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Synthesis and characterization of benzylselenolate complexes of palladium(II) and platinum(II)

Sandip Dey [a], Vimal K. Jain [a,*], Babu Varghese [b]

[a] *Novel Materials and Structural Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India*

[b] *Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Chennai 600036, India*

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Abstract

Reactions of sodium benzylselenolate with several palladium(II) and platinum(II) complexes were carried out and a variety of products isolated and characterized. Reactions of Na_2PdCl_4 or K_2PtCl_4 with NaSeBz gave $[M(SeBz)_2]_n$ (M = Pd or Pt; Bz = CH_2Ph) which when treated with tertiary phosphines yielded $[M(SeBz)_2(L\text{-}L)]$. The latter can also be prepared by the reaction of $MCl_2(L\text{-}L)$ (L-L = dppm, dppe or $2PPh_3$) with NaSeBz. Treatment of $[M_2X_2(\mu\text{-}Cl)_2(PR_3)_2]$ with NaSeBz in 1:2 molar ratio afforded complexes of the type $[M_2X_2(\mu\text{-}SeBz)_2(PR_3)_2]$ (M = Pd or Pt; X = Cl or Me; $PR_3 = PEt_3$, PPr^n_3, PBu^n_3, PMe_2Ph, $PMePh_2$ or PPh_3) which existed predominantly as a *cis* isomer. Reaction of $[M_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ with $[M_2Cl_2(\mu\text{-}SeBz)_2(PR_3)_2]$ gave heterobridged complexes $[M_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeBz)(PR_3)_2]$, the bridging chloride in the latter can be substituted with SBu^t or pz. All the complexes were characterized by elemental analysis and NMR (^1H, ^{31}P, ^{77}Se, ^{195}Pt) spectral data. Stereochemistry of these complexes has been discussed on the basis of NMR data. The crystal structure of $[Pt_2Cl_2(\mu\text{-}SeBz)_2(PPr^n_3)_2]$ has established a *cis* configuration with a bent four-membered Pt_2Se_2 ring. The complex $[Pd(SeBz)_2]_n$ on thermolysis at 630°C yields $Pd_{17}Se_{15}$. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Palladium; Platinum; Benzylselenolate; NMR; Binuclear compounds; Tertiaryphosphines

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1. Introduction

The chemistry of transition metal complexes with chalcogen ligands is expanding at a rapid pace. Besides diverse structural possibilities [1], they have been used as molecular precursors for the preparation of advanced materials [2] and industrial catalysis [3]. Platinum group chalcogenides M_xE_y (M = platinum group metal; E = S, Se, Te) find extensive applications in catalysis [4] and materials science [5]. We have recently demonstrated that the methylallyl palladium complexes $[Pd_2(\mu\text{-}ER)_2(\eta^3\text{-}C_4H_7)_2]$ on thermolysis yield Pd_4E (E = S or Se)/Pd_3Te_2 at moderately low temperatures (140°C) [6]. Similarly $[Pd(Epy)\{S_2P(OR)_2\}(PPh_3)]$ affords PdSE (E = S, Se) on pyrolysis [7].

The chemistry of palladium and platinum with chalcogenolates has been dominated by molecules containing thiolate groups [1]. Complexes with heavier chalcogens (E = Se or Te) are rare [8]. We have recently examined some chemistry of palladium and platinum complexes with SeEt [9], SePh [10], Sepy [11], and TePh [12] ligands. The increasing continued interest in selenium/tellurium containing materials [2c,8b] and a drive to replace volatile toxic Se/Te containing precursors (such as H_2Se or R_2E_2 etc.) have motivated us to explore single source precursors. The photosensitivity and cleaner cleavage of the benzyl group in Bz_2E_2 (E = Se or Te) [13] has attracted our attention to examine the chemistry of palladium(II) and platinum(II) with the $BzSe^-$ ligand. Results of this work are reported herein.

2. Results and discussion

2.1. Mononuclear complexes

Reaction of Na_2PdCl_4/K_2PtCl_4 with sodium benzylselenolate, prepared by reductive cleavage of the

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* Corresponding author. Tel.: +91-22-550-5148; fax: +91-22-550-5151.

E-mail address: jainvk@apsara.barc.ernet.in (V.K. Jain).

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Se–Se bond in Bz_2Se_2 with sodium borohydride in methanol, afforded sparingly soluble complexes of composition $[M(SeBz)_2]$ (**1**) [M = Pd (**1a**) or Pt (**1b**)]. Several thiolates of composition $[M(SR)_2]$ are reported as polymeric species; structures of palladium complexes $[Pd(SPr^n)_2]_n$ ($n = 6$ or 8) [14] have been confirmed by X-ray diffraction. Treatment of **1** with phosphine ligands readily gave monomeric complexes $[M(SeBz)_2(L\text{-}L)]$ (**2**) (M = Pt; L-L = $2PPh_3$) and (**3**) (Scheme 1). The latter two can be obtained readily by the reaction of $MCl_2(L\text{-}L)$ with NaSeBz.

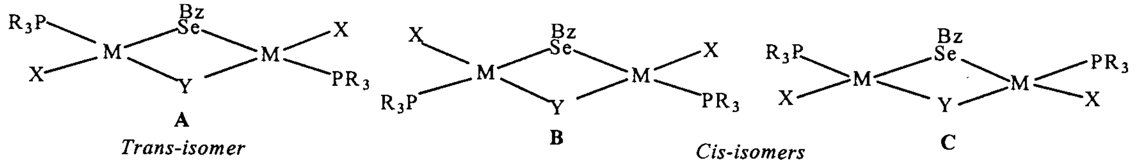
The compound **2** has been isolated as a *cis* product. The presence of $^4J(P–H)$ for the methylene protons of the SeBz group and the magnitude of $^1J(Pt–P)$ (2964 Hz) indicates a *cis* geometry. The magnitude of $^1J(Pt–P)$ (Table 1) can be compared with *cis*-$[Pt(SePh)_2(PPh_3)]$ (2969 Hz) while the *trans* isomer has a smaller $^1J(Pt–P)$ (2860 Hz) [15]. **2** reacts with methyl iodide in benzene to yield a pale yellow solid which is characterized as *trans*-$[PtI_2(PPh_3)_2]$ from analysis and NMR data.

The $^{31}P\{^1H\}$-NMR resonances for **3** are deshielded relative to the corresponding *cis*-$MCl_2(L\text{-}L)$ species and the magnitude of $^1J(Pt–P)$ is reduced significantly indicating strong *trans* influence of the SeBz group *trans* to phosphines. The ^1H-NMR spectra exhibited a doublet for the CH_2 protons of the SeBz group due to $^4J(P–H)$ couplings (~ 3 Hz). The $^{195}Pt\{^1H\}$-NMR spectra of **3b** and **3c** displayed a triplet at δ −4205 ($^1J(^{195}Pt–^{31}P) = 2377$ Hz) and −4917 ($^1J(^{195}Pt–^{31}P) = 2853$ Hz) ppm, respectively, due to coupling with two equivalent phosphorus nuclei. ^{195}Pt-NMR data can be compared with the spectra of *cis*-$[Pt(ER)_2(L\text{-}L)]$ (E = S, Se, Te; L = dppm or dppe) [15b]. The ^{195}Pt resonance is shielded on substituting dppm for dppe, though the overall stereochemistry is same in the two complexes. The observed shielding may be attributed to the ring size effects.

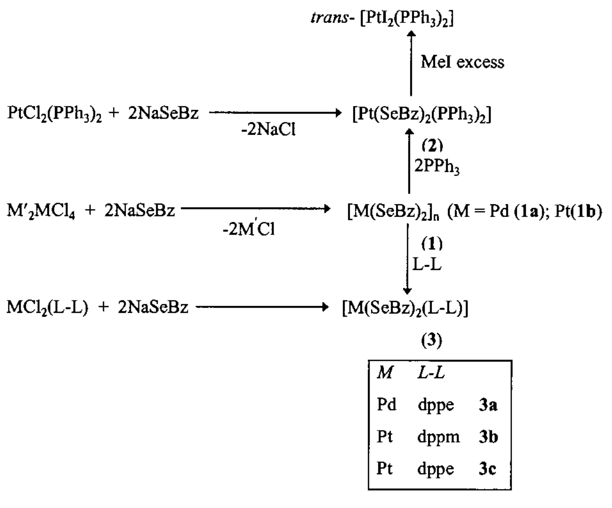
2.2. Binuclear complexes

Treatment of $[M_2X_2(\mu\text{-}Cl)_2(PR_3)_2]$ with NaSeBz afforded benzylselenolato-bridged complexes, $[M_2X_2(\mu\text{-}SeBz)_2(PR_3)_2]$ (**4**) as orange (Pd) or yellow (Pt) crystalline solids (Scheme 2). The reaction of halogen-bridged complexes $[M_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ with $[M_2Cl_2(\mu\text{-}SeBz)_2(PR_3)_2]$ in refluxing dichloromethane yields heterobridged complexes $[M_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeBz)(PR_3)_2]$ (**5**) in quantitave yields. The bridging chloride in the latter can be substituted with pyrazolato ligand, by treatment with pyrazole in the presence of aqueous NaOH to yield $[M_2Cl_2(\mu\text{-}pz)(\mu\text{-}SeBz)(PR_3)_2]$ (**6**) or SBu^t by the reaction of Bu^tSH to give $[M_2Cl_2(\mu\text{-}SBu^t)(\mu\text{-}SeBz)(PR_3)_2]$ (**7**).

The NMR spectra of these complexes (**4**–**7**) are consistent with the $[Pt_2X_2(\mu\text{-}Y)(\mu\text{-}SeBz)(PR_3)_2]$ arrangement which exhibits *trans* (**A**) and *cis* (**B** and **C**) isomerism as depicted below:



(M = Pd or Pt; X = Cl or Me; Y = SeBz, Cl, pz or SBu^t)



Scheme 1.

The NMR spectra of **4** revealed that these complexes were formed exclusively as the *cis* isomer except in a few cases where a small quantity of *trans* isomer also formed. The ^1H-NMR spectra for the *cis* complexes exhibited two sets of methylene proton resonances of SeBz groups each flanked by ^{77}Se satellites ($^2J(^{77}Se–^1H) \sim 10$ Hz). The downfield signal, appearing as a triplet due to phosphorus coupling, has been attributed to the SeBz group *trans* to the phosphine ligand. The high field signal, appearing as a singlet, has been assigned to the SeBz group *trans* to the terminal chloride ligand. The methylene proton resonances of the benzyl group for platinum complexes were further flanked by ^{195}Pt satellites. The *trans* isomer, as expected, showed only one methylene proton resonance.

The $^{31}P\{^1H\}$-NMR spectra (Table 1) displayed a single set of resonances for *cis* and *trans* isomers, the signal for the latter is considerably deshielded com-

Table 1
^{31}P- and ^{1}H-NMR data for benzylselenolate complexes of palladium and platinum

Complex	^{31}P-NMR data			^{1}H-NMR data
	δ ^{31}P (ppm)	^{1}J(Pt–P) (Hz)	Other couplings (Hz)	δ ^{1}H (ppm)
2	17.9	2964		4.46 (d, J(P–H) = 4.3 Hz; J(Pt–H) = 36.5 Hz, Se$\mathit{CH_2}$); 7.04–7.52 (m, Ph)
3a	49.8			2.23 (d, 21.4 Hz, P$\mathit{CH_2}$); 3.87 (d, J(P–H) = 3.5 Hz, Se$\mathit{CH_2}$); 7.01–7.17 (m), 7.36–7.51 (m), 7.70–7.82 (m) Ph
3b	−51.8	2389	^{2}J(Se–P) = 29	3.74 (s, J(Pt–H) = 18.6 Hz, Se$\mathit{CH_2}$); 4.40 (t, J(P–H) = 10.4 Hz, J(Pt–H) = 45 Hz, P$\mathit{CH_2}$); 7.01–7.17 (m), 7.42–7.52 (m), 7.88–7.94 (m) Ph
3c	47.0	2842		2.17 (d, 18.9 Hz, P$\mathit{CH_2}$); 3.83 (d, J(P–H) = 3 Hz, J(Pt–H) = 25 Hz, Se$\mathit{CH_2}$); 7.01–7.24 (m); 7.30–7.48 (m); 7.70–7.91 (m) Ph
4a	(*cis*) 13.8; (*trans*) 31.2		^{2}J(Se–P) = 62.6	1.03 (t, 7.1 Hz, $\mathrm{PCH_2CH_2}\mathit{CH_3}$); 1.44–1.55 (m, $\mathrm{PCH_2}\mathit{CH_2}$–); 1.69–1.79 (m, P$\mathit{CH_2}$–); 3.80 (s, J(Se–H) = 12 Hz), SeCH$_2$ *trans* to Cl); 4.51 (t, 4.7 Hz, SeCH$_2$ *trans* to P); 4.40 (s, Se$\mathit{CH_2}$ J(Se–H) = 11 Hz *trans* isomer); 7.15–7.65 (m, *Ph*) for *cis* and *trans* isomers
4b	14.1		^{2}J(Se–P) = 64	0.94 (t, 6.9 Hz, $\mathrm{PCH_2CH_2CH_2}\mathit{CH_3}$); 1.43 (br, $\mathrm{PCH_2}\mathit{CH_2CH_2}$–); 1.71–1.81 (m, P$\mathit{CH_2}$–); 3.80 (s, Se$\mathit{CH_2}$ *trans* to Cl); 4.50 (t, ^{4}J(P–H) = 4.6 Hz, Se$\mathit{CH_2}$ *trans* to P); 7.15 (t, 7.4 Hz, 4H, C_6H_5); 7.40 (d, 7.4 Hz, C_6H_5); 7.65 (d, 7.1 Hz, 2H C_6H_5); 7.23–7.31(m, Ph)
4c [a]	(*cis*) −3.8; (*trans*) 10.1		^{2}J(Se–P) = 65	1.50 (d), 1.64 (d) (each 11 Hz, P$\mathit{Me_2}$, major *cis* isomer), 1.59 (d), 1.77 (d) (each 12.4 Hz, P$\mathit{Me_2}$, *trans* isomer); 3.38 (s, ^{2}J(Se–H) = 10 Hz, SeCH$_2$ *trans* to Cl); 4.54 (t, ^{4}J(P–H) = 5.1 Hz, SeCH$_2$ *trans* to P) [*cis* isomer]; 3.90 (s, Se$\mathit{CH_2}$, *trans* isomer, 10%);7.14–7.47 (m); 7.64 (d), (*Ph*)
4d	21.2		^{2}J(Se–P) = 64	3.23 (s, *trans* to Cl, Se$\mathit{CH_2}$); 4.83 (t, ^{4}J(P–H) = 4.9 Hz, Se$\mathit{CH_2}$ *trans* to PPh$_3$,); 6.84–7.76 (m, *Ph*)
4e	33.1			0.46 (d, J(P–H) = 3.3 Hz,, Pd–*Me*); 3.13–3.83 (br, Se$\mathit{CH_2}$); 7.01–7.13 (m); 7.32–7.41 (m); 7.60–7.74 (m) (*Ph*)
4f	7.5	3219	^{2}J(^{77}Se–^{31}P) = 57; ^{2}J(^{195}Pt–^{195}Pt) = 846	1.07 (td, 16.7 Hz, d; 7.6 Hz, t; $\mathrm{PCH_2}\mathit{CH_3}$); 1.60–1.94 (m, P$\mathit{CH_2}$); 3.93 (s, ^{3}J(Pt–H) = 41 Hz; ^{2}J(Se–H) = 11 Hz; Se$\mathit{CH_2}$ *trans* to Cl); 4.64 (t, ^{4}J(P–H) = 3.7 Hz; ^{3}J(Pt–H) = 21 Hz; Se$\mathit{CH_2}$ *trans* to PEt$_3$); 7.14 (t, 7.3 Hz, 4H, C_6H_5); 7.41–7.44 (m, 3H, C_6H_5); 7.60 (d, 7.3 Hz, 2H, C_6H_5)} (Ph, SeBz *trans* to P); 7.23–7.31 (m) (Ph, SeBz *cis* to P)
4g	−0.8	3194	^{2}J(^{77}Se–^{31}P) = 57; ^{2}J(^{195}Pt–^{195}Pt) = 860	1.02 (t, 7 Hz, $\mathrm{PCH_2CH_2}\mathit{CH_3}$); 1.42–1.58 (m, $\mathrm{PCH_2}\mathit{CH_2}$–); 1.61–1.86 (m, P$\mathit{CH_2}$–); 3.91 (s, ^{2}J(Se–H) = 10 Hz), ^{3}J(Pt–H) = 41 Hz; Se$\mathit{CH_2}$ *trans* to Cl); 4.63 (t, ^{4}J(P–H) = 3.7 Hz, ^{3}J(Pt–H) = 21 Hz, SeCH$_2$ *trans* to P); 7.13 (t, 6.2 Hz, 4H, C_6H_5); 7.40 (m, 3H, C_6H_5); 7.60 (d, 7.6 Hz, 2H, C_6H_5)} (Ph, SeBz *trans* to P); 7.25–7.30 (m) (Ph, SeBz *cis* to P)
4h	−1.3	3323	^{2}J(^{77}Se–^{31}P) = 60	2.03 (d, J(P–H) = 11 Hz; ^{3}J(Pt–H) = 30 Hz, PMe); 3.19 (s, ^{3}J(Pt–H) = 40 Hz, SeCH$_2$, *trans* to Cl); 4.78 (t, ^{4}J(P–H) = 4 Hz, ^{3}J(Pt–H) = 23 Hz; Se$\mathit{CH_2}$, *trans* to P); 6.90–7.68 (m, *Ph*)
4i	−13.2	3823		0.70 (d, ^{3}J(P–H) = 4.4 Hz; ^{2}J(Pt–H) = 73 Hz; Pt*Me*); 1.59 (d, ^{2}J(P–H) = 10 Hz; ^{3}J(Pt–H) = 41 Hz, P$\mathit{Me_2}$); 3.69 (s, ^{3}J(Pt–H) = 15 Hz, Se$\mathit{CH_2}$, *trans* to Pt*Me*); 4.15 (t, ^{4}J(P–H) = 3.4 Hz, ^{3}J(Pt–H) = 26 Hz; Se$\mathit{CH_2}$, *trans* to P); 7.04–7.47 (m), 7.65–7.71 (m) (Ph)
5a	31.2			1.03 (t, 7.1 Hz, $\mathrm{PCH_2CH_2}\mathit{Me}$); 1.47–1.59 (m, $\mathrm{PCH_2}\mathit{CH_2}$–); 1.69–1.84 (m, P$\mathit{CH_2}$–); 4.39 (s, Se$\mathit{CH_2}$ *cis* to P); 7.29–7.34 (m, 3, 4, 5H, *Ph*); 7.54 (d, 7.2 Hz, 2, 6H, *Ph*)
5b	0.1	3950		1.03 (t, 7.2 Hz, $\mathrm{PCH_2CH_2}\mathit{Me}$); 1.48–1.59 (m, $\mathrm{PCH_2}\mathit{CH_2}$–); 1.62–1.87 (m, P$\mathit{CH_2}$–); 4.36 (s, ^{3}J(Pt–H) 38 Hz); 7.29–7.34 (m, 3, 5H, Ph), 7.51–7.55(m, 2, 6H, Ph)
5c	−4.4	4192		2.06 (d, ^{2}J(P–H) = 12 Hz; ^{3}J(Pt–H) = 39 Hz, P*Me*); 3.62 (s, ^{3}J(Pt–H) = 32 Hz, Se$\mathit{CH_2}$ *trans* to Cl); 7.00–7.60 (m, Ph)
6a	18.3			1.03 (t, 7.2 Hz, $\mathrm{PCH_2CH_2}\mathit{Me}$); 1.42–1.59 (m, $\mathrm{PCH_2}\mathit{CH_2}$–); 1.71–1.87 (m, P$\mathit{CH_2}$–); 3.50 (s, Se$\mathit{CH_2}$ *trans* to Cl); 6.18 (t, 1.9 Hz, 3H, *pz trans* to P); 7.25–7.35 (m, Ph); 8.01 (s, br, 2,4H, *pz*)
6b	−8.6	3170	^{3}J(Pt–P) = 39	1.02 (t, 7.1 Hz, $\mathrm{PCH_2CH_2}\mathit{Me}$); 1.40–1.49 (m, $\mathrm{PCH_2}\mathit{CH_2}$); 1.74–1.83 (m, P$\mathit{CH_2}$); 3.43 (s, ^{3}J(Pt–H) = 40 Hz, Se$\mathit{CH_2}$); 6.29 (s, br, 3H, pz); 7.24–7.33 (m, Ph); 8.11 (s, 2-,4H, pz)
7	−2.2 [b]; −0.8 [c]	3102; 3190		1.09 (m, $\mathrm{PCH_2CH_2}\mathit{Me}$); 1.42–1.53 (m, $\mathrm{PCH_2}\mathit{CH_2}$); 1.57–1.75 (m, P$\mathit{CH_2}$); 1.80 (s, SBu^{t}); 4.11 (s, ^{2}J(Se–H) = 10 Hz, ^{3}J(Pt–H) = 42 Hz, SeBz *trans* to Cl); 4.63 (t, ^{4}J(P–H) = 3.7 Hz, SeBz *trans* to P); 7.15 (t, 4H); 7.45–7.48 (m, 3H); 7.60 (d, 6.9 Hz, 2H; Ph for SeBz *trans* to P); 7.25–7.39 (m, Ph for SeBz *trans* to Cl)

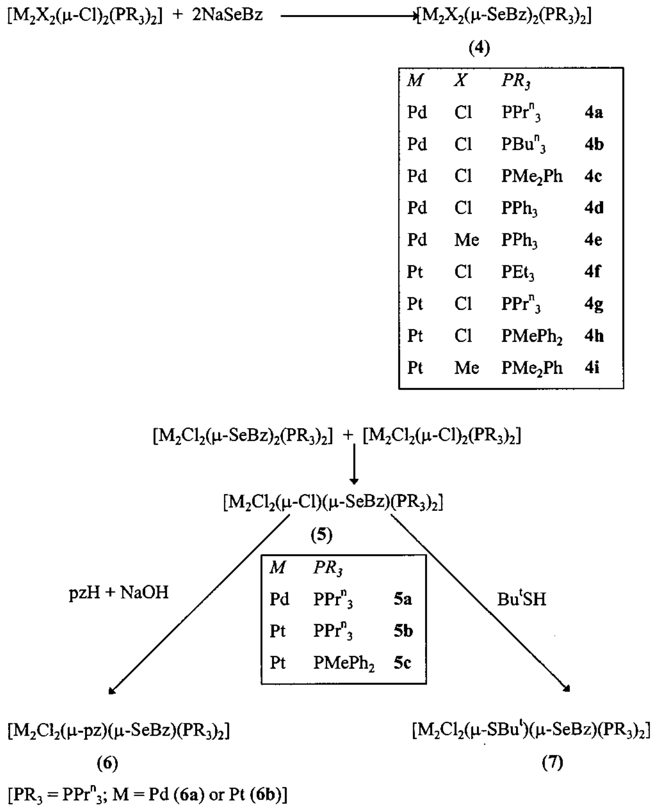
[a] *cis:trans* ratio 9:1.

[b] Phosphine *trans* to bridging SBu^{t}; major isomer.

[c] Phosphine *trans* to bridging SeBz; minor isomer (by integration of ^{31}P-NMR spectrum).

pared with that for the former. These signals were flanked by the ^{77}Se isotope with ^{2}J(Se–P) ~ 60 Hz. The spectra of platinum complexes displayed ^{1}J(Pt–P) couplings which can be compared with the couplings reported for organochalcogenolate bridged complexes $[Pt_2Cl_2(\mu\text{-}ER)_2(PR_3)_2]$ (E = S, Se, Te) [9,10,16,17].

The ^{195}Pt-NMR spectra of **4g** (δ −4072, $^{1}J(^{195}Pt–^{31}P)$ 3200 Hz, $^{2}J(^{195}Pt–^{195}Pt) = 841$ Hz) and **4h** (δ −4107, $^{1}J(^{195}Pt–^{31}P)$ 3310 Hz, $^{2}J(^{195}Pt–^{195}Pt) = 929$ Hz) displayed the expected doublet due to coupling with phosphorus nuclei. The magnitude of $^{2}J(^{195}Pt–^{195}Pt)$ couplings can be compared with bis(organochalcogenolato)-bridged complexes, $[Pt_2Cl_2(\mu\text{-}ER)_2(PR_3)_2]$ [10,18]. The ^{77}Se{^{1}H}-NMR spectra of **4b** [δ 38.8 (*cis* to P), 29.1 (*trans* to P)] and **4g** [δ 11.8, $^{1}J(^{195}Pt–^{77}Se) = 134$ Hz (*cis* to P); −25.3, $^{1}J(^{195}Pt–^{77}Se) = 229$ Hz, $^{2}J(^{77}Se–^{31}P) = 39$ Hz (*trans* to P)] exhibited two signals attributable to bridging SeBz groups, each *trans* to chloride and phosphine ligands. The ^{77}Se-NMR spectra of **4g** (Fig. 1) showed couplings due to ^{195}Pt and ^{31}P nuclei. The BzSe group *trans* to phosphine exhibited phosphorus couplings ($^{2}J(^{77}Se–^{31}P) = 39$ Hz) while for the BzSe *trans* to chloride such couplings are not resolved as the $^{2}J(Se–P)_{cis}$ are < 10 Hz [15b]. The magnitude of $J(^{195}Pt–^{77}Se)$ for BzSe *trans* to P is greater than that of the *trans* to Cl. The compound **7** also existed in two *cis* configurations (**B** and **C**; Y = SBu^t, Cl), thus the ^{31}P-NMR spectra displayed two signals, and the isomer with the phosphines *trans* to SBu^t predominated.



M	*X*	*PR$_3$*	
Pd	Cl	PPr$^n_3$	**4a**
Pd	Cl	PBu$^n_3$	**4b**
Pd	Cl	PMe$_2$Ph	**4c**
Pd	Cl	PPh$_3$	**4d**
Pd	Me	PPh$_3$	**4e**
Pt	Cl	PEt$_3$	**4f**
Pt	Cl	PPr$^n_3$	**4g**
Pt	Cl	PMePh$_2$	**4h**
Pt	Me	PMe$_2$Ph	**4i**

M	*PR$_3$*	
Pd	PPr$^n_3$	**5a**
Pt	PPr$^n_3$	**5b**
Pt	PMePh$_2$	**5c**

Scheme 2.

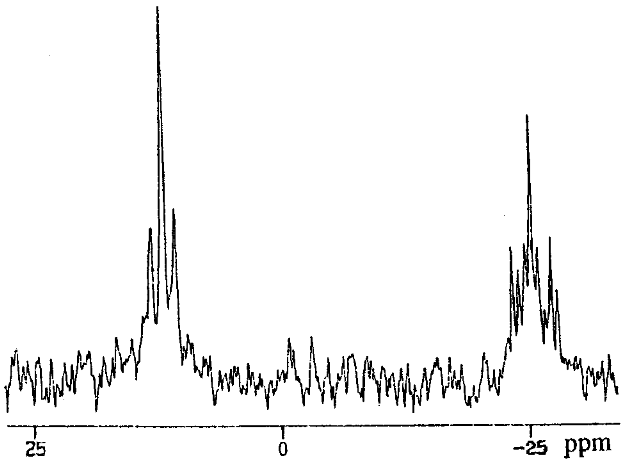


Fig. 1. ^{77}Se{^{1}H}-NMR spectrum of **4g** in CDCl$_3$.

On the basis of NMR data **5** and **6** have been assigned a *cis* configuration with phosphine ligands *trans* to bridging Y (Y = Cl or pz) (**C**). Accordingly the methylene proton signal of SeBz in the ^{1}H-NMR spectra did not show ^{4}J(P–H) couplings. The ^{31}P-NMR spectra of **5b** and **5c** showed considerably large ^{1}J(Pt–P) couplings. ^{195}Pt and ^{77}Se-NMR spectra of **5b** were recorded in CDCl$_3$. The ^{195}Pt-NMR spectrum exhibited the expected doublet at δ −3986 with $^{1}J(^{195}Pt–^{31}P) = 3955$ Hz. The ^{77}Se-NMR spectrum showed a triplet at δ 69.2 with $^{1}J(^{195}Pt–^{77}Se) = 113$ Hz. The magnitude of ^{2}J(Se–P) appears to be small which further suggests that phosphine is *cis* to the bridging SeBz group. Recently we have reported a series of organochalcogenolato-bridged complexes of type **5** and **6** for which a *cis* configuration (**C**) has been established by X-ray diffraction data [16,19–22].

2.3. Structure of $[Pt_2Cl_2(\mu\text{-}SeBz)_2(PPr^n_3)_2]$ (4g)

The crystal and molecular structure of $[Pt_2Cl_2(\mu\text{-}SeBz)_2(PPr^n_3)_2]$ (**4g**) together with atomic numbering scheme is shown in Fig. 2. Selected bond lengths and angles are summarized in Table 2. The molecule consists of two slightly distorted square planar platinum atoms which are bridged together by two benzylselenolato groups. The platinum atoms Pt(1) and Pt(2) showed deviation of 0.046 and 0.032 Å, respectively, from the mean planes defined by P(1)Cl(1)Se(1)Se(2) and P(2)Cl(2)Se(1)Se(2). The molecule has a sym-*cis* configuration with a non-planar four-membered ‘Pt$_2$Se$_2$’ ring (hinge angle 131.1°). This is in contrast to the ethylselenato-bridged complex $[Pt_2Cl_2(\mu\text{-}SeEt)_2(PEt_3)_2]$ which has a planar Pt$_2$Se$_2$ ring [9]. Alkylthiolato-bridged palladium and platinum complexes adopt a non-planar conformation for the four-

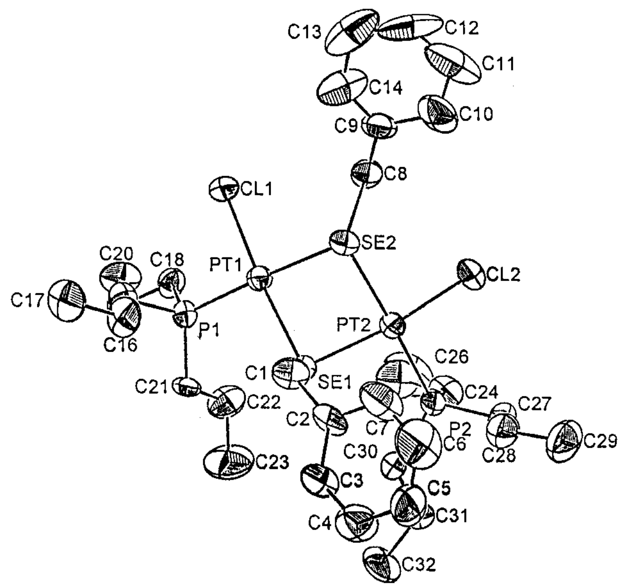


Fig. 2. Molecular structure with atomic numbering scheme of $[Pt_2Cl_2(\mu\text{-SeBz})_2(PPr^n_3)_2]$ (**4g**).

Table 2
Selected bond lengths(Å) and angles(°) for $[Pt_2Cl_2(\mu\text{-SeBz})_2(PPr^n_3)_2]$ (**4g**)

Pt(1)–P(1)	2.253(3)	Pt(2)–P(2)	2.257(3)
Pt(1)–Cl(1)	2.338(2)	Pt(2)–Cl(2)	2.345(3)
Pt(1)–Se(1)	2.3885(10)	Pt(2)–Se(1)	2.3874(12)
Pt(1)–Se(2)	2.4829(13)	Pt(2)–Se(2)	2.4734(11)
Se(1)–C(1)	2.015(10)	Se(2)–C(8)	1.979(10)
Pt(1)–Se(1)–Pt(2)	89.99(4)	Pt(1)–Se(2)–Pt(2)	85.89(4)
P(1)–Pt(1)–Cl(1)	89.19(10)	P(2)–Pt(2)–Cl(2)	88.63(10)
P(1)–Pt(1)–Se(1)	96.09(7)	P(2)–Pt(2)–Se(1)	96.03(8)
Cl(1)–Pt(1)–Se(1)	174.72(8)	Cl(2)–Pt(2)–Se(1)	171.06(9)
P(1)–Pt(1)–Se(2)	175.26(8)	P(2)–Pt(2)–Se(2)	175.49(9)
Cl(1)–Pt(1)–Se(2)	93.88(8)	Cl(2)–Pt(2)–Se(2)	94.69(8)
Se(1)–Pt(1)–Se(2)	80.88(4)	Se(1)–Pt(2)–Se(2)	81.10(4)
Se(1)–C(1)–C(2)	112.2(8)	Se(2)–C(8)–C(9)	110.9(8)

membered 'M_2SRX' (X = SR or Cl) with dihedral angle varying in the range 130–154° between the two coordination planes [16,20,23–26].

The Pt–Cl [2.338(2), 2.345(3) Å], Pt–P, Se–C and P–C distances are in agreement with the values reported in the literature [1,4,5,8–10,16,24]. There are distinctly two types of Pt–Se bonds, the one *trans* to phosphine is longer (~ 0.1 Å) than that *trans* to chloride, in accordance with the *trans* influence of the PR_3 and Cl ligands. These distances can be compared with those observed in $[Pt_2Cl_2(\mu\text{-SeEt})_2(PEt_3)_2]$ [9], $[Pt_2Cl_2(\mu\text{-Cl})(\mu\text{-SeEt})(PMe_2Ph)_2]$ [22] and similar other complexes [27–29]. The two Pt–Se–Pt angles [89.99(4), 85.89(4)°] are significantly smaller than those observed in $[Pt_2Cl_2(\mu\text{-SeEt})_2(PEt_3)_2]$ [9] (96.9°), but can be compared with the alkylthiolato bridged complex $[Pt_2Cl_2(\mu\text{-SEt})_2(PR_3)_2]$ [85.1(2), 89.7(2)°] [24]. The benzyl groups adopt an *anti* configuration.

2.4. Thermal studies

In order to evaluate whether the benzylselenolate complexes reported here can serve as precursors for the synthesis of palladium selenides, thermolysis of one representative complex, $[Pd(SeBz)_2]_n$ (**1a**) was studied. The thermogravimetric analysis (TGA) (Fig. 3) of **1a** was carried out in a flowing argon atmosphere. The TG trace (Fig. 3) shows two stages of decomposition. The product formed after the first stage of decomposition (in the temperature range 210–500°C) was identified as a mixture of $PdSe_2$ and $Pd_{17}Se_{15}$ contaminated with carbon (typical analysis of a sample heated at 300°C: C, 7.7; H, 0.6; Se, 49.1; Pd, 40.4%, XRD pattern showed peaks due to $PdSe_2$ and $Pd_{17}Se_{15}$). In the second stage of decomposition (above 600°C) selenium is eleminated leading to the formation of $Pd_{17}Se_{15}$ as indicated by the weight loss and XRD pattern which compares well with the reported pattern (JCPDS-ICDD 29-1437; 11-508). The carbon contents (C 5.7%) in this product were reduced slightly.

3. Experimental details

The complexes $[MCl_2(L\text{-}L)]$ [30,31], $[M_2Cl_2(\mu\text{-Cl})_2(PR_3)_2]$ [32] (M = Pd or Pt; L-L = dppm, dppe, $2PPh_3$; $PR_3 = PEt_3$, PPr^n_3, PBu^n_3, PMe_2Ph; $PMePh_2$ or PPh_3), $[M_2Me_2(\mu\text{-Cl})_2(PR_3)_2]$ [33,34] and Bz_2Se_2 (Bz = $PhCH_2$–) were prepared according to literature methods. Due to slow photodecomposition of Bz_2Se_2, it was recrystallized every month from petroleum ether, m.p.

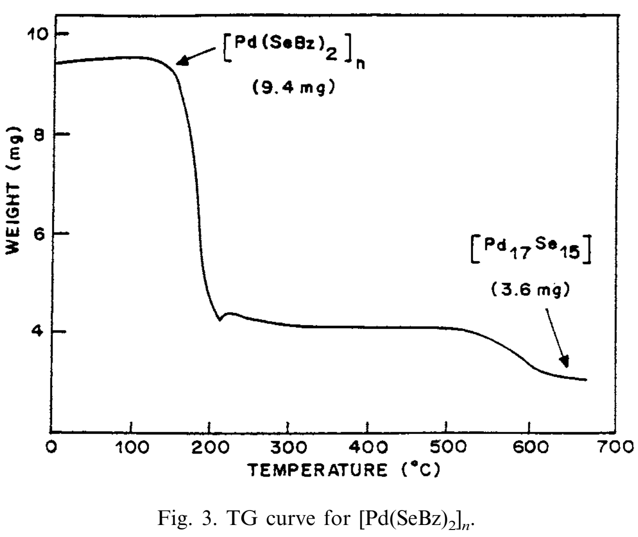


Fig. 3. TG curve for $[Pd(SeBz)_2]_n$.

Table 3
Physical and analytical data for benzylselenolate complexes of palladium and platinum

Complex		Recrystallization solvent	Yield (%)	M.p. (°C)	Analysis: found (calc.) (%)	
					C	H
$[\{Pd(SeBz)_2\}_n]$	**1a**	CH_2Cl_2	82	135	37.3 (37.6)	3.0 (3.2)
$[\{Pt(SeBz)_2\}_n]$	**1b**	CH_2Cl_2	37	160	31.6 (31.4)	2.4 (2.6)
$[Pt(SeBz)_2(PPh_3)_2]$	**2**	C_6H_6–hexane	40	112	56.1 (56.6)	3.9 (4.2)
$[Pd(SeBz)_2(dppe)]$	**3a**	CH_2Cl_2–hexane	69	171	56.3 (56.8)	4.4 (4.5)
$[Pt(SeBz)_2(dppm)]$	**3b**	CH_2Cl_2–hexane	65	157	50.5 (50.9)	3.6 (3.9)
$[Pt(SeBz)_2(dppe)]$	**3c**	CH_2Cl_2–hexane	55	187	51.2 (51.4)	3.8 (4.1)
$[Pd_2Cl_2(\mu\text{-}SeBz)_2(PPr^n_3)_2]$	**4a**	CH_2Cl_2–hexane	58	156	40.4 (40.7)	5.9 (5.9)
$[Pd_2Cl_2(\mu\text{-}SeBz)_2(PBu^n_3)_2]$	**4b**	CH_2Cl_2–ethanol	66	137	44.2 (44.4)	7.1 (6.7)
$[Pd_2Cl_2(\mu\text{-}SeBz)_2(PMe_2Ph)_2]$	**4c**	CH_2Cl_2–hexane	38	169	39.7 (40.0)	3.8 (4.0)
$[Pd_2Cl_2(\mu\text{-}SeBz)_2(PPh_3)_2]$	**4d**	CH_2Cl_2–hexane	80	150	51.9 (52.3)	3.7 (3.9)
$[Pd_2Me_2(\mu\text{-}SeBz)_2(PPh_3)_2]$	**4e**	CH_2Cl_2–methanol	75	149	55.9 (56.4)	4.4 (4.5)
$[Pt_2Cl_2(\mu\text{-}SeBz)_2(PEt_3)_2]$	**4f**	CH_2Cl_2–ethanol	43	205(d)	29.8 (30.1)	5.3 (4.3)
$[Pt_2Cl_2(\mu\text{-}SeBz)_2(PPr^n_3)_2]$	**4g**	CH_2Cl_2–hexane	60	184	34.1 (34.3)	5.3 (5.0)
$[Pt_2Cl_2(\mu\text{-}SeBz)_2(PMePh_2)_2]$	**4h**	CH_2Cl_2–hexane	70	178(d)	39.8 (40.0)	3.4 (3.4)
$[Pt_2Me_2(\mu\text{-}SeBz)_2(PMe_2Ph)_2]$	**4i**	CH_2Cl_2–hexane	70	178(d)	36.7 (37.0)	4.0 (4.1)
$[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeBz)(PPr^n_3)_2]$	**5a**	CH_2Cl_2–hexane	94	145	36.7 (37.1)	6.1 (6.1)
$[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeBz)(PPr^n_3)_2]$	**5b**	CH_2Cl_2–hexane	68	144	29.9 (30.4)	4.7 (5.0)
$[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeBz)(PMePh_2)_2]$	**5c**	CH_2Cl_2–ethanol	72	185(d)	37.2 (37.1)	3.2 (3.1)
$[Pd_2Cl_2(\mu\text{-}pz)(\mu\text{-}SeBz)(PPr^n_3)_2]$ [a]	**6a**	CH_2Cl_2–hexane	55	146	39.6 (40.0)	5.9 (6.2)
$[Pt_2Cl_2(\mu\text{-}pz)(\mu\text{-}SeBz)(PPr^n_3)_2]$ [b]	**6b**	CH_2Cl_2–ethanol	48	149	33.1 (33.0)	5.0 (5.1)
$[Pt_2Cl_2(\mu\text{-}SBu^t)(\mu\text{-}SeBz)(PPr^n_3)_2]$	**7**	CH_2Cl_2–hexane	40	136	33.1 (33.5)	5.6 (5.6)

[a] N: found 3.1; calcd. 3.3%.

[b] N: found 2.9; calcd. 2.7%.

90°C (lit. 90–91°C) [35]. ^1H-NMR in $CDCl_3$: $\delta = 3.86$ (s, $^2J(Se\text{–}H)$ 14.5 Hz; SeCH_2), 7.25–7.31 (m, Ph). $^{77}Se\{^1H\}$-NMR in $CDCl_3$: $\delta = 400.3$. The tertiary phosphines (Strem Chemicals, USA) and $NaBH_4$ were obtained from commercial sources. Reactions were carried out under nitrogen using Schlenk techniques in dry and distilled analytical grade solvents. The ^1H, $^{31}P\{^1H\}$, $^{77}Se\{^1H\}$ and $^{195}Pt\{^1H\}$-NMR spectra were recorded on a Bruker DPX-300 NMR spectrometer operating at 300.00, 121.49, 57.31, and 64.52 MHz, respectively. Chemical shifts are relative to internal chloroform (δ 7.26 ppm) for ^1H, external 85% H_3PO_4 for ^{31}P, Me_2Se for ^{77}Se and Na_2PtCl_6 in D_2O for ^{195}Pt. A 90° pulse was used in every case. Thermogravimetric analysis (TGA) was carried out on a Setaram 92-16-18 instrument. The TG curves were recorded at a heating rate of 10°C min^{-1} under a flow of argon. Microanalyses of the complexes were carried out in the Analytical Chemistry Division of this research centre.

3.1. $[\{Pd(SeBz)_2\}_n]$ (**1a**)

To a dichloromethane solution (10 cm^3) of Bz_2Se_2 (1.112 gm, 3.27 mmol) was added a methanolic solution of $NaBH_4$ (255 mg, 6.74 mmol) at room temperature with stirring for 5 min whereupon the yellow coloured solution became colourless. To this an aqueous solution (10 cm^3) of Na_2PdCl_4 (954 mg, 3.24 mmol) was added immediately. A brown precipitate formed. The reactants were stirred for 5 h. The brown insoluble product was filtered off, washed with water, ethanol and diethylether and dried in vacuo (yield 1.19 g, 82%). The product was sparingly soluble in dichloromethane. It was extracted in 90% yield from dichloromethane using Soxhlet apparatus. Pertinent data are summarized in Table 3.

3.2. $[\{Pt(SeBz)_2\}_n]$ (**1b**)

This was prepared in 95% yield in an analogous manner to complex **1a** from Bz_2Se_2 (259 mg, 0.76 mmol), $NaBH_4$ (62 mg, 1.64 mmol) and K_2PtCl_4 (309 mg, 0.74 mmol). It was extracted in 37% yield from dichloromethane using Soxhlet apparatus.

3.3. $[Pt(SeBz)_2(PPh_3)_2]$ (**2**)

(a) Analogously as described for **3a**, by using $[PtCl_2(PPh_3)_2]$ (458 mg, 0.58 mmol) and NaSeBz [prepared from Bz_2Se_2 (199 mg, 0.59 mmol) and $NaBH_4$ (47.3 mg, 1.24 mmol) as starting materials]. Recrystallized from benzene–hexane as orange crystals in 40% yield.

(b) To a dichloromethane suspension (8 cm^3) of $[\{Pt(SeBz)_2\}_n]$ (55 mg, 0.10 mmol) was added solid PPh_3 (56 mg, 0.21 mmol) and the mixture was stirred for 1 h. The clear solution was filtered and the filtrate concentrated in vacuo, and washed with hexane and dried to give 28% title complex. The NMR spectra were consistent with the product obtained in (a).

*3.4. Reaction of **2** with methyl iodide*

To a dichloromethane solution (15 cm^3) of $[Pt(\text{-}SeBz)_2(PPh_3)_2]$ (50 mg, 0.05 mmol) excess MeI was added, and the yellow coloured solution was stirred for 4 h. The solvent was evaporated in vacuo. The residue was washed with hexane, diethylether and dichloromethane to leave a pale yellow residue. ^1H-NMR ($CDCl_3$): $\delta = 7.38\text{–}7.43$ (br); 7.72–7.75 (br) (Ph). $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta = 12.6$ [$^1J(Pt\text{–}P) = 2497$ Hz]. Anal. Calc. for $C_{36}H_{30}P_2I_2Pt$ (973.5): C, 44.4; H, 3.2. Found: C, 43.9; H, 2.9%.

*3.5. $[Pd(SeBz)_2(dppe)]$ (**3a**)*

(a) To a methanolic solution (15 cm^3) of NaSeBz (prepared from Bz_2Se_2 (125 mg, 0.37 mmol) and $NaBH_4$ (30 mg, 0.79 mmol) a dichloromethane suspension of $[PdCl_2(dppe)]$ (204 mg, 0.35 mmol) was added at once and the resulting orange coloured mixture was stirred for 4 h. The solvents were evaporated in vacuo and the orange red residue was extracted with dichloromethane (3×8 cm^3), and was passed through a Florisil column. The solvent was evaporated in vacuo and the residue obtained as an orange crystalline solid.

Similarly **3b** and **3c** were prepared. **3a** can also be prepared from $[Pd(SeBz)_2]_n$ and dppe as described for **2** (method (b)).

*3.6. $[Pd_2Cl_2(\mu\text{-}SeBz)_2(PPr^n_3)_2]$ (**4a**)*

A dichloromethane solution (10 cm^3) of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PPr^n_3)_2]$ (325 mg, 0.48 mmol) was added to a freshly prepared methanolic solution of NaSeBz [prepared from Bz_2Se_2 (165 mg, 0.49 mmol) and $NaBH_4$ (39 mg, 1.03 mmol)] with stirring at room temperature. After stirring the mixture for 4 h, the solvents were evaporated in vacuo. The yellow-orange coloured residue was extracted with dichloromethane (3×8 cm^3), the solution was passed through a Florisil column and the solvents evaporated in vacuo. The residue was dissolved in acetone to leave some orange–red coloured solid (yield 193 mg, m.p. 182°C; found: C, 40.0; H, 4.8%) and the filtrate afforded yellow crystals (m.p. 156°C; 128 mg; 28%) which can be recrystallized with dichloromethane–hexane.

Other binuclear bis(selenolato) bridged complexes were prepared in a similar manner.

*3.7. $[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeBz)(PPr^n_3)_2]$ (**5a**)*

To a dichloromethane solution (20 cm^3) of $[Pd_2Cl_2(\mu\text{-}SeBz)_2(PPr^n_3)_2]$ (224 mg, 0.24 mmol) solid $[Pd_2Cl_2(\mu\text{-}Cl)_2(PPr^n_3)_2]$ (162 mg, 0.24 mmol) (yellow or a mixture of yellow and orange-red forms can be taken) was added, and stirred for 5 h. The solvent was evaporated in vacuo. Similarly **5b** and **5c** were prepared in refluxing CH_2Cl_2.

*3.8. $[Pd_2Cl_2(\mu\text{-}pz)(\mu\text{-}SeBz)(PPr^n_3)_2]$ (**6a**)*

To a solution of $[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeBz)(PPr^n_3)_2]$ (104 mg, 13 mmol) was added a methanolic solution (2 cm^3) of pzH (11 mg, 0.16 mmol) containing aq. NaOH solution (1.62 cm^3, 0.1 N) with vigorous stirring which continued for 5 h. The solvent was evaporated in vacuo. It was extracted with dichloromethane and passed through a Florisil column. The solvent was evaporated in vacuo and the residue was recrystallized from dichloromethane–hexane as a yellow solid in 55% (60 mg) yield.

3.9. $[Pt_2Cl_2(\mu\text{-}SBu^t)(\mu\text{-}SeBz)(PPr^n_3)_2]$ (7)

To a dichloromethane solution (20 cm^3) of $[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeBz)(PPr^n_3)_2]$ (81 mg, 0.08 mmol) Bu^tSH (0.5 cm^3) was added in excess, and stirred for 5 h at room temperature. The solvent was evaporated in vacuo. The residue was washed with hexane to remove the excess Bu^tSH; the residue on recrystallization from dichloromethane–hexane gave a pale yellow fibrous compound:

*3.10. X-ray crystallographic study of **4g***

X-ray data on yellow crystals of $[Pt_2Cl_2(\mu\text{-}SeBz)_2(PPr^n_3)_2]$ (**4g**) were collected at room temperature on an Enraf–Nonius CAD-4 diffractometer using graphite monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å) employing the $\omega\text{–}2\theta$ scan technique. The unit cell parameters (Table 4) were determined from 25 reflections measured by random search routine and indexed by the method of short vectors followed by least-squares refinement. The intensity data were corrected for Lorentz-polarization and absorption effects. The structure was solved using SHELXS-86 [36] and SHELXL-97 [37] computer programs. The non-hydrogen atoms were refined anisotropically.

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Table 4
Crystallographic data for $[Pt_2Cl_2(\mu\text{-}SeBz)_2(PPr^n_3)_2]$ **(4g)**

Empirical formula	$C_{32}H_{56}Cl_2P_2Pt_2Se_2$
Formula weight	1121.71
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Orthorhombic, *Pbca*
Unit cell dimensions	
a (Å)	16.774(4)
b (Å)	20.575(3)
c (Å)	23.602(4)
Volume (Å^3)	8146(3)
Z	8
D_{calc} (mg m^{-3})	1.829
Absorption coefficient (mm^{-1})	8.878
F(000)	4288
Crystal size(mm)	0.2 × 0.2 × 0.1
θ range for data collection (°)	2.11–24.99
Index ranges	$0 \le h \le 19$, $0 \le k \le 24$, $0 \le l \le 28$
Reflections collected/unique	7102/7102 [$R_{int} = 0.0000$]
Completeness to $2\theta = 24.99$ (%)	90.6
Absorption correction	Ψ scan
Maximum and minimum transmission	0.99 and 0.61
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7102/0/362
Goodness of fit on F^2	1.055
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0401$, $wR_2 = 0.0651$
Largest difference peak and hole (e Å^{-3})	0.764 and −0.818

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