



1-Selenolato-2-phenyl-*o*-carborane complexes of palladium(II) and platinum(II): Synthesis, spectroscopy and structures

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ABSTRACT

The reactions of $\text{PhCb}^{\text{o}}\text{SeNa}$ ($\text{Cb}^{\text{o}} = o\text{-C}_2\text{B}_{10}\text{H}_{10}$), prepared by reductive cleavage of Se–Se bond in $(\text{PhCb}^{\text{o}}\text{Se})_2$ by NaBH_4 in methanol, with Na_2PdCl_4 , $\text{MCl}_2(\text{PR}_3)_2$ and $[\text{M}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{PR}_3)_2]$ afforded a variety of complexes, viz., $[\text{Pd}(\text{SeCb}^{\text{o}}\text{Ph})\text{Cl}]$ (**1**), $[\text{M}(\text{SeCb}^{\text{o}}\text{Ph})_2(\text{PR}_3)_2]$, $[\text{M}_2\text{Cl}_2(\mu\text{-SeCb}^{\text{o}}\text{Ph})(\mu\text{-Cl})(\text{PR}_3)_2]$ ($\text{M} = \text{Pd}, \text{Pt}$) and $[\text{Pd}_2\text{Cl}(\text{SeCb}^{\text{o}}\text{Ph})(\mu\text{-Cl})(\mu\text{-SeCb}^{\text{o}}\text{Ph})(\text{PET}_3)_2]$ (**7**) have been isolated. These complexes were characterized by elemental analyses and NMR (^1H , ^{31}P , ^{77}Se , ^{195}Pt) spectroscopy. The structures of $[\text{Pd}(\text{SeCb}^{\text{o}}\text{Ph})_2(\text{PET}_3)_2]$ (**2**), $[\text{Pt}(\text{SeCb}^{\text{o}}\text{Ph})_2(\text{PMe}_2\text{Ph})_2]$ (**3**), $[\text{Pd}_2\text{Cl}_2(\mu\text{-SeCb}^{\text{o}}\text{Ph})(\mu\text{-Cl})(\text{PMe}_2\text{Ph})_2]$ (**5**) and $[\text{Pd}_2\text{Cl}(\text{SeCb}^{\text{o}}\text{Ph})(\mu\text{-Cl})(\mu\text{-SeCb}^{\text{o}}\text{Ph})(\text{PET}_3)_2]$ (**7**) were established by X-ray crystallography. The latter represents the first example of asymmetric coordination of selenolate ligands in binuclear bis chalcogenolate complexes of palladium and platinum. Thermolysis of $[\text{Pd}(\text{SeCb}^{\text{o}}\text{Ph})_2(\text{PET}_3)_2]$ (**2**) in HDA (hexadecylamine) at $330\text{ }^\circ\text{C}$ gave nano-crystals of $\text{Pd}_{17}\text{Se}_{15}$.

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1. Introduction

Platinum group metal organochalcogenolates are attractive not only because of their rich reaction chemistry and structural diversity [1–3], but also due to their applications as catalysts in organic transformations [4–7], enzymatic models in biological systems, in cancer chemotherapy [8,9] and more recently as molecular precursors for metal chalcogenides, M_xE_y ($\text{M} = \text{Pd}$ or Pt ; $\text{E} = \text{S}$, Se , and Te) [10–12]. Several of these chalcogenides show semiconducting properties and find numerous applications in electronic industry and catalysis [10]. Recently we have described the synthesis of mononuclear palladium and platinum complexes derived from 2-mercapto carboranes [13]. The three dimensional steric demand of carborane has led to subtle differences in the reactivity of these complexes when compared with those containing simple thiolate ligands. In the above perspective and in pursuance of our interest in palladium/platinum complexes, it was considered worthwhile to explore the chemistry of heavier chalcogen containing carboranes with the following objectives (i) to identify structural motifs generated by these ligands and (ii) facile

synthesis of palladium selenides by cleavage of C–Se bond. Accordingly, reactions of 2-phenyl-*o*-carboraneselenolate with palladium and platinum compounds have been examined. The results of this work are reported herein.

2. Experimental

The compounds, bis(2-phenyl-*o*-carborane)diselenide, $(\text{PhCb}^{\text{o}}\text{Se})_2$ [14,15], $[\text{MCl}_2(\text{PR}_3)_2]$ and $[\text{M}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{PR}_3)_2]$ [16] were prepared according to literature methods. All reactions were carried out in anhydrous conditions under a nitrogen atmosphere. Melting points were determined in capillary tubes and are uncorrected. Elemental analyses were carried out on a Flash EA-1112 CHNS instrument. ^1H , ^{31}P $\{^1\text{H}\}$, $^{77}\text{Se}\{^1\text{H}\}$ and $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker Avance-II 300 MHz spectrometer operating at 300, 121.5, 57.24 and 64.29 MHz, respectively. Chemical shifts are relative to internal chloroform peak (7.26 ppm) for ^1H and external 85% H_3PO_4 (for ^{31}P), Me_2Se (Ph_2Se_2 in CDCl_3 , 463 ppm relative to Me_2Se for ^{77}Se) and Na_2PtCl_6 in D_2O (for ^{195}Pt). Mass spectra were measured on a Kratos MS 890 mass spectrometer. X-ray powder diffractometer data were collected on a Phillips X-ray diffractometer (Model PW1729) using $\text{Cu-K}\alpha$ ($\lambda = 1.5406\text{ \AA}$) radiation. SEM (scanning electron microscopy) and EDX (energy dispersive X-ray analysis) measurements were made on a Tesca Vega 2300T/40 instrument.

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Table 1
Crystallographic and structure refinement data for [Pd(SeCb^oPh)₂(PEt₃)₂] (**2**), [Pt(SeCb^oPh)₂(PMe₂Ph)₂] (**3**), [Pd₂Cl₂(μ-Cl)(μ-SeCb^oPh)(PMe₂Ph)₂] (**5**) and [Pd₂Cl(SeCb^oPh)(μ-Cl)(μ-SeCb^oPh)(PEt₃)₂] (**7**).

	[Pd(SeCb ^o Ph) ₂ (PEt ₃) ₂] (2)	[Pt(SeCb ^o Ph) ₂ (PMe ₂ Ph) ₂] (3)	[Pd ₂ Cl ₂ (μ-Cl)(μ-SeCb ^o Ph)(PMe ₂ Ph) ₂] (5)	[Pd ₂ Cl(SeCb ^o Ph)(μ-Cl)(μ-SeCb ^o Ph)(PEt ₃) ₂] (7)
Chemical Formula	C ₂₈ H ₆₀ B ₂₀ P ₂ PdSe ₂ ·2CHCl ₃	C ₃₂ H ₅₂ B ₂₀ P ₂ PtSe ₂	C ₂₄ H ₃₇ B ₁₀ Cl ₃ P ₂ Pd ₂ Se ₂ ·0.25CH ₂ Cl ₂ ·0.5CH ₄ O	C ₂₈ H ₆₀ B ₂₀ Cl ₂ Pd ₂ P ₂ Se ₂ ·CH ₂ Cl ₂
M	1177.96	1067.89	930.94	1201.45
T/K	100 (2)	298 (2)	100 (2)	298 (2)
Size/color	0.5 × 0.4 × 0.3/red prism	0.4 × 0.15 × 0.15/yellow	0.3 × 0.2 × 0.15/colorless plate	0.5 × 0.4 × 0.3/red
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> – 1	<i>P</i> – 1	<i>P</i> – 1	<i>P</i> 2 _{1/n}
<i>a</i> /Å	13.5794 (8)	11.898 (5)	10.3010 (9)	18.006 (4)
<i>b</i> /Å	13.9325 (8)	14.387 (6)	10.9728 (9)	13.859 (6)
<i>c</i> /Å	15.4689 (8)	14.965 (3)	18.9447 (19)	22.433 (6)
α /°	75.1030 (10)	107.43(3)	86.614 (2)	
β /°	67.6280 (10)	103.97 (3)	76.019 (2)	110.47 (2)
γ /°	75.0970 (10)	98.81 (4)	64.7840 (10)	
<i>V</i> /Å ³	2567.2 (2)	2300.3 (16)	1877.5 (3)	5245 (3)
<i>Z</i>	2	2	2	4
<i>d</i> _{calc} /g cm ⁻³	1.542	1.542	1.647	1.522
Diffractometer	Bruker APEX 2	Rigaku AFC7S	Bruker APEX 2	Rigaku AFC7S
μ (mm ⁻¹)/F(000)	2.180/1176	4.727/1040	2.281/915	2.363/2376
θ for data collection/°	1.45 to 28.00	2.55 to 27.50	4.00 to 27.00	2.51 to 27.51
Limiting indices	-17 ≤ <i>h</i> ≤ 17 -18 ≤ <i>k</i> ≤ 18 -20 ≤ <i>l</i> ≤ 20	-15 ≤ <i>h</i> ≤ 8 -18 ≤ <i>k</i> ≤ 18 -18 ≤ <i>l</i> ≤ 19	-13 ≤ <i>h</i> ≤ 13 -14 ≤ <i>k</i> ≤ 13 -24 ≤ <i>l</i> ≤ 24	-21 ≤ <i>h</i> ≤ 23 -10 ≤ <i>k</i> ≤ 18 -29 ≤ <i>l</i> ≤ 16
Absorption correction	SADABS	Psi-Scan	SADABS	Psi-Scan
<i>T</i> _{max} and <i>T</i> _{min}	0.521 and 0.356	0.5374 and 0.2536	0.705 and 0.581	0.5375 and 0.3846
No. of unique reflns/	12373	10574	8085	12022
No. of obsd reflns with <i>I</i> > 2σ(<i>I</i>)	10768	8431	5628	4660
Data/restraints/parameters	12373/0/649	10574/0/586	8085/1/411	12022/0/532
Final <i>R</i> ₁ , ω <i>R</i> ₂ indices (R _{factor} _gt/ wR _{factor} _gt)	0.0227/0.0535	0.0330/0.0663	0.0394/0.0829	0.0555/0.1077
<i>R</i> ₁ , ω <i>R</i> ₂ (all data) (R _{factor} _all/ wR _{factor} _ref)	0.0291/0.0561	0.0549/0.0730	0.0709/0.0909	0.2112/0.1450
GOF	0.990	0.991	1.018	0.963
Largest difference peak and hole (e Å ⁻³)	1.037 and -0.732	0.924 and -1.436	2.158 and -1.043	0.694 and -0.811

2.1. Preparation of [Pd(SeCb^oPh)Cl]_n (**1**)

To a methanolic solution (15 ml) of Na₂PdCl₄ (59 mg, 0.20 mmol), a methanolic solution of NaSeCb^oPh (prepared from reduction of (PhCb^oSe)₂ (119 mg 0.20 mmol) in 5 ml benzene by methanolic solution of NaBH₄ (15 mg, 0.40 mmol)) was added with vigorous stirring which continued for 4 h. The solvent was evaporated under vacuum and the residue was extracted with dichloromethane and filtered. The filtrate was concentrated under vacuum and kept for recrystallization to give dark brown crystals (62 mg, 70% yield), m.p. 130 °C. Anal. Calcd. for C₈H₁₅B₁₀ClPdSe: C, 21.8; H, 3.4%. Found: C, 22.0; H, 3.8%. Mass spectrum (*m/e*): 519.4 (Pd(SeCb^oPh)(Cl)Se); 439.4 (PdCl(SeCb^oPh)); 235.4; 219.5 (Cb^oPh). ¹H NMR (dmso-*d*₆) δ : 7.32–7.40 (m); 7.51 (d, 7.7 Hz); 7.66 (m). ⁷⁷Se{¹H} NMR (dmso-*d*₆) δ : 839 ppm.

2.2. Preparation of [Pd(SeCb^oPh)₂(PEt₃)₂] (**2**)

To a dichloromethane solution (15 ml) of [PdCl₂(PEt₃)₂] (83 mg, 0.20 mmol), a methanolic solution of NaSeCb^oPh (prepared from reduction of (PhCb^oSe)₂ (119 mg 0.20 mmol) in 5 ml benzene by methanolic solution of NaBH₄ (15 mg, 0.40 mmol)) was added with vigorous stirring which continued for 4 h. The solvent was evaporated under vacuum and the residue was extracted with dichloromethane and then filtered. The filtrate was concentrated under vacuum and the residue was recrystallized from chloroform as a red crystalline solid (113 mg, 60% yield); m.p. 133 °C. Anal. Calcd. for C₂₈H₆₀B₂₀P₂PdSe₂·2CHCl₃: C, 30.5; H, 5.3%. Found: C, 30.6; H, 5.3%. ¹H NMR (CDCl₃) δ : 0.83–0.91 (m, PCH₂Me); 1.72–1.78 (m, PCH₂);

7.36–7.44 (m); 7.71 (d, 7.0 Hz). ³¹P{¹H} NMR (CDCl₃) δ : 0.5 ppm; ⁷⁷Se{¹H} NMR (CDCl₃) δ : 257 ppm.

2.3. Preparation of [Pt(SeCb^oPh)₂(PMe₂Ph)₂] (**3**)

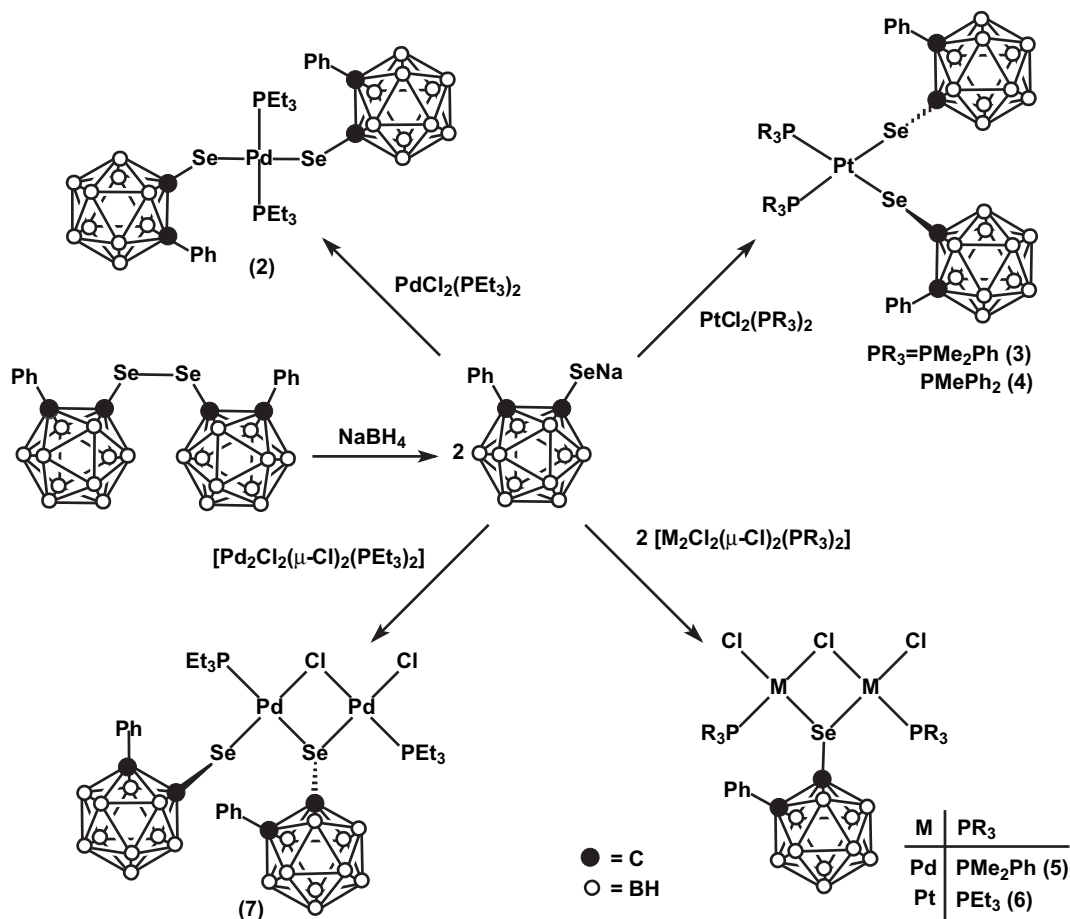
Prepared similar to **2** as a yellow crystalline solid in 73% yield, m.p. 170 °C. Anal. Calcd. for C₃₂H₅₂B₂₀P₂PtSe₂: C, 36.0; H, 4.9%. Found: C, 35.9; H, 4.9%. ¹H NMR (CDCl₃) δ : 1.50 (d, 10 Hz); 1.75 (d, 13 Hz); 2.20 (d, 13 Hz, PMe₂); 7.14–7.72 (m, Ph). ³¹P{¹H} NMR (CDCl₃) δ : -19.5 (¹J(Pt–P) = 3022 Hz). ⁷⁷Se{¹H} NMR (CDCl₃) δ : 289 ppm.

2.4. Preparation of [Pt(SeCb^oPh)₂(PMePh)₂] (**4**)

Prepared similar to **2** as a yellow crystalline solid in 74% yield, m.p. 185 °C. Anal. Calcd. for C₄₂H₅₆B₂₀P₂PtSe₂: C, 42.3; H, 4.7%. Found C, 42.6; H, 4.7%. ¹H NMR (CDCl₃) δ : 1.91 (d, J(P–H) = 10 Hz; J(Pt–H) = 32 Hz); 7.22–7.45 (m); 7.60 (d, 7 Hz). ³¹P{¹H} NMR (CDCl₃) δ : -7.8 (¹J(Pt–P) = 3054 Hz). ⁷⁷Se{¹H} NMR (CDCl₃) δ : 320 ppm.

2.5. Preparation of [Pd₂Cl₂(μ-SeCb^oPh)(μ-Cl)(PMe₂Ph)₂] (**5**)

To a dichloromethane solution (20 ml) of [Pd₂Cl₂(μ-Cl)₂(PMe₂Ph)₂] (126 mg, 0.2 mmol), a methanolic solution of NaSeCb^oPh (prepared from (PhCb^oSe)₂ (119 mg 0.20 mmol) and NaBH₄ (15 mg, 0.40 mmol) in methanol) was added and the reaction mixture was stirred at room temperature for 4 h. The solvents were evaporated under a reduced pressure and the residue was extracted with dichloromethane which on concentration to 10 ml and on cooling



Scheme 1.

afforded yellow crystals (98 mg, 55% yield), m.p. 200 °C (dec.). Anal. Calcd. for C₂₄H₃₇B₁₀Cl₃P₂Pd₂Se. CH₂Cl₂: C, 30.7; H, 4.0%. Found: C, 31.0; H, 3.9%. ¹H NMR (dms_o-d₆) δ: 1.69, 1.82 (each d, 12.5 Hz, PMe₂); 7.45–7.65 (m, Ph), 7.86–7.91 (m). ³¹P{¹H} NMR (dms_o-d₆) δ: 10.8, 14.2 (each s). ⁷⁷Se{¹H} NMR (dms_o-d₆) δ: 452 (s) ppm.

2.6. Preparation of [Pt₂Cl₂(μ-SeC⁰Ph)(μ-Cl)(PEt₃)₂] (6)

Prepared similar to **5** in 74% yield, m.p. 165 °C. Anal. Calcd. for C₂₀H₄₅B₁₀Cl₃P₂Pt₂Se: C, 23.3; H, 4.4%. Found: C, 23.7; H, 4.3%. ¹H NMR (CDCl₃) δ: 1.06–1.18 (m, PCH₂CH₃); 1.77–1.84 (m, PCH₂); 7.27–7.70 (m, Ph). ³¹P{¹H} NMR (CDCl₃) δ: 9.1 (¹J(Pt–P) = 3836 Hz). ⁷⁷Se{¹H} NMR (CDCl₃) δ: 244 (¹J(Pt–Se) = 118 Hz). ¹⁹⁵Pt{¹H} NMR (CDCl₃) δ: –3894 (d, ¹J(Pt–P) = 3812 Hz).

Preparation of [Pd₂Cl(SeC⁰Ph)(μ-Cl)(μ-SeC⁰Ph)(PEt₃)₂] (7)

Prepared by a method similar to **5** by using [Pd₂Cl₂(μ-Cl)₂(PEt₃)₂] and NaSeC⁰Ph in 1:2 M ratio. Yield 65%, m.p. 210 °C. Anal. Calcd. for C₂₈H₆₀B₂₀Cl₂P₂Pd₂Se₂: C, 30.1; H, 5.4%. Found: C, 30.7; H, 5.4%. ¹H NMR (CDCl₃) δ: 1.02–1.26 (m, PCH₂CH₃); 1.62–1.85 (m, PCH₂); 7.42–7.77 (m, Ph). ³¹P{¹H} NMR (CDCl₃) δ: 27.2, 42.4 (each s). ⁷⁷Se{¹H} NMR (CDCl₃) δ: 352 (s); 157 (d, J(⁷⁷Se–³¹P) = 152 Hz).

2.8. Thermolysis of [Pd(SeC⁰Ph)₂(PEt₃)₂]

In a typical experiment **2** (70 mg) and HDA (hexadecylamine) (2.5 g) were taken in a round bottom flask and heated at 330 °C for

1.5 h. This was cooled to 70 °C and methanol was added. The contents were centrifuged leaving a black residue, which was washed with methanol (15 ml × 3) and dried *in vacuo*.

2.9. Crystallographic experiment

Single-crystal X-ray diffraction measurements were made on a Bruker APEX-2 diffractometer for **2** and **5** and Rigaku AFC 7S diffractometer for **3** and **7** using graphite monochromated Mo-Kα (λ = 0.71069 Å) radiation. Low temperature diffraction data were collected by keeping the crystal at low temperature using a cryo-stream (Oxford Cryo-Systems) open-flow N₂ gas cryostat. The structures were solved by direct methods [17] and refinement was on F² [17] using data that had been corrected for Lorentz and polarization effects with an empirical procedure [18]. The non-hydrogen atoms were refined anisotropically. The experimental data had been corrected for absorption effects with sadabs (for **2** and **5**) [19] and psi-scans (for **3** and **7**) procedures [20], the carbaborane hydrogen atoms were located from the difference Fourier syntheses, the H(C) atoms were placed in geometrically calculated positions. All hydrogen atom positions were refined in isotropic approximation in riding model with the Uiso(H) parameters equal to nUeq(Ci), where Ueq(Ci) are the equivalent thermal parameters of the atoms to which corresponding H atoms are bonded, n = 1.2 for CH– and CH₂–groups, n = 1.5 for CH₃–groups. Molecular structures were drawn using ORTEP [21]. Crystallographic data, together with data collection and refinement details are given in Table 1.

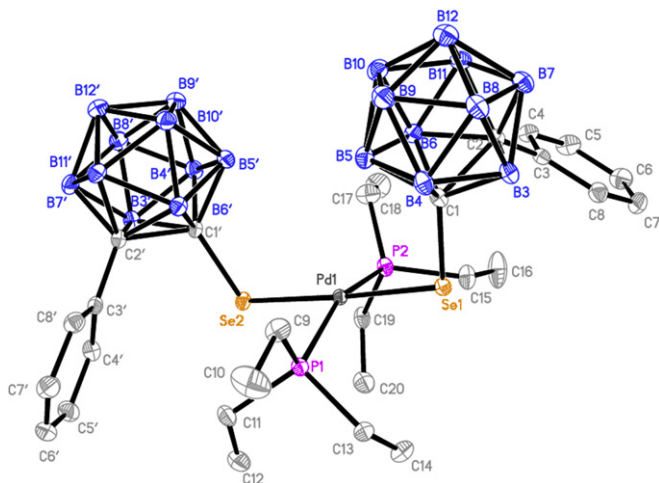


Fig. 1. ORTEP drawing of $[\text{Pd}(\text{SeCb}^{\text{o}}\text{Ph})_2(\text{PEt}_3)_2]$ (**2**) with atomic numbering scheme (ellipsoids drawn with 25% probability).

3. Results and discussion

Treatment of Na_2PdCl_4 with $\text{NaSeCb}^{\text{o}}\text{Ph}$, prepared by reductive cleavage of Se–Se bond of $(\text{PhCb}^{\text{o}}\text{Se})_2$ by methanolic NaBH_4 , affords a dark brown complex of composition, $[\text{Pd}(\text{SeCb}^{\text{o}}\text{Ph})\text{Cl}]_n$ (**1**). The reactions of $\text{MCl}_2(\text{PR}_3)_2$ with two equivalents of $\text{NaSeCb}^{\text{o}}\text{Ph}$ yield bis(selenolate) complexes, $[\text{M}(\text{SeCb}^{\text{o}}\text{Ph})_2(\text{PR}_3)_2]$ ($\text{M}/\text{PR}_3 = \text{Pd}/\text{PEt}_3$ (**2**); $\text{Pt}/\text{PMe}_2\text{Ph}$ (**3**) and Pt/PMePh_2 (**4**)). The reaction of $[\text{M}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{PR}_3)_2]$ with $\text{NaSeCb}^{\text{o}}\text{Ph}$ in 1:1 M ratio gives complexes of composition $[\text{M}_2\text{Cl}_2(\mu\text{-Cl})(\mu\text{-SeCb}^{\text{o}}\text{Ph})(\text{PR}_3)_2]$ ($\text{M}/\text{PR}_3 = \text{Pd}/\text{PMe}_2\text{Ph}$ (**5**) and Pt/PEt_3 (**6**)) whereas similar reaction (when $\text{M} = \text{Pd}$) in 1:2 stoichiometry yields $[\text{Pd}_2\text{Cl}(\text{SeCb}^{\text{o}}\text{Ph})(\mu\text{-Cl})(\mu\text{-SeCb}^{\text{o}}\text{Ph})(\text{PEt}_3)_2]$ (**7**) as a red crystalline solid (Scheme 1).

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **3** and **4** displayed a singlet with $^1J(\text{Pt}–\text{P})$ of ~ 3000 Hz indicating a *cis* configuration [22]. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **6** exhibited a single resonance suggesting the presence of only one isomeric species. Similarly, in the $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectrum a doublet centered at $\delta -3894$ ppm was observed

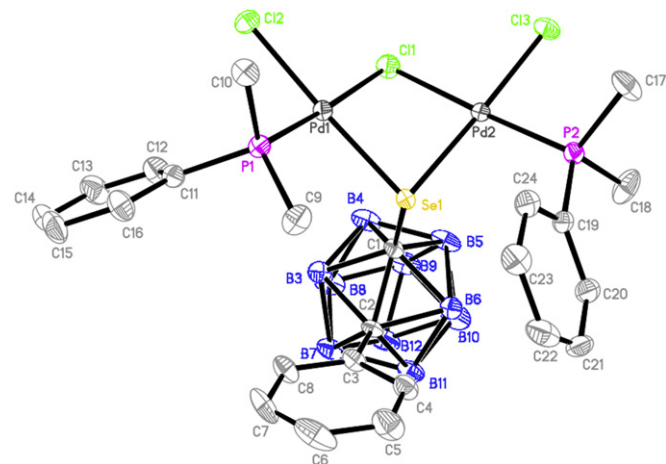


Fig. 3. ORTEP drawing of $[\text{Pd}_2\text{Cl}_2(\mu\text{-Cl})(\mu\text{-SeCb}^{\text{o}}\text{Ph})(\text{PMe}_2\text{Ph})_2]$ (**5**) with atomic numbering scheme (ellipsoids drawn with 25% probability).

suggestive of coupling with one ^{31}P nucleus. The magnitude of $^1J(\text{Pt}–\text{P})$ (~ 3800 Hz) coupling constant is in conformity with the *sym-cis* configuration having phosphine ligands *trans* to bridging chloride [1]. The $^{31}\text{P}\{^1\text{H}\}$ NMR of **7** showed two resonances which can be assigned to the phosphine ligands coordinated to two different palladium atoms. The $^{77}\text{Se}\{^1\text{H}\}$ NMR spectra of **1–6** displayed a single resonance in the region $\delta 244–839$ ppm while the spectrum of **7** showed two such resonances due to two different selenolate groups. The mass spectrum of **1** displayed a peak of highest mass at m/e 519.4 with the isotopic pattern corresponding to $[\text{Pd}(\text{SeCb}^{\text{o}}\text{Ph})(\text{Cl})\text{Se}]$. Another peak at m/e 439.4 is assigned for $[\text{PdCl}(\text{SeCb}^{\text{o}}\text{Ph})]$ fragment. Several complexes of composition $[\text{PdCl}(\text{ER})]_n$ ($\text{E} = \text{S}, \text{Se}, \text{Te}$) have been described in literature. Polymeric insoluble complexes are formed when R is an aryl (e.g. Ph) or pyridyl group [23]. However, with internally functionalized alkyl group, bi and tri-nuclear complexes, $[\text{PdCl}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)_3]$ [12] and $[\text{PdCl}(\text{ECH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)_2]$ ($\text{E} = \text{S}, \text{Se}, \text{Te}$) [24] are formed.

The molecular structures of $[\text{Pd}(\text{SeCb}^{\text{o}}\text{Ph})_2(\text{PEt}_3)_2]$ (**2**), $[\text{Pt}(\text{SeCb}^{\text{o}}\text{Ph})_2(\text{PMe}_2\text{Ph})_2]$ (**3**) $[\text{Pd}_2\text{Cl}_2(\mu\text{-Cl})(\mu\text{-SeCb}^{\text{o}}\text{Ph})(\text{PMe}_2\text{Ph})_2]$ (**5**) and $[\text{Pd}_2\text{Cl}(\text{SeCb}^{\text{o}}\text{Ph})(\mu\text{-Cl})(\mu\text{-SeCb}^{\text{o}}\text{Ph})(\text{PEt}_3)_2]$ (**7**) have been established unambiguously by single crystal X-ray diffraction analyses. The crystals of **2**, **5** and **7** contain solvent of crystallization. The ORTEP drawings with atomic number scheme are shown in Figs. 1–4 and selected bond lengths and angles are given in Tables

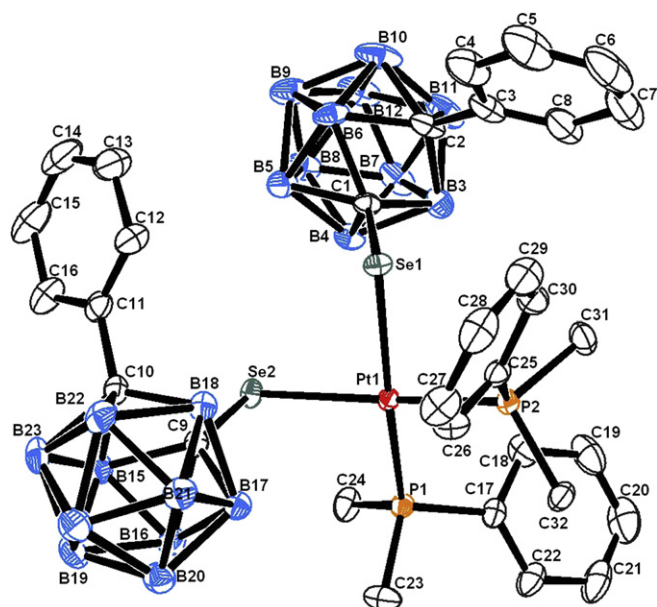


Fig. 2. ORTEP drawing of $[\text{Pt}(\text{SeCb}^{\text{o}}\text{Ph})_2(\text{PMe}_2\text{Ph})_2]$ (**3**) with atomic numbering scheme (ellipsoids drawn with 25% probability).

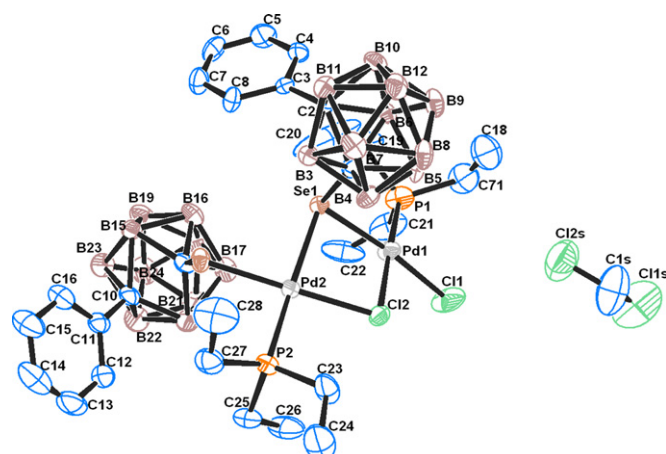


Fig. 4. ORTEP drawing of $[\text{Pd}_2\text{Cl}(\mu\text{-Cl})(\mu\text{-SeCb}^{\text{o}}\text{Ph})(\text{SeCb}^{\text{o}}\text{Ph})(\text{PEt}_3)_2]$ (**7**) with atomic numbering scheme (ellipsoids drawn with 25% probability).

Table 2

The selected bond lengths (Å) and angles (°) for *trans*-[Pd(SeCb^oPh)₂(PEt₃)₂].2CHCl₃ (**2**) and [Pt(SeCb^oPh)₂(PMe₂Ph)₂] (**3**).

	[Pd(SeCb ^o Ph) ₂ (PEt ₃) ₂].2CHCl ₃ (2) ^a	[Pt(SeCb ^o Ph) ₂ (PMe ₂ Ph) ₂] (3) ^b
M1–Se1	2.4945 (2)	2.4945 (11)
M1–Se2	2.4794 (2)	2.5094 (10)
M1–P1	2.3495 (4)	2.2749 (14)
M1–P2	2.3508 (4)	2.2706 (14)
Se1–C1	1.9240 (16)	1.939 (4)
Se2–C9	1.9242 (16)	1.928 (4)
C1–C2	1.752 (2)	1.742 (6)
C9–C10	1.747 (2)	1.760 (6)
C2–C3(Ph)	1.505 (2)	1.508 (6)
C10–C11(Ph)	1.505 (2)	1.509 (6)
Se1–M1–Se2	176.850 (7)	90.09 (4)
Se1–M1–P1	86.931 (12)	170.64 (3)
Se1–M1–P2	94.620 (12)	83.65 (5)
Se2–M1–P1	94.178 (12)	89.54 (5)
Se2–M1–P2	85.931 (12)	167.66 (3)
P1–M1–P2	160.297 (16)	98.35 (5)

^a C–B distances lie between 1.699 (2) and 1.730 (2) Å.

^b C–B distances lie between 1.683 (9) and 1.740 (9) Å.

2–4. The C–Se distances in all the complexes are similar to those observed in selenocarboranes, e.g. (PhCb^oSe)₂ (1.947 Å (av)) [15].

The coordination environment around the metal atoms in **2** and **3** is distorted square planar and is defined by the two Se and two P atoms of selenolate and tertiary phosphine ligands. In the former the neutral atoms (P) are mutually *trans* disposed while in the latter they occupy *cis* positions. Because of severe crowding from carboranes as well as phosphine ligands in **2** distortion in the coordination environment around palladium is evident. Thus the dihedral angles between “P₂Pd” and “Se₂Pd” and “P1Pd1Se2” and “P2Pd1Se1” planes in **2** are 84.78(1) and 19.77°, respectively. The P1–Pd1–P2 and Se1–Pd1–Se2 angles are also reduced to 160.30 and 176.85°, respectively from the ideal value of 180°. The carborane fragments in **2** are *syn* oriented with the phenyl groups pointing outward while in **3** they are mutually *anti*. The two M–P bonds in each molecule are essentially similar. However, the two M–Se distances in each molecule differ slightly (0.015 Å) as has been reported earlier for palladium/platinum selenolate complexes [22]. Both M–P and M–Se distances are within the range reported for mononuclear palladium/platinum selenolate complexes [11,22].

Complex **5** consists of two square planar palladium atoms which are held together by one selenium and chlorine bridges, a configuration observed for [M₂Cl₂(μ-Cl)(μ-ER)(PR₃)₂] complexes [1]. The other two terminal chlorine atoms are in *cis* configuration. The dihedral angle between “PdPSeCl₂” planes is 48.02(3)°. The two

Table 3

The selected bond lengths (Å) and angles (°) for [Pd₂Cl₂(μ-Cl)(μ-SeCb^oPh)(PMe₂Ph)₂] (**5**).

Pd1–Se1	2.3978 (6)	Pd2–Se1	2.4070 (6)
Pd1–Cl1	2.4031 (13)	Pd2–Cl1	2.4053 (13)
Pd1–Cl2	2.3145 (13)	Pd2–Cl3	2.3272 (12)
Pd1–P1	2.2301 (13)	Pd2–P2	2.2233 (13)
Se1–C1	1.963 (4)	C1–C2	1.718 (6)
C2–C3 (Ph)	1.508 (6)	Pd1–Pd2	3.2027 (6)
Se1–Pd1–Cl1	87.98 (3)	Se1–Pd2–Cl1	87.72 (3)
Se1–Pd1–Cl2	177.28	Se1–Pd2–Cl3	177.87(4)
Se1–Pd1–P1	93.67 (4)	Se1–Pd2–P2	94.07 (4)
Pd1–Se1–C1	105.90 (14)	Pd2–Se1–C1	102.03 (14)
Cl1–Pd1–Cl2	89.87 (5)	Cl1–Pd2–Cl3	90.36 (5)
Cl1–Pd1–P1	173.83 (5)	Cl1–Pd2–P2	177.62 (5)
Cl2–Pd1–P1	88.29 (5)	Cl3–Pd2–P2	87.83 (5)
Pd1–Cl1–Pd2	83.53 (4)	Pd1–Se1–Pd2	83.60 (2)

^a C–B distances lie in the region 1.705 (7) and 1.740 (7) Å.

Table 4

The selected bond lengths (Å) and angles (°) for [Pd₂Cl₂(SeCb^oPh)(μ-Cl)(μ-SeCb^oPh)(PEt₃)₂] (**7**).^a

Pd1–Cl1	2.315 (2)	Pd2–Cl2	2.3835 (19)
Pd1–Cl2	2.428 (2)	Pd2–Se1	2.5278 (11)
Pd1–Se1	2.4139 (10)	Pd2–Se2	2.3996 (11)
Pd1–P1	2.235 (3)	Pd2–P2	2.274 (2)
Se1–C1	1.966 (6)	Se2–C9	1.942 (7)
C1–C2	1.717 (9)	C9–C10	1.745 (9)
C2–C3(Ph)	1.497 (9)	C10–C11(Ph)	1.486 (10)
Pd1–Pd2	3.461		
Pd1–Cl2–Pd2	91.97 (7)	Pd1–Se1–Pd2	88.87 (3)
Cl1–Pd1–Se1	174.32 (9)	Cl2–Pd2–Se1	84.74 (6)
Cl1–Pd1–Cl2	90.21 (9)	Cl2–Pd2–Se2	173.42 (6)
Cl1–Pd1–P1	87.16 (10)	Cl2–Pd2–P2	94.44 (8)
Cl2–Pd1–P1	177.36 (8)	Se1–Pd2–P2	173.35 (6)
Cl2–Pd1–Se1	86.30 (5)	Se1–Pd2–Se2	91.71 (4)
Se1–Pd1–P1	96.32 (7)	P2–Pd2–Se2	89.72 (6)
C1–Se1–Pd1	104.21 (19)	Pd2–Se1–C1	98.76 (19)
		Pd2–Se2–C9	103.0 (2)

^a C–B distances lie in the region 1.685 (12) and 1.758 (11) Å.

Pd–Se distances are essentially similar and are as expected [25,26]. Various angles around each palladium atom are normal and lie in the range reported for [M₂Cl₂(μ-Cl)(μ-ER)(PR₃)₂] complexes [1]. The Pd–Pd separation (3.2027 (6) Å) is significantly large to account for any Pd–Pd interaction.

The molecular structure of **7** represents the first example of asymmetric coordination environment around each metal centre for the binuclear complexes of composition [M₂X₂(ER)₂(PR₃)₂] which are stabilized invariably by two bridging chalcogenolate ligands [1]. Because of this asymmetry, there is significant distortion around the metal atom. Coordination environment around one of the palladium atoms is defined by two *cis* Se atoms, a bridging chloride and a P atom while a P atom, two chlorides (one terminal and another bridging) and a bridging Se surround the other palladium atom. The four-membered ‘Pd₂SeCl’ ring is puckered with the hinge angle of 150.3°. To reduce steric crowding the two-carborane fragments on two selenolate ligands are directed in opposite directions. The palladium-bridging ligand distances are dissimilar due to different *trans* influence of the terminal ligands. Accordingly Pd(2)–Se(1) distance (*trans* to PEt₃) is longer than the Pd(1)–Se(1) bond length (*trans* to Cl) by ~0.1 Å. Similarly Pd(1)–Cl(2) (*trans* to

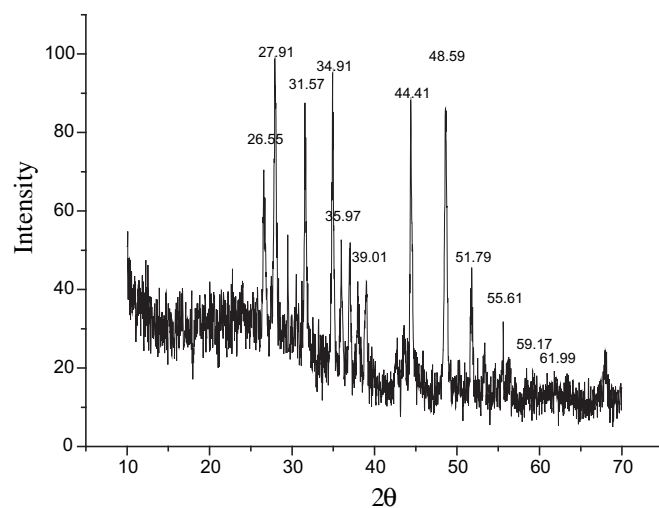


Fig. 5. XRD pattern of Pd₁₇Se₁₅ obtained from thermolysis of Pd(SeCb^oPh)₂(PEt₃)₂ (**2**) in HDA at 330 °C.

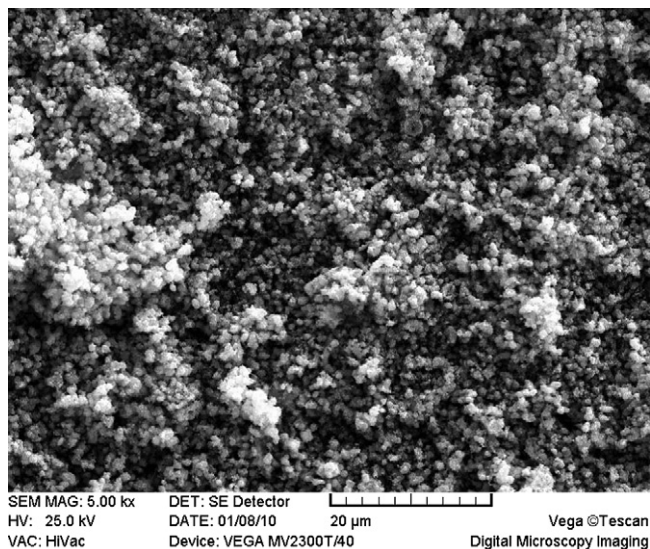


Fig. 6. SEM micrograph of Pd₁₇Se₁₅ obtained from thermolysis of Pd(SeCb^oPh)₂(PEt₃)₂ (**2**) in HDA at 330 °C.

PEt₃) is longer than Pd(2)–Cl(2) (*trans* to SeCb^oPh) by 0.044 Å. The Pd–Se distances (bridging and terminal) are well within the range reported for palladium selenolate complexes [25,26]. It is worth noting that while both *cis* and *trans* [M(SeCb^oPh)₂(PR₃)₂] could be isolated (*vide supra*), isolation of asymmetric structure **7** reflects severe steric demands of selenocarborane ligand which would be exerted in the expected bis-selenolato bridged complexes.

3.1. Thermal behavior

Palladium chalcogenides are of interest because of their relevance in catalysis and electronic industry [10]. Palladium chalcogenolates have been successfully employed for the preparation of palladium chalcogenides. Depending on the nature of precursor, different compositions and morphologies of Pd_xE_y have been isolated. Thus, thermolysis of complex **2** was carried out. The complex on heating in HDA (hexadecylamine) at 330 °C for 1.5 h gave a black residue which was characterized as Pd₁₇Se₁₅ by EDX (Calcd. for Pd₁₇Se₁₅; Pd, 60.4; Se, 39.6; found Pd, 60.6; Se, 39.4%) and XRD pattern (Fig. 5) (JCPDS File No 73-1424). The SEM micrograph (Fig. 6) showed particles are spherical in shape with an average diameter of 100 nm. Recently extrusion of carborane in metal complexes has been reported [13,27].

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Appendix A. Supplementary data

CCDC-Nos. 772666 (for **2**), 772667 (for **5**), 773677 (for **7**) and 773678 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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