
Space group	$P\bar{1}$	$P2_{1/n}$	$P\bar{4}2_1c$	$P\bar{1}$
Unit cell dimensions				
a (Å)	10.003(3)	13.487(3)	25.1730(11)	12.110(3)
b (Å)	11.383(4)	18.823(4)	25.1730(11)	12.363(3)
c (Å)	11.647(4)	14.763(3)	16.5105(16)	14.297(4)
α (°)	77.879(5)	90.00	90.00	93.057(5)
β (°)	67.470(5)	112.861(4)	90.00	111.197(5)
γ (°)	86.041(6)	90.00	90.00	98.359(5)
Volume (Å^3)/Z	1197.5(7)/1	3453.4(14)/4	10462.4(12)/8	1961.4(9)/2
μ (mm^{-1})/F(000)	2.492/584	9.488/1872	4.006/5408	6.978/1248
θ Range (°)	1.83–27.5	1.85–26.37	1.81–26.0	1.83–26.7
Limiting indices	$-13 \leqslant h \leqslant 13$, $-14 \leqslant k \leqslant 15$, $-15 \leqslant l \leqslant 15$	$-16 \leqslant h \leqslant 16$, $-23 \leqslant k \leqslant 22$, $-16 \leqslant l \leqslant 18$	$-31 \leqslant h \leqslant 6$, $-25 \leqslant k \leqslant 24$, $-19 \leqslant l \leqslant 20$	$-15 \leqslant h \leqslant 15$, $-15 \leqslant k \leqslant 15$, $-17 \leqslant l \leqslant 17$
Number of reflections/unique	14058/5562	27401/7048	26842/9159	21128/7964
Number of data/restraints/parameters	5562/0/271	7048/0/296	9159/8/488	7964/0/409
Final R_1 [$I > 2\sigma(I)$], ωR_2	0.0489, 0.0756	0.0423, 0.0783	0.0552, 0.1226	0.0462, 0.0934
R_1, ωR_2 (all data)	0.1489, 0.1766	0.1430, 0.1904	0.0971, 0.1204	0.1018, 0.1236
Goodness-of-fit on F^2	0.733	0.687	0.919	0.899

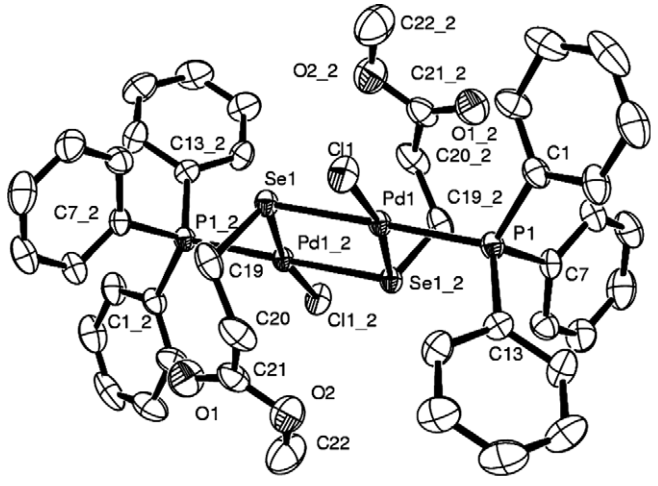


Fig. 3. Molecular structure of *trans*-$[Pd_2Cl_2(\mu\text{-}SeCH_2CH_2COOMe)_2(PPh_3)_2]$ (**2d**) (ORTEP drawn with 50% probability; hydrogen atoms are omitted for clarity).

The molecule $[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeCH_2CH_2COOMe)(P^nPr_3)_2]$ (**3e**) (Fig. 4) has a *syn-cis* configuration with the phosphine ligands mutually *trans* to the bridging chloride. The ester group on Se adopts the axial position relative to the non-planar "PtClSePt" ring. The two Pt–Se bonds are essentially the same (Table 3) and are in agreement with the reported values. Various angles around both the platinum atoms are normal and fall within the expected range. The Pt–Se–Pt angle [88.80 (4)°] is within the range reported for binuclear chalcogenolate bridged complexes (85.5–92.0°) [24].

Table 2
Selected bond lengths (Å) and bond angles (°) for *trans*-$[Pd_2Cl_2(\mu\text{-}SeCH_2CH_2COOMe)_2(PPh_3)_2]$ (**2d**)

Pd1–Se1	2.4590(9)	C21–O1	1.196(9)
Pd1–Se1_2	2.4090(9)	C21–O2	1.313(10)
Pd1–P1	2.3076(16)	C22–O2	1.418(13)
Pd1–Cl1	2.3480(17)	P1–C1	1.826(6)
Se1–C19	1.964(7)	P1–C7	1.816(6)
C19–C20	1.510(12)	P1–C13	1.817(6)
C20–C21	1.509(12)	Pd–Pd	3.696(1)
Se1–Pd1–Se1_2	81.21(3)	C19–Se1–Pd1	99.5(2)
Pd1–Se1–Pd1_2	98.79(3)	C19–Se1_2–Pd1	108.4(2)
Cl1–Pd1–Se1	89.75(5)	Se1–C19–C20	115.0(5)
Cl1–Pd1Se1_2	167.93(5)	C19–C20–C21	113.4(6)
Cl1–Pd1–P1	92.69(5)	Pd1–P1–C1	114.9(2)
P1–Pd1–Se1	177.56(5)	Pd1–P1–C7	115.07(19)
P1–Pd1–Se1_2	96.37(5)	Pd1–P1–C13	111.4(2)

_2 Denotes symmetrical moiety with respect to centre of inversion.

The molecular structure of $[Pd_3Cl_2(\mu\text{-}SeCH_2CH_2COOMe)_4(P^nPr_3)_2]$ (**5**) (Fig. 5) comprises of three distorted square planar palladium atoms which are held together by bridging selenolate groups. The metal square planes are tilted towards each other (plane 1 and plane 2 = 62.08(3)°, plane 1 and plane 3 = 67.20(5)° and plane 2 and plane 3 = 50.85(4)°; where planes 1, 2 and 3 are through Pd(1), Pd(2) and Pd(3), respectively) resulting in a zig-zag shape of the molecule. A similar shape is observed for $[Pd_3Cl_2(\mu\text{-}S\text{-}cyclohexyl)_4(PMe_3)_2]$ [25] and $[Pt_3(\mu\text{-}SC_6H_4Me\text{-}4)_4(dppm)_2]^{2+}$ [26]. The coordination environment around the central palladium and the peripheral metal atoms can be defined by the "$PdSe_4$" and "$PdClPSe_2$"

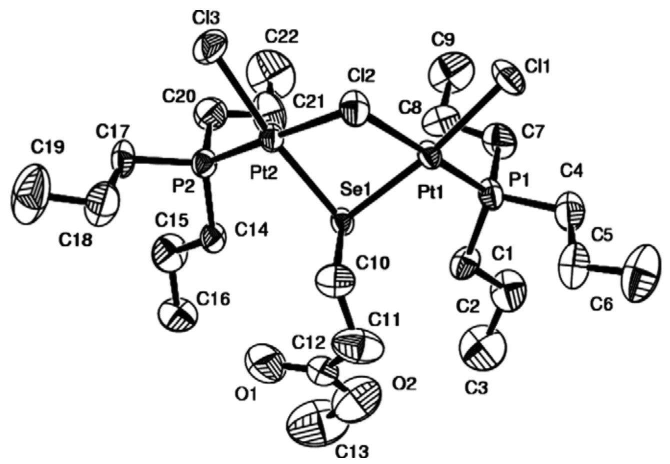


Fig. 4. Molecular structure of $[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeCH_2CH_2COOMe)(P^nPr_3)_2]$ (**3e**) (ORTEP drawn with 50% probability; hydrogen atoms are omitted for clarity).

Table 3
Selected bond lengths (Å) and bond angles (°) for $[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeCH_2CH_2COOMe)(P^nPr_3)_2]$ (**3e**)

Pt1–Se1	2.3819(12)	C11–C12	1.51 (2)
Pt2–Se1	2.3820(12)	C12–O1	1.225(18)
Pt1–P1	2.214(3)	C12–O2	1.228(17)
Pt2–P2	2.217(3)	C13–O2	1.60(3)
Pt1–Cl1	2.338(3)	P1–C1	1.813(13)
Pt1–Cl2	2.424(3)	P1–C4	1.828(15)
Pt2–Cl2	2.430(3)	P1–C7	1.829(15)
Pt2–Cl3	2.331(3)	P2–C14	1.800(12)
Se1–C10	1.981(13)	P2–C17	1.814(12)
C10–C11	1.48 (2)	P2–C20	1.805(20)
Se1–Pt1–Cl2	83.23(8)	Cl2–Pt1–Cl1	91.36(13)
Se1–Pt2–Cl2	83.10(8)	Cl2–Pt2–Cl3	91.60(13)
Se1–Pt1–Cl1	173.11(11)	P1–Pt1–Cl2	178.45(12)
Se1–Pt2–Cl3	173.82(11)	P2–Pt2–Cl3	89.99(13)
Pt1–Se1–Pt2	88.80(4)	P2–Pt2–Cl2	177.84(11)
Pt1–Cl2–Pt2	86.73(9)	P2–Pt2–Se1	95.22(9)
P1–Pt1–Cl1	89.80(13)	Pt1–Se1–C10	102.7(5)
P1–Pt1–Se1	95.54(9)	Pt2–Se1–C10	102.3(4)

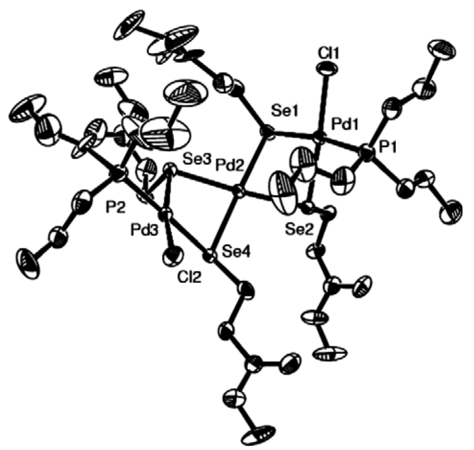


Fig. 5. Molecular structure of $[Pd_3Cl_2(\mu\text{-}SeCH_2CH_2COOMe)_4(P^nPr_3)_2]$ (**5**) (ORTEP drawn with 50% probability; hydrogen atoms are omitted for clarity).

cores. The phosphine ligands are *trans* disposed whereas the $–CH_2CH_2COOMe$ fragments on bridging selenolates are in *anti* conformations. All the four Pd–Se distances for the central palladium atom are essentially similar (Table 4), but for peripheral palladium atoms the Pd–Se distance *trans* to phosphine is longer than the one *trans* to Cl atom. This has been attributed to strong *trans* influence of phosphine ligand. Various angles around palladium atoms are as expected for chalcogenolato-bridged complexes. The Pd–Pd distances (Pd1–Pd2 = 3.352(1) and Pd2–Pd3 = 3.204(1) Å) do not support the existence of metal–metal interactions. A number of trinuclear palladium complexes have been reported and in general they have ‘Y’ shape (e.g., $[M_3(\mu\text{-}S)_2(P^\cap P)]^{2+}$ [7,27]) or triangular structures (e.g., $[Pd(OAc)_2]_3$ [28]). Only few examples with linear chain arrangement, $[Pd_3Cl_2(\mu\text{-}S\text{-cyclohexyl})_4(PMe_3)_2]$ [25] and $[Pd_3(\eta\text{-allyl})_2(\mu\text{-}X)_4]$ (X = OAc, Cl) [29–31], are reported. The structure of complex **4**, to our knowledge, is the first example of selenolato-bridged linear trinuclear palladium complex.

The complex $[Pd(SeCH_2CH_2COOMe)_2]_6$ (**6**) (Fig. 6) has a centrosymmetric hexameric structure in which each palladium atom has a square planar configuration defined by $PdSe_4$ core and each ligand moiety bridges two palladium atoms through Se ends. The PdSe coordination planes are inclined to each other by planes 1 and 2 = 52.92(2), planes 2 and 3 = 61.95(2) and planes 1 and 3 = 65.12(2)° where planes 1, 2 and 3 are through Pd(1), Pd(2) and Pd(3), respectively leading to the formation of Pd_6Se_{12} hexagon. The structure is isomorphous to $[Pd(SeCH_2CH_2CH_2N\text{-}Me_2)_2]_6$ [32] and thiolate complexes $[Pd(SR)_2]_6$

Table 4
Selected bond lengths (Å) and bond angles (°) for $[Pd_3Cl_2(\mu\text{-}SeCH_2CH_2COOMe)_4(P^nPr_3)_2]$ (**5**)

Pd1–Se1	2.4791(15)	Pd2–Se3	2.4363(15)
Pd1–Se2	2.4004(15)	Pd2–Se4	2.4237(15)
P1–Pd1	2.271(4)	Pd3–Se3	2.4050(16)
Cl1–Pd1	2.318(3)	Pd3–Se4	2.4803(16)
C31–Se1	1.935(18)	Cl2–Pd3	2.335(4)
C10–Se2	1.937(12)	P2–Pd3	2.267(4)
Pd2–Se1	2.4267(14)	C14–Se4	1.953(14)
Pd2–Se2	2.4281(15)	C27–Se3	1.976(12)
Pd1–Pd2	3.352 (1)	Pd2–Pd3	3.204 (1)
P1–Pd1–Se1	171.31(11)	Se4–Pd2–Se2	98.17(5)
P1–Pd1–Se2	89.68(11)	Pd2–Se1–Pd1	86.20(5)
P1–Pd1–Cl1	94.00(14)	Pd1–Se2–Pd2	87.94(5)
Cl1–Pd1–Se1	94.25(10)	Pd3–Se3–Pd2	82.92(5)
Cl1–Pd1–Se2	176.14(10)	Pd2–Se4–Pd3	81.63(5)
Se2–Pd1–Se1	82.02(5)		
C31–Se1–Pd1	109.4(7)	Se3–Pd3–Se4	82.10(5)
C31–Se1–Pd2	109.4(6)	P2–Pd3–Se3	92.63(11)
C10–Se2–Pd1	101.8(4)	Cl2–Pd3–Se3	169.14(10)
C10–Se2–Pd2	103.3(4)	P2–Pd3–Se4	173.05(12)
		Cl2–Pd3–Se4	95.29(10)
Se1–Pd2–Se2	82.55(5)	P2–Pd3–Cl2	90.72(14)
Se1–Pd2–Se3	99.05(5)	C27–Se3–Pd3	107.6(4)
Se4–Pd2–Se1	170.07(6)	C27–Se3–Pd2	107.1(4)
Se2–Pd2–Se3	166.20(6)	C14–Se4–Pd2	111.8(4)
Se4–Pd2–Se3	82.64(5)	C14–Se4–Pd3	110.7(4)

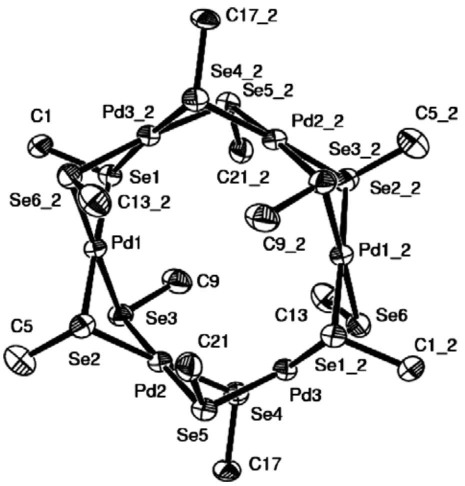


Fig. 6. Molecular structure of $[Pd(\mu\text{-}SeCH_2CH_2COOMe)_2]_6$ (**6**) (ORTEP drawn with 50% probability; except C–Se, other atoms of selenolate ligands as well as all hydrogen atoms are omitted for clarity).

(R = Pr^n [33], CH_2COOMe [34]). The Se–Pd–Se angles around individual palladium atom are acute (~82°; within the ring plane) and obtuse (~97°, parallel to the ring axis) while diagonal angles deviate slightly from ideal value of 180°. The average Pd–Se bond distance of 2.439 Å (Table 5) can be compared with that reported for $[Pd(SeCH_2CH_2\text{-}CH_2NMe_2)_2]_6$ (2.437 Å) [32] and related selenolato-bridged complexes, $[Pd_2Cl_2(\mu\text{-}SeCH_2CH_2\text{-}CH_2NMe_2)_2]$ (2.3858 (7) and 2.4037(7) Å) [10] and $[Pd_2(SePh)_4(PPh_3)_2]$ (2.464(2), 2.494(2) Å) [35]. The Pd–Pd separation of 3.1656(10) and 3.2082(10) Å is shorter than the sum of the van der Waals radii for two Pd atoms (3.26 Å). These distances can be compared to $[Pd(SeCH_2CH_2CH_2NMe_2)_2]_6$.

Table 5
Selected bond lengths (Å) and bond angles (°) for $[Pd(\mu\text{-}SeCH_2CH_2\text{-}COOMe)_2]_6$ (**6**)

Pd1–Se1	2.4405(11)	Pd3–Se5	2.4413(12)
Pd1–Se2	2.4348(11)	Pd3–Se6	2.4368(12)
Pd1–Se3	2.4467(11)	Pd3–Se1_2	2.4397(12)
Pd1–Se6_2	2.4419(11)	Se1–C1	1.971(8)
Pd2–Se2	2.4353(11)	Se2–C5	1.984(9)
Pd2–Se3	2.4396(11)	Se3–C9	1.984(8)
Pd2–Se4	2.4441(11)	Se4–C17	1.973(8)
Pd2–Se5	2.4337(11)	Se5–C21	1.977(8)
Pd3–Se4	2.4427(12)	Se6–C13	1.987(9)
Se2–Pd1–Se1	178.25(4)	Se6–Pd3–Se1_2	82.79(3)
Se1–Pd1–Se3	96.16(4)	Se6–Pd3–Se5	175.29(4)
Se1–Pd1–Se6	82.66(3)	Se6–Pd3–Se4	97.31(4)
Se2–Pd1–Se3	83.95(3)	Se5–Pd3–Se4	82.38(3)
Se2–Pd1–Se6_2	97.21(4)	Se1_2–Pd3–Se5	97.11(4)
Se6_2–Pd1–Se3	178.71(4)	Se1_2–Pd3–Se4	175.06(4)
Se2–Pd2–Se3	84.09(4)	Pd1–Se2–Pd2	84.59(4)
Se2–Pd2–Se4	177.30(4)	Pd1–Se3–Pd2	84.24(4)
Se5–Pd2–Se2	96.10(4)	Pd2–Se5–Pd3	82.31(3)
Se5–Pd2–Se3	177.96(4)	Pd2–Se4–Pd3	82.07(4)
Se3–Pd2–Se4	97.22(4)	Pd3–Se1_2–Pd1–2	80.88(3)
Se5–Pd2–Se4	82.51(4)	Pd3–Se6–Pd1_2	80.91(3)

_2 Denotes symmetrical moiety with respect to centre of inversion.

2.4. Thermal behaviour

The TG curves of $[M_2Cl_2(\mu\text{-}SeCH_2CH_2COOMe)_2\text{-}(P^nPr)_2]$ (M = Pd (**2b**); Pt (**2f**)) showed a two step decomposition with the formation of $Pd_{17}Se_{15}$ and Pt_5Se_4, respectively as suggested from weight loss (Calc. for $Pd_{17}Se_{15}$ = 62.4%; Found = 64%. Calc. for Pt_5Se_4 = 53.6%; Found = 54%). The complex **2b** was pyrolized in a furnace at 315 °C. The XRD pattern can be compared with the standard patterns reported for $Pd_{17}Se_{15}$. Solvothermal decomposition of **2b** in TBP at 195 °C for 1 h gave a black residue which has been identified as $Pd_{17}Se_{15}$ from XRD (Fig. 7) [36] and EDAX (Calc.: Pd = 60.4%; Se = 39.6%. Found for **2b**: Pd = 62.9%; Se = 37.1% (furnace heating) and Pd = 63.0%; Se = 37.0% (solvothermal)). The broadening observed in the XRD peaks of the sample obtained from complex **2b** suggested that the particles were in the nanometer regime.

3. Experimental

3.1. General

Microanalyses were carried out on a Carlo-Erba EA-1110 CHN-O instrument. UV–Vis absorption spectra were recorded in CH_2Cl_2 on a Chemito Spectrascan double

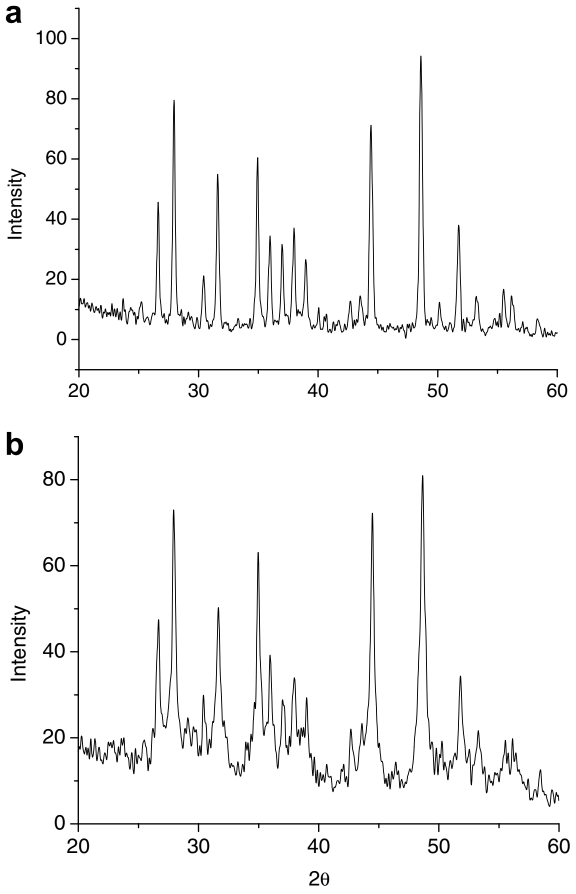


Fig. 7. XRD pattern of $Pd_{17}Se_{15}$ obtained from $[Pd_2Cl_2(\mu\text{-}SeCH_2CH_2\text{-}COOMe)_2(P^nPr_3)_2]$ (**2b**) by heating in (a) furnace, (b) TBP.

beam UV–Vis spectrophotometer. ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, $^{77}Se\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra were recorded in $CDCl_3$ on a Bruker DPX-300 NMR spectrometer operating at 300, 75.47, 121.49, 57.24 and 64.52 MHz, respectively and chemical shifts are relative to internal $CHCl_3$ for ^1H and ^{13}C, external 85% H_3PO_4 for $^{31}P\{^1H\}$, Me_2Se for ^{77}Se (secondary reference Ph_2Se_2, δ 463 ppm) and Na_2PtCl_6 in D_2O for $^{195}Pt\{^1H\}$. TG curves were obtained at a heating rate of 10 °C min^{-1} under flowing argon on a Setaram 92-16.18 instrument. Solvothermal decomposition of $[Pd_2Cl_2(\mu\text{-}SeCH_2CH_2COOMe)_2(P^nPr_3)_2]$ (**2b**) was carried out by adding a saturated dichloromethane solution of the complex to preheated tributyl phosphate (TBP) at 195 °C with stirring under an argon atmosphere. The black residue was separated by centrifugation which was repeatedly washed with ethanol and dried under vacuum. Powder XRD patterns were recorded on a Philips PW 1710 using Cu Kα radiation.

3.2. Materials

The complexes, Na_2PdCl_4, K_2PtCl_4 and $[M_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ (M = Pd, Pt; PR_3 = PEt_3, P^nPr_3, P^nBu_3, PMe_2Ph, $PMePh_2$, PPh_3) were prepared according to literature methods [37]. 3,3′-Diselenopropionic acid, $(HOOCCH_2CH_2Se)_2$ was prepared by reacting an aqueous Na_2Se_2 solution with 3-bromo propionic acid (1:2 mol) and recrystallized from hot water, in 63% yield [38]. All reactions were carried out under argon in dry and distilled solvents.

3.3. Preparation of the ligand $(MeOOCCH_2CH_2Se)_2$ (*1*)

A methanolic solution (25 cm^3) of $(HOOCCH_2CH_2Se)_2$ (3.5 g, 11.5 mmol) containing 2 cm^3 of conc. H_2SO_4 was refluxed for 24 h. Excess methanol was distilled out and the resulting contents were dissolved in ether (25 cm^3). Ether solution was repeatedly washed with three portions (10 cm^3) of water and dried over anhydrous sodium sulfate. The solvent was stripped off by distillation and the residue was distilled off under reduced pressure (2 mm) at 145 °C as a yellow-orange oil. Yield: 2.6 g (68%). Anal. Calc. for $C_8H_{14}O_4Se_2$: C, 28.9; H, 4.2. Found: C, 29.3; H, 4.2%. IR (Nujol) $\nu_{C=O}$: 1734 cm^{-1}. UV–Vis (CH_2Cl_2), λ (ε, M^{-1} cm^{-1}): 235 (867), 307 (552) nm. ^1H NMR ($CDCl_3$): 2.81 (t, 7.2 Hz, 4H, $SeCH_2$); 3.09 (t, 7.1 Hz, 4H, $SeCH_2CH_2$); 3.69 (s, 6H, COOMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 23.3 (COO*Me*); 35.7 ($SeCH_2$); 51.6 ($SeCH_2CH_2$); 172.2 (CO). $^{77}Se\{^1H\}$ NMR ($CDCl_3$): 325.4 ppm. *Caution: Skin contact should be avoided as it causes rashes/itching. Wash with soap solution.*

3.4. Preparation of complexes

3.4.1. $[Pd_2Cl_2(\mu\text{-}SeCH_2CH_2COOMe)_2(PEt_3)_2]$ (**2a**)

A dichloromethane solution (15 cm^3) of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2]$ (247 mg, 0.42 mmol) was added to a methanolic solution (10 cm^3) of $NaSeCH_2CH_2COOMe$ [prepared from $(MeOOCCH_2CH_2Se)_2$ (141 mg, 0.43 mmol) and $NaBH_4$ (32 mg, 0.84 mmol)]. Reaction mixture was stirred under argon for 1 h to obtain an orange solution. The solvents were evaporated under vacuum and the residue was extracted with dichloromethane (20 cm^3). The dichloromethane solution was passed through a Florisil column (0.5 cm × 7 cm) and dried to give an orange oil which was dissolved in CH_2Cl_2–ethyl acetate–hexane mixture and refrigerated to yield orange crystals of the title complex in 45% yield (159 mg); mp = 99–100 °C. Anal. Calc. for $C_{20}H_{44}Cl_2O_4P_2Pd_2Se_2$: C, 28.2; H, 5.2. Found: C, 27.8; H, 5.1%. IR (Nujol) ν, cm^{-1}: 1728 (C=O); 314 (Pd–Cl). UV–Vis (CH_2Cl_2), λ (ε, M^{-1} cm^{-1}): 236 (2.7×10^4), 274 (1.8×10^4), 340 (1.9×10^4) nm. ^1H NMR ($CDCl_3$): 1.22 (m, 18H, PCH_2CH_3); 1.92 (m, 12H, PCH_2–); 2.79 (q) 2.88 (q) ($SeCH_2$ for *cis* and *trans*); 3.06 (t, 8 Hz, –CH_2–); 3.22–3.26 (m, –CH_2–); 3.64, 3.70 (each s, COOMe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 21.7; 23.6 (s). $^{77}Se\{^1H\}$ NMR ($CDCl_3$): −47.0 (t, $^2J(^{77}Se\text{–}^{31}P)$ = 135 Hz, *trans* isomer); −74.7, −99.8 ppm (each s, *cis* isomer).

3.4.2. $[Pd_2Cl_2(\mu\text{-}SeCH_2CH_2COOMe)_2(P^nPr_3)_2]$ (**2b**)

Prepared similar to complex **2a** from $[Pd_2Cl_2(\mu\text{-}Cl)_2(P^nPr_3)_2]$ (559 mg, 0.83 mmol) and $NaSeCH_2CH_2COOMe$ [$(MeOOCCH_2CH_2Se)_2$ (280 mg, 0.84 mmol) and $NaBH_4$ (65 mg, 1.71 mmol)] and recrystallized from ethyl acetate–hexane in 58% yield (450 mg); mp = 120–121 °C. Anal. Calc. for $C_{26}H_{56}Cl_2O_4P_2Pd_2Se_2$: C, 33.4; H, 6.0. Found: C, 33.9; H, 6.0%. IR (Nujol) ν, cm^{-1}: 1734 (C=O); 316 (Pd–Cl). UV–Vis (CH_2Cl_2), λ (ε, M^{-1} cm^{-1}): 238 (2.4×10^4), 274 (1.7×10^4), 295 (1.5×10^4), 338 nm (1.9×10^4). ^1H NMR ($CDCl_3$): 1.07 (t, 7 Hz, 18H, $PCH_2CH_2CH_3$); 1.56–1.68 (m, 12H, PCH_2CH_2); 1.81–1.90 (m, 12H, PCH_2–); 2.76 (q), 2.87 (*cis*/*trans* $SeCH_2$–); 3.04 (t, 7 Hz, –CH_2–); 3.18–3.23 (m, –CH_2–); 3.63, 3.70 (each s, *cis* and *trans* isomer). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 12.9; 14.3 (s). $^{77}Se\{^1H\}$ NMR ($CDCl_3$): −79.4 (s, *trans* isomer); −58.8, −107.6 (*cis* isomer).

3.4.3. $[Pd_2Cl_2(\mu\text{-}SeCH_2CH_2COOMe)_2(PMePh_2)_2]$ (**2c**)

Prepared similar to complex **2a** from $[Pd_2Cl_2(\mu\text{-}Cl)_2(PMePh_2)_2]$ (245 mg, 0.32 mmol) and $NaSeCH_2CH_2COOMe$ [$(MeOOCCH_2CH_2Se)_2$ (113 mg, 0.34 mmol) and $NaBH_4$ (26 mg, 0.68 mmol)] and recrystallized from $CHCl_3$–ether–hexane in 62% yield (203 mg); mp = 179–180 °C. Anal. Calc. for $C_{34}H_{40}Cl_2O_4P_2Pd_2Se_2$: C, 40.2; H, 4.0. Found: C, 40.0; H, 3.8%. IR (Nujol) ν, cm^{-1}: 1730 (C=O). UV–Vis (CH_2Cl_2), λ (ε, M^{-1} cm^{-1}): 235 (3.5×10^4), 275 (2.1×10^4), 353 (2.2×10^4) nm. ^1H NMR ($CDCl_3$): 1.94 (t, 6.8 Hz); 2.11(d, 10.8 Hz, PMe); 2.20 (d, 10.6 Hz, PMe), 3.20 (t, 8 Hz) 3.44 (m, –CH_2–), 3.60, 3.69 (each 1:1 *cis* isomer), 3.72 (*trans* isomer) (COOMe); 7.19–7.35 [m, Ph]. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 8.6 (s, *cis* isomer); 10.6 (s, *trans* isomer).

3.4.4. $[Pd_2Cl_2(\mu\text{-}SeCH_2CH_2COOMe)_2(PPh_3)_2]$ (**2d**)

Prepared similar to complex **2a** from $[Pd_2Cl_2(\mu\text{-}Cl)_2(PPh_3)_2]$ (249 mg, 0.28 mmol) and $NaSeCH_2CH_2COOMe$ $[(MeOOCCH_2CH_2Se)_2$ (99 mg, 0.30 mmol) and $NaBH_4$ (22 mg, 0.59 mmol)] and recrystallization by $CHCl_3$–ether–hexane in 59% yield (192 mg); mp = 160–161 °C. Anal. Calc. for $C_{44}H_{44}Cl_2O_4P_2Pd_2Se_2$: C, 46.3; H, 3.9. Found: C, 46.2; H, 3.9%. IR (Nujol) ν, cm^{-1}: 1733 (C=O), 302 (Pd–Cl). UV–Vis (CH_2Cl_2), λ (ε, $M^{-1}\,cm^{-1}$): 235 (4.1×10^4), 308 (1.7×10^4), 361 (2.4×10^4) nm. ^1H NMR ($CDCl_3$): 1.94 (t, 7 Hz); 2.14 (t, 7 Hz); 3.20 (t, 8 Hz), 3.48 (m) ($-CH_2-$); 3.61 (s), 3.63 (s) (*cis*); 3.65 (s, *trans*) (COOMe); 7.30–7.68 (m, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 19.6, 22.6 (each s 1:1); 20.4 (br); 36.6, 38.0 (each singlet 1:1); 51.6, 51.9 (each singlet 1:1); 51.8 (s), 128.1–134.8 (complex pattern, Ph). 170.9, 171.9, 172.7 (each s, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 20.2 (s, *cis*); 23.1 (s, *trans*).

3.4.5. $[Pt_2Cl_2(\mu\text{-}SeCH_2CH_2COOMe)_2(PEt_3)_2]$ (**2e**)

Prepared similar to complex **2a** from $[Pt_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2]$ (210 mg, 0.27 mmol) and $NaSeCH_2CH_2COOMe$ $[(MeOOCCH_2CH_2Se)_2$ (95 mg, 0.29 mmol) and $NaBH_4$ (22 mg, 0.57 mmol)] and recrystallized from ethyl acetate–hexane as yellow crystalline solid in 46% yield (128 mg); mp = 123–125 °C. Anal. Calc. for $C_{20}H_{44}Cl_2O_4P_2Pt_2Se_2$: C, 23.3; H, 4.3. Found: C, 23.6; H, 4.1%. IR (Nujol) ν, cm^{-1}: 1734 (C=O). UV–Vis (CH_2Cl_2), λ (ε, $M^{-1}\,cm^{-1}$): 248 (2.0×10^4), 266 (2.0×10^4), 311 (sh, 6.6×10^4) nm. ^1H NMR ($CDCl_3$): 1.18 (m, 18H, PCH_2CH_3); 1.88 (m, 12H, PCH_2); 2.80 ($SeCH_2$); 2.90 ($SeCH_2$); 3.15 (t, 7 Hz, $-CH_2-$) 3.40 (br, $-CH_2-$); 3.64 (s, *trans* isomer, COOMe); 3.69 (s, *cis* isomer, COOMe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 7.8 $[^1J(^{195}Pt–^{31}P) = 3166$ Hz (*cis* isomer)]; 8.6 $[^1J(^{195}Pt–^{31}P) = 3111$ Hz (*trans* isomer)]. $^{77}Se\{^1H\}$ NMR ($CDCl_3$): −104.2 [t, $^1J(^{195}Pt–^{77}Se) = 168$ Hz], −122.4 [t, $^1J(^{195}Pt–^{77}Se) = 241$ Hz] (*cis* isomer); −242.4 [d, $(^{195}Pt–^{77}Se) = 143$ Hz] (*trans* isomer). $^{195}Pt\{^1H\}$ NMR ($CDCl_3$): −3976 [(d, $^1J(Pt–P) = 3110$ Hz, $^2J(^{195}Pt–^{195}Pt) = 1015$ Hz)] (*trans* isomer); −4073 [(d, $^1J(^{195}Pt–^{31}P) = 3161$ Hz, $^2J(^{195}Pt–^{195}Pt) = 943$ Hz)] (*cis* isomer).

3.4.6. $[Pt_2Cl_2(\mu\text{-}SeCH_2CH_2COOMe)_2(P^nPr_3)_2]$ (**2f**)

Prepared similar to complex **2a** from $[Pt_2Cl_2(\mu\text{-}Cl)_2(P^nPr_3)_2]$ (170 mg, 0.20 mmol) and $NaSeCH_2CH_2COOMe$ $[(MeOOCCH_2CH_2Se)_2$ (69 mg, 0.21 mmol) and $NaBH_4$ (16 mg, 0.42 mmol)] and recrystallized from ethyl acetate–hexane in 54% yield (120 mg); mp = 144–146 °C. Anal. Calc. for $C_{26}H_{56}Cl_2O_4P_2Pt_2Se_2$: C, 28.0; H, 5.1. Found: C, 28.3; H, 4.9%. IR (Nujol) ν, cm^{-1}: 1732 (C=O), 312 (Pt–Cl). UV–Vis (CH_2Cl_2), λ (ε, $M^{-1}\,cm^{-1}$): 247 (2.7×10^4), 267 (2.7×10^4), 309 (9.4×10^3) nm. ^1H NMR ($CDCl_3$): 1.07 (t, 7 Hz, 18H, $PCH_2CH_2CH_3$); 1.61 (m, 12H, PCH_2CH_2); 1.85 (m, 12H, PCH_2); 2.78 (t, $SeCH_2$); 2.92 (t, $SeCH_2$); 3.15 (t, CH_2) 3.40 (br, $-CH_2-$); 3.64 (s, *trans* isomer, COOMe); 3.70 (s, *cis* isomer, COOMe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): −1.0 ppm $[^1J(^{195}Pt–^{31}P) = 3141$ Hz, $^2J(^{77}Se–^{31}P) = 122$ Hz] (*cis* isomer); −0.1 $[^1J(^{195}Pt–^{31}P) = 3090$ Hz] (*trans* isomer). $^{77}Se\{^1H\}$ NMR ($CDCl_3$): −106.5 [t, $^1J(^{195}Pt–^{77}Se) = 177$ Hz]; −128.1 $[^1J(^{195}Pt–^{77}Se) = 242$ Hz] (*cis* isomer); −241.0 [(d, $J(^{195}Pt–^{31}P) = 144$ Hz, $J(^{195}Pt–^{77}Se) = 132$ Hz] (*trans* isomer). $^{195}Pt\{^1H\}$ NMR ($CDCl_3$): −3960 [d, $^1J(^{195}Pt–^{31}P) = 3102$ Hz, $^2J(^{195}Pt–^{195}Pt) = 986$ Hz] (*trans* isomer); −4056 [d, $^1J(^{195}Pt–^{31}P) = 3160$ Hz, $^2J(^{195}Pt– ^{195}Pt) = 922$ Hz) (*cis* isomer).

3.4.7. $[Pt_2Cl_2(\mu\text{-}SeCH_2CH_2COOMe)_2(P^nBu_3)_2]$ (**2g**)

Prepared similar to complex **2a** from $[Pt_2Cl_2(\mu\text{-}Cl)_2(P^nBu_3)_2]$ (145 mg, 0.16 mmol) and $NaSeCH_2CH_2COOMe$ $[(MeOOCCH_2CH_2Se)_2$ (51 mg, 0.16 mmol) and $NaBH_4$ (12 mg, 0.31 mmol)] and recrystallized from ethyl acetate–hexane in 62% yield (115 mg); mp 110–112 °C. Anal. Calc. for $C_{32}H_{68}Cl_2O_4P_2Pt_2Se_2$: C, 32.1; H, 5.7. Found: C, 32.5; H, 5.7%. IR (Nujol) ν, cm^{-1}: 1737 (C=O), 310 cm^{-1} (Pt–Cl). UV–Vis (CH_2Cl_2), λ (ε, $M^{-1}\,cm^{-1}$): 246 (2.3×10^4), 268 (2.3×10^4), 309 (8.6×10^3) nm. ^1H NMR ($CDCl_3$): 0.95 (t, 7 Hz, 18H, $PCH_2CH_2CH_2CH_3$); 1.44–1.55 (br, m, 24H, $PCH_2CH_2CH_2$); 1.86 (br, 12H, PCH_2); 2.81 (br, $SeCH_2$); 2.99 (br, $SeCH_2$); 3.24 (br, $-CH_2-$) 3.34 (br, $-CH_2-$); 3.63 (s, *trans* isomer), 3.69 (s, *cis* isomer) (COOMe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): −0.3 $[^1J(^{195}Pt–^{31}P) = 3133$ Hz, $^2J(^{77}Se–^{31}P) = 122$ Hz] (*cis* isomer); 0.9 ppm $[^1J(^{195}Pt–^{31}P) = 3105$ Hz] (*trans* isomer). $^{77}Se\{^1H\}$ NMR ($CDCl_3$): −113.6 $[^1J(^{195}Pt–^{77}Se) = 183$ Hz]; −139.9 $[^1J(^{195}Pt–^{77}Se) = 245$ Hz] (*cis* isomer); −243.1 [d, $J(^{77}Se–^{31}P) = 143$ Hz, $J(^{195}Pt–^{77}Se) = 190$ Hz] (*trans* isomer). $^{195}Pt\{^1H\}$ NMR ($CDCl_3$): −3964 (d, $^1J(^{195}Pt–^{31}P) = 3111$ Hz, *trans* isomer); −4051 [d, $^1J(^{195}Pt–^{31}P) = 3135$ Hz, $^2J(^{195}Pt–^{195}Pt) = 1007$ Hz] (*cis* isomer).

3.4.8. $[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeCH_2CH_2COOMe)(PEt_3)_2]$ (**3a**)

A dichloromethane solution (10 cm^3) of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2]$ (59 mg, 0.10 mmol) was added to a solution (10 cm^3) of $[Pd_2Cl_2(\mu\text{-}SeCH_2CH_2COOMe)_2(PEt_3)_2]$ (85 mg, 0.10 mmol) in the same solvent. The resulting light orange solution was stirred for 1 h. The solvent was removed under vacuum to yield a yellow solid which was recrystallized from CH_2Cl_2–hexane at −10 °C as deep yellow crystals (yield 123 mg, 86%); mp = 156–157 °C. Anal. Calc. for $C_{16}H_{37}Cl_3O_2P_2Pd_2Se$: C, 26.6; H, 5.2. Found: C, 27.0; H, 5.1%. IR (Nujol) ν, cm^{-1}: 1731 (C=O), 322 (Pd–Cl). UV–Vis (CH_2Cl_2), λ (ε, $M^{-1}\,cm^{-1}$): 237 (2.7×10^4), 296 (2.0×10^4), 355 (6.1×10^3) nm. ^1H NMR ($CDCl_3$): 1.22 (m, 18H, PCH_2CH_3); 2.02 (m, 12H, PCH_2); 2.97 (t, 6.9 Hz, 2H, $SeCH_2$); 3.38 (t, 6.6 Hz, 2H, $SeCH_2CH_2$); 3.73 (s, 3H, COOMe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 41.1. $^{77}Se\{^1H\}$ NMR ($CDCl_3$): 21.5 ppm.

3.4.9. $[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeCH_2CH_2COOMe)(P^nPr_3)_2]$ (**3b**)

Prepared similar to complex **3a** from $[Pd_2Cl_2(\mu\text{-}Cl)_2(P^nPr_3)_2]$ (73 mg, 0.11 mmol) and $[Pd_2Cl_2(\mu\text{-}SeCH_2CH_2COOMe)_2(P^nPr_3)_2]$ (100 mg, 0.1 mmol) and recrystallized from CH_2Cl_2–hexane (137 mg, 79% yield) as orange crystals; mp = 175–176 °C. Anal. Calc. for $C_{22}H_{49}Cl_3O_2P_2Pd_2Se$: C, 32.8; H, 6.1. Found: C, 32.5; H, 6.2%. IR (Nujol) ν, cm^{-1}: 1734 (C=O), 320 (Pd–Cl). UV–Vis (CH_2Cl_2), λ (ε, M^{-1} cm^{-1}): 237 (2.7×10^4), 295 (2.0×10^3), 358 (6.2×10^3) nm. ^{1}H NMR ($CDCl_3$): 1.09 (t, 7 Hz, 18H, $PCH_2CH_2C\mathit{H}_3$); 1.69 (br, m, 12H, $PCH_2C\mathit{H}_2$); 1.93 (m, 12H, PCH_2); 2.95 (t, 6.6 Hz, 2H, $SeCH_2$); 3.38 (t, 6.6 Hz, 2H, $SeCH_2C\mathit{H}_2$); 3.73 (s, 3H, COOMe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 31.4. $^{77}Se\{^1H\}$ NMR ($CDCl_3$): 16.4.

3.4.10. *[$Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeCH_2CH_2COOMe)(PMe_2Ph)_2$] (**3c**)*

A dichloromethane solution (15 cm^3) of [$Pd_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2$] (217 mg, 0.34 mmol) was added to a methanolic solution (10 cm^3) of $NaSeCH_2CH_2COOMe$ [prepared from $(SeCH_2CH_2COOMe)_2$ (57 mg, 0.17 mmol) and $NaBH_4$ (13 mg, 0.34 mmol)] and recrystallized from $CHCl_3$–ether (159 mg, 61% yield) as yellow crystals; mp 136–138 °C. Anal. Calc. for $C_{20}H_{29}Cl_3O_2P_2Pd_2Se$: C, 31.5; H, 3.8. Found: C, 31.9; H, 3.7%. IR (Nujol) ν, cm^{-1}: 1721 (C=O), 314 (Pd–Cl). UV–Vis (CH_2Cl_2), λ (ε, M^{-1} cm^{-1}): 239 (2.1×10^4), 293 (2.2×10^4), 365 (7.5×10^4) nm. ^{1}H NMR ($CDCl_3$): 1.90, 1.98 (each d, *J*(P–H) 12 Hz, PMe_2); 2.58 (t, 6.9 Hz, 2H, $SeCH_2$); 2.78 (t, 6.6 Hz, 2H, $SeCH_2C\mathit{H}_2$), 3.66 (s, 3H, COOMe); 7.45, 7.61–7.66 (m) [Ph]. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 10.3. $^{77}Se\{^1H\}$ NMR ($CDCl_3$): 56.3 ppm.

3.4.11. *[$Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeCH_2CH_2COOMe)(PEt_3)_2$] (**3d**)*

Prepared similar to complex **3a** from [$Pt_2Cl_2(\mu\text{-}SeCH_2\text{-}CH_2COOMe)_2(PEt_3)_2$] (86 mg, 0.08 mmol) and [$Pt_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2$] (64 mg, 0.08 mmol) in CH_2Cl_2 and recrystallized from CH_2Cl_2–hexane at −10 °C as yellow crystals (117 mg, 78% yield); mp = 187–189 °C. Anal. Calc. for $C_{16}H_{37}Cl_3O_2P_2Pt_2Se$: C, 21.4; H, 4.1. Found: C, 21.7; H, 4.1%. IR (Nujol) ν, cm^{-1}: 1741 (C=O), 315 (Pt–Cl). UV–Vis (CH_2Cl_2), λ (ε, M^{-1} cm^{-1}): 246 (2.1×10^4), 280 (6.7×10^3), 332 (1.5×10^3) nm. ^{1}H NMR ($CDCl_3$): 1.16 (m, 18H, $PCH_2C\mathit{H}_3$); 1.90–2.10 (m, 12H, PCH_2); 2.99 (t, 7 Hz, 2H, $SeCH_2$); 3.25 (t, br, 6.9 Hz, 2H, $SeCH_2C\mathit{H}_2$); 3.73 (s, 3H, COOMe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 9.3 [$^1J(^{195}Pt\text{–}^{31}P) = 3936$ Hz, $^2J(^{195}Pt\text{–}^{195}Pt) = 432$ Hz]. $^{77}Se\{^1H\}$ NMR ($CDCl_3$): −15.3 [$^1J(^{195}Pt\text{–}^{77}Se) = 147$ Hz]. $^{195}Pt\{^1H\}$ NMR ($CDCl_3$): −4017 [d, $^1J(^{195}Pt\text{–}^{31}P) = 3922$ Hz, $^2J(^{195}Pt\text{–}^{195}Pt) = 446$ Hz].

3.4.12. *[$Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeCH_2CH_2COOMe)(P^nPr_3)_2$] (**3e**)*

Prepared similar to complex **3a** using [$Pt_2Cl_2(\mu\text{-}Cl)_2(P^nPr_3)_2$] (65 mg, 0.076 mmol) and [$Pt_2Cl_2(\mu\text{-}SeCH_2CH_2COOMe)_2(P^nPr_3)_2$] (85 mg, 0.076 mmol) and recrystallized from CH_2Cl_2–hexane as yellow crystals (121 mg, 81% yield); mp = 177–179 °C. Anal. Calc. for $C_{22}H_{49}Cl_3O_2P_2Pt_2Se$: C, 26.9; H, 5.0. Found: C, 27.1; H, 4.9%. IR (Nujol) ν, cm^{-1}: 1737 (C=O), 315 (Pt–Cl). UV–Vis (CH_2Cl_2), λ (ε, M^{-1} cm^{-1}): 238 (2.4×10^4), 246 (2.5×10^4), 280 (8.2×10^3), 344 (2.1×10^3) nm. ^{1}H NMR ($CDCl_3$): 1.07 (t, 6.9 Hz, 18H, $PCH_2CH_2C\mathit{H}_3$); 1.65 (m, 12H, $PCH_2C\mathit{H}_2$); 1.89 (m, 12H, PCH_2); 2.94 (t, 2H, 6.9 Hz, $SeCH_2$), 3.25 (br, 2H, $SeCH_2CH_2$); 3.72 (s, 3H, COOMe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 0.4 [$^1J(^{195}Pt\text{–}^{31}P) = 3912$ Hz]. $^{77}Se\{^1H\}$ NMR ($CDCl_3$): −18.1 [$^1J(^{195}Pt\text{–}^{77}Se) = 134$ Hz]. $^{195}Pt\{^1H\}$ NMR ($CDCl_3$): −3992 [d, $^1J(^{195}Pt\text{–}^{31}P) = 3902$ Hz, $^2J(^{195}Pt\text{–}^{195}Pt) = 500$ Hz].

3.4.13. *[$Pd_2(SeCH_2CH_2COOMe)_4(P^nPr_3)_2$] (**4**)*

A dichloromethane solution (15 cm^3) of [$Pd_2Cl_2(\mu\text{-}Cl)_2(P^nPr_3)_2$] (185 mg, 0.27 mmol) was added to a methanolic solution (15 cm^3) of $NaSeCH_2CH_2COOMe$ [prepared from $(MeOOCCH_2CH_2Se)_2$ (192 mg, 0.58 mmol) and $NaBH_4$ (44 mg, 1.15 mmol)]. Reaction mixture was stirred for 2 h under argon and the solvents were removed under reduced pressure. Contents were extracted with dichoromethane and extract was passed through a Florisil column. Solvent was stripped off from the filtrate *in vacuo* whereupon an oily residue was obtained. Repeated washing with hexane and subsequent drying yielded a red oil of title compound (230 mg, 74% Yield). Anal. Calc. for $C_{34}H_{70}O_8P_2Pd_2Se_4$: C, 34.1; H, 5.9. Found: C, 34.6; H, 5.8%. IR (Nujol) $\nu_{C=O}$: 1740 cm^{-1}. ^{1}H NMR ($CDCl_3$): 1.04 (t, 18H, $PCH_2CH_2C\mathit{H}_3$); 1.55 (br, 12H, $PCH_2C\mathit{H}_2$); 1.87 (br, PCH_2); 2.73–2.95 (m, 16H, $SeCH_2CH_2$); 3.38 (s); 3.66 (s) (COOMe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 7.7; 8.6. $^{77}Se\{^1H\}$ NMR ($CDCl_3$): −271.1; 93.7; 97.7; 141.5 (each s).

3.4.14. *[$Pd_3Cl_2(\mu\text{-}SeCH_2CH_2COOMe)_4(P^nPr_3)_2$] (**5**)*

The complex **2b**, when left for recrystallization gave two types of crystals viz. yellow orange (**2a**), and deep red (**5**). The latter was mechanically separated. A dichloromethane solution (15 cm^3) of [$Pd_2Cl_2(\mu\text{-}Cl)_2(P^nPr_3)_2$] (189 mg, 0.28 mmol) was added to a methanolic solution (10 cm^3) of $NaSeCH_2CH_2COOMe$ [prepared from $(MeOOCCH_2CH_2Se)_2$ (126 mg, 0.38 mmol) and $NaBH_4$ (29 mg, 0.76 mmol)]. Reaction mixture was stirred under argon for 2 h to obtain a red solution. The solvents were evaporated under vacuum and the residue was extracted with dichloromethane (20 cm^3). Extract was passed through a Florisil column (0.5 cm × 7 cm) and dried to get a red oil which was dissolved in CH_2Cl_2–ethyl acetate–hexane mixture and cooled at −10 °C yield red crystals of the title compound (103 mg, 68% yield); mp = 124–125 °C. Anal. Calc. for $C_{34}H_{70}Cl_2O_8P_2Pd_3Se_4$: C, 29.7; H, 5.1. Found: C, 30.2; H, 5.1%. IR (Nujol) $\nu_{C=O}$: 1732 cm^{-1}. UV–Vis (CH_2Cl_2), λ (ε, M^{-1} cm^{-1}): 236 (3.1×10^4), 259 (2.7×10^4), 291 (2.8×10^4), 342 (2.6×10^4), 372 (sh, 2.4×10^4). ^{1}H NMR ($CDCl_3$): 1.06 (t, 18H, $PCH_2CH_2C\mathit{H}_3$); 1.60 (br, 12H, $PCH_2C\mathit{H}_2$); 1.86 (br, 12H, PCH_2); 2.76, 2.78 (each m); 3.06 (m), 3.22 (br); 3.62, 3.69 (each s, COOMe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 13.0 (s).

3.4.15. *[$Pd(SeCH_2CH_2COOMe)_2]_6$ (**6**)*

A methanolic solution (15 cm^3) of Na_2PdCl_4 (307 mg, 1.04 mmol) was added to a solution (10 cm^3) of NaSe-

CH_2CH_2COOMe [prepared from $(MeOOCCH_2CH_2Se)_2$ (350 mg, 1.05 mmol) and $NaBH_4$ (82 mg, 2.2 mmol)]. Reaction mixture was stirred for 2 h under argon and the solvent was dried under vacuum. Residue was extracted with dichloromethane which was evaporated *in vacuo* to yield a deep red powder. Recrystallisation from dichloromethane–hexane–ethyl acetate gave deep red crystals (228 mg, 50% yield); mp = 140–141 °C. Anal. Calc. for $[C_8H_{14}O_4PdSe_2]_6$: C, 21.9; H, 3.2. Found: C, 22.3; H, 3.2%. IR (Nujol) $\nu_{C=O}$: 1732 cm^{-1}. UV–Vis (CH_2Cl_2), λ (ε, $M^{-1}\,cm^{-1}$): 235 (4.5×10^4), 257 (4.7×10^4), 279 (5.4×10^4), 297 (6.5×10^4), 331(5.0×10^4), 439 (2.7×10^4) nm. ^1H NMR ($CDCl_3$): 2.65–2.79 (m), 2.92 (t, 7 Hz) ($SeCH_2CH_2$); 3.68, 3.72 (each s, OMe). ^{13}C NMR ($CDCl_3$): 17.7, 20.6 (each s, $SeCH_2$); 36.5, 38.9 (each s, CH_2); 51.5, 51.7 (each s, OMe); 171.6 (s, CO). $^{77}Se\{^1H\}$ NMR ($CDCl_3$): −33.0; −172 (each s).

3.5. Crystallography

The unit cell parameters and intensity data for single crystals of **2d**, **3e**, **5** and **6** were collected at 293(2) K on a Bruker Smart Apex CCD diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å), employing the ω scan technique. The intensity data were collected for Lorentz, polarization and absorption effects. The structure was solved and refined with SHELX program [39]. Non-hydrogen atoms were refined anisotropically. Selected crystallographic data are given in Table 1.

4. Conclusion

A variety of bi-, tri- and hexa-nuclear palladium(II) and platinum(II) complexes have been isolated by the reaction of $NaSeCH_2CH_2COOMe$ with different palladium(II) and platinum(II) precursors. The selenolate functions as a bridging ligand with free ester group making it akin to simple selenolate group. Nevertheless, subtle differences are quite obvious like facile formation of a trinuclear complex **5** and high solubility of polynuclear homoleptic complexes such as **6**, providing an opportunity to study homoleptic derivatives which are otherwise difficult to characterize due to their insolubility/poor solubility. These complexes have also served as precursors for the preparation of metal selenides at moderately low temperature.

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Appendix A. Supplementary material

CCDC 619561, 619562, 619559, and 619560 contain the supplementary crystallographic data for $[Pd_2Cl_2(\mu\text{-}SeCH_2CH_2COOMe)_2(PPh_3)_2]$, $[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeCH_2CH_2COOMe)(P^nPr_3)_2]$, $[Pd_3Cl_2(\mu\text{-}SeCH_2CH_2COOMe)_4(P^nPr_3)_2]$ and $[Pd(\mu\text{-}SeCH_2CH_2COOMe)_2]_6$. 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; 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.jorganchem.2006.12.003.

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