

Platinum(II) Complexes of 2-(Dimethylamino)ethylselenolate – Donor–Acceptor Inter-Ligand Interactions as Evident from Experimental and TD-DFT Computational Analysis

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Several platinum(II) complexes of 2-(dimethylamino)ethane-selenolate with the formulae, $[\text{PtCl}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PR}_3)]$ (**1**), $[\text{PtPh}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PnBu}_3)]$ (**2**), $[\text{Pt}_2\text{Ph}_2(\text{Cl})(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PnBu}_3)_2]$ (**3**), $[\text{Pt}_2\text{Cl}_3(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PR}_3)_2]$ (**4**), $[\text{Pt}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)_2(\text{P-P})]$ (**5**), $[\text{Pt}_2(\text{SeCH}_2\text{CH}_2\text{NMe}_2)_2(\text{P-P})_2]^{++}$ (**6**), and $[\text{Pt}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PPh}_3)]_n[\text{PF}_6]_n$ (**7**) have been synthesized and characterized by elemental analysis, UV/Vis and NMR (^1H , ^{31}P , ^{77}Se , ^{195}Pt) spectroscopy. The stereochemistry of these complexes (**1–7**) has been deduced

from NMR spectroscopic data. A weak absorption in the UV/Vis spectrum of **1** has been assigned to a ligand (Se)-to-ligand (PR_3) charge transfer (LLCT), supported by TD-DFT calculations. The structures of $[\text{PtCl}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PPh}_3)]$ and $[\text{Pt}_2\text{Ph}_2(\text{Cl})(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PnBu}_3)_2]$ have been established by single crystal X-ray diffraction analysis. Each platinum atom in the latter is coordinated to four different ligands and $\text{Me}_2\text{NCH}_2\text{CH}_2\text{Se}$ behaves as μ_2 -bridging and is also simultaneously chelated to one of the platinum atoms.

Introduction

Platinum group metal chalcogenolates have attracted considerable attention during the last 15 years or so due to their wide structural diversity^[1] and relevance in catalysis,^[2–5] and as a result of being precursors for the synthesis of metal chalcogenides^[6–8] for electronic devices.^[9] The area of metal chalcogenolates has been dominated by molecules containing the M–SR linkage.^[1] In most cases these molecules have been isolated as non-volatile, insoluble (or sparingly soluble) polymers, thus making them inconvenient as precursors for the synthesis of metal chalcogenides. Although several strategies have been adopted to suppress polymerisation, the use of hybrid ligands containing both soft chalcogen and hard N donor atoms has been quite successful, such as pyridine-2-thiolate^[10] or aliphatic mercapto amines.^[11–14] The continued current interest in selenium containing inorganic materials^[15] and in pursuance of our program on the design and development of molecular precursors, we explored some chemistry of internally functionalized selenolates, viz. $\text{pySe}^{[16]}$ and $\text{Me}_2\text{NCH}_2\text{CH}_2\text{Se}^-$.^[8] Herein we now report the synthesis, spectroscopy, electrochemistry, structures, and TD-DFT calculations of platinum complexes derived from the latter ligand.

Results and Discussion

Synthesis and Spectroscopy

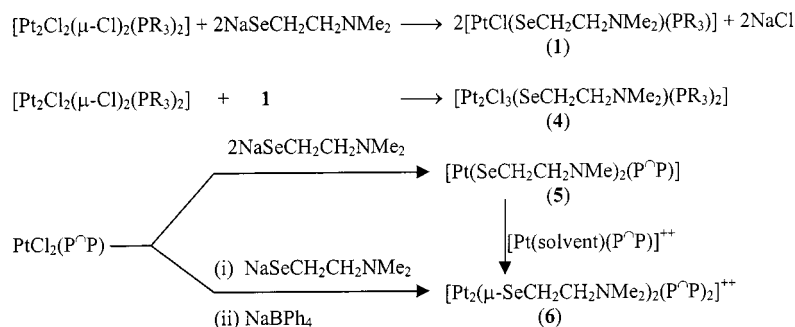
Treatment of $[\text{Pt}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{PR}_3)_2]$ with two equivalents of $\text{NaSeCH}_2\text{CH}_2\text{NMe}_2$, prepared by the reductive cleavage of the Se–Se bond in $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{Se})_2$ with sodium borohydride, afforded dimethylaminoethylselenolate complexes of the type $[\text{PtCl}(\eta^2\text{-SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PR}_3)]$ (**1**) [$\text{PR}_3 = \text{PEt}_3$ (**1a**), PnPr_3 (**1b**), PnBu_3 (**1c**), PMe_2Ph (**1d**), or PMePh_2 (**1e**)] (Scheme 1). The analogous triphenylphosphane complex, $[\text{PtCl}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PPh}_3)]$ (**1f**) can be readily prepared by the reaction of $\text{PtCl}_2(\text{PPh}_3)_2$ with one equivalent of $\text{NaSeCH}_2\text{CH}_2\text{NMe}_2$.

The ^1H NMR spectra of **1** showed the expected integration and peak multiplicities. The selenolate proton resonances, i.e., SeCH_2 , NMe_2 , NCH_2 were flanked with platinum satellites with $^3J(\text{Pt-H})$ being 24–27, 14–18, and 36–42 Hz, respectively. The observed magnitudes of $^3J(\text{Pt-H})$ can be compared with platinum complexes containing neutral $\text{RSeCH}_2\text{CH}_2\text{NMe}_2$ ligands.^[17,18] The ^{31}P NMR spectra of **1** exhibited single resonances flanked with ^{195}Pt satellites. The magnitude of $^1J(\text{Pt-P})$, (3434–3662 Hz) indicates that the phosphane ligand is *trans* to the nitrogen atom of the chelated $[\text{SeCH}_2\text{CH}_2\text{NMe}_2]^-$ group.^[16,19,20] The $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectra of these complexes displayed a doublet due to coupling with a single ^{31}P nucleus. The doublet appeared in a narrow range of $\delta = -4266$ to -4308 . As is evident from Table 1, there is shielding of the ^{195}Pt resonances as the phosphane ligand is changed from PMe_2Ph to PMePh_2 through PPh_3 . A similar trend is evident for ^{77}Se and ^{31}P chemical shifts which, however, showed deshielding. The ^{77}Se NMR resonances for **1** appeared as a triplet owing to the coupling with the ^{195}Pt nucleus. The resonance for **1f**, however, appeared as a broad signal and

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Scheme 1

Table 1. $^{31}\text{P}\{^1\text{H}\}$, $^{77}\text{Se}\{^1\text{H}\}$ and $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectroscopic data (δ in ppm, J in Hz) for dimethylaminoethaneselenolate complexes of platinum(II)

Complex	$^{195}\text{Pt}\{\text{}^1\text{H}\}$	$^1J(^{195}\text{Pt}\text{-}^{31}\text{P})$	$^{77}\text{Se}\{\text{}^1\text{H}\}$	$^1J(^{195}\text{Pt}\text{-}^{77}\text{Se})$	$^{31}\text{P}\{\text{}^1\text{H}\}$	$^1J(^{195}\text{Pt}\text{-}^{31}\text{P})$
	δ		δ			
[PtCl(SeCH ₂ CH ₂ NMe ₂)(PEt ₃)] (1a)	−4308(d)	3407	140.1	147	4.5	3434
[PtCl(SeCH ₂ CH ₂ NMe ₂)(P <i>n</i> Pr ₃)] (1b)	−4283(d)	3400	138.5	129	−4.7	3415
[PtCl(SeCH ₂ CH ₂ NMe ₂)(P <i>n</i> Bu ₃)] (1c)	−4284(d)	3394	137.8	138	−4.0	3416
[PtCl(SeCH ₂ CH ₂ NMe ₂)(PMe ₂ Ph)] (1d)	−4266	3439	164(d)	123	−21.8	3454
				$^2J(\text{Se-P}) = 24$		
[PtCl(SeCH ₂ CH ₂ NMe ₂)(PMePh ₂)] (1e)	−4293(d)	3555	190.6(d)	104	−6.8	3571
				$^2J(\text{Se-P}) = 30$		
[PtCl(SeCH ₂ CH ₂ NMe ₂)(PPh ₃)] (1f)	−4305	3658	218.6(br)	—	7.4	3662
[Pt(Ph)(SeCH ₂ CH ₂ NMe ₂)(P <i>n</i> Bu ₃)] (2)	−4245	3845	—	—	−3.1	3834
[Pt ₂ (Ph) ₂ Cl(SeCH ₂ CH ₂ NMe ₂)(P <i>n</i> Bu ₃) ₂] (3)	−4295	3776	—	—	−1.0	3783
	−4073	3761	—	—	−4.2	3829
[Pt ₂ Cl ₃ (SeCH ₂ CH ₂ NMe ₂)(PEt ₃) ₂] (4a)	—	—	—	—	5.1	3203
					3.5	3355
[Pt ₂ Cl ₃ (SeCH ₂ CH ₂ NMe ₂)(PMe ₂ Ph) ₂] (4b)	—	—	—	—	−21.0	3581
					−22.4	3359
[Pt(SeCH ₂ CH ₂ NMe ₂) ₂ (dppm)] (5a)	−4251(t)	2429	78.0	294	−52.9	2412
[Pt(SeCH ₂ CH ₂ NMe ₂) ₂ (dppe)] (5b)	−4958(t)	2884	29.3	264	46.7	2859
				$J(\text{Se-P}) = 11$		
[Pt(SeCH ₂ CH ₂ NMe ₂) ₂ (dppp)] (5c)	−4913(t)	2783	53.5	279	−1.8	2849
[Pt ₂ (SeCH ₂ CH ₂ NMe ₂) ₂ (dppm) ₂][BPh ₄] ₂ (6a)	−4065(d,d)	2738	255.0	472	−39.3(d)	2286
					−44.8(d)	2745
						$J(\text{P-P}) = 65$
[Pt ₂ (SeCH ₂ CH ₂ NMe ₂) ₂ (dppe) ₂][BPh ₄] ₂ (6b)	−4680(d,d)	2852	276.6	385	47.3	2822
					36.9	3158
[Pt ₂ (SeCH ₂ CH ₂ NMe ₂) ₂ (dppp) ₂][BPh ₄] ₂ (6c)	−4534(d,d)	2706	309.8	316	−1.8(d)	2676
					−13.7(d)	3048
						$J(\text{P-P}) = 31$
						$J(\text{P-P}) = 31$
[Pt(SeCH ₂ CH ₂ NMe ₂)(PPh ₃)] _{<i>n</i>} [PF ₆] _{<i>n</i>} (7)	−4071(d)	3323	49.8	—	5.3	3330
	(major)				(major)	
	−3854	3337	17.9	—	3.1	3353
	(minor)				(minor)	

hence platinum coupling could not be resolved. The magnitude of $^1J(^{195}\text{Pt}\text{-}^{77}\text{Se})$ is comparable to that of the values reported for mononuclear platinum selenolates.^[16,21,22] The appearance of a single resonance in ^{77}Se NMR spectra suggests that the phosphane is *cis* to the selenium atom as the $^2J(^{77}\text{Se}\text{-}^{31}\text{P})_{\text{cis}}$ couplings are usually small (> 10 Hz).^[22,23] However, such couplings are slightly larger for **1d** and **1e** (24 and 30 Hz, respectively) and could thus be resolved in the ^{77}Se NMR spectra.

Reaction of $[\text{Pt}_2\text{Ph}_2(\mu\text{-Cl})_2(\text{P}^n\text{Bu}_3)_2]$ with two equivalents of $\text{NaSeCH}_2\text{CH}_2\text{NMe}_2$, affords a mixture of products, $[\text{PtPh}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{P}^n\text{Bu}_3)]$ (**2**) and $[\text{Pt}_2\text{Ph}_2(\text{Cl})(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{P}^n\text{Bu}_3)_2]$ (**3**). Compound **3** appears to be an intermediate product in the reaction, which on further reaction with $\text{NaSeCH}_2\text{CH}_2\text{NMe}_2$ yields **2**. The calculated values of C, H, and N for the two are not significantly different, hampering an unambiguous identification of **2** and **3**. The two can, however, be separated by repeated

recrystallization. The NMR spectroscopic data for **2** can be compared with **1** as described above. Although the magnitude of $^1J(\text{Pt-P})$ is greater (418 Hz) than that of **1c**, it is in compliance with ArPt^{II} complexes in which the phosphane is *trans* to nitrogen, e.g. $[\text{Pt}_2\text{R}_2(\mu\text{-N-N})_2(\text{PR}_3)_2]$ ($\text{R} = \text{Me}$ or aryl, $\text{N-N} = \text{pyrazole}$).^[24] The ^{31}P and ^{195}Pt NMR spectra of **3** exhibited two separate resonances attributable to “ $\text{PtPhCl}(\text{PnBu}_3)$ ” and “ $\text{PtPh}(\text{Se-N})(\text{PnBu}_3)$ ” fragments. The magnitude of $^1J(\text{Pt-P})$ suggests that the phosphane ligand is *trans* to Cl in the former and *trans* to N in the latter fragment.^[25] This stereochemistry is unambiguously established by X-ray structural analysis (see later).

The chloro analogue of **3**, $[\text{Pt}_2\text{Cl}_3(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PR}_3)_2]$ (**4**) [$\text{PR}_3 = \text{PEt}_3$ (**4a**), PMe_2Ph (**4b**)] can be obtained readily by treatment of $[\text{Pt}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{PR}_3)_2]$ with **1** in 1:2 molar ratio. The ^{31}P NMR spectra of a freshly prepared solution exhibited two singlets each flanked with platinum satellites. The signal of lower frequency may be attributed to the phosphane attached to the metal atom containing the chelating Se-N ligand. The magnitude of $^1J(\text{Pt-P})$ coupling associated with this signal is reduced (≈ 90 Hz) relative to that of the corresponding mononuclear complex. The second resonance at higher frequency may be assigned to the phosphane coordinated to the metal atom containing two chlorines and the selenium atom. Similar NMR spectroscopic data have been reported for $[\text{Pt}_2\text{Cl}_3(\mu\text{-Sepy})(\text{PR}_3)_2]$.^[16] Although the spectra of **4b** did not change with time, **4a** slowly isomerised in solution to establish an equilibrium with another species **4a'**. Thus, a CDCl_3 solution of **4a**, after 2 h, displayed four resonances ($\delta = 5.1, 3.4, 3.1, 2.4$), each showing platinum satellites, the intensity of which changed with time until an equilibrium is reached after two days. No change occurs after a week. It is likely that the “ $\text{PtCl}_2(\text{PR}_3)$ ” fragment of **4a** isomerises from *cis*-“ PtCl_2 ” to the *trans*-“ PtCl_2 ” configuration, a structure observed for palladium complex, $[\text{Pd}_2\text{Cl}_3(\text{Sepy})(\text{PR}_3)_2]$.^[16] Thus, the second set of resonances ($\delta = 3.1, ^1J(\text{Pt-P}) = 3504$ Hz; $\delta = 2.4, ^1J(\text{Pt-P}) = 3218$ Hz) may be attributed to **4a'** in which “ PtCl_2 ” has a *trans* configuration.

Reaction of $\text{PtCl}_2(\text{P-P})$ with two equivalents of $\text{Na-SeCH}_2\text{CH}_2\text{NMe}_2$ yields, mononuclear $[\text{Pt}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)_2(\text{P-P})]$ (**5**) [$\text{P-P} = \text{dppm}$ (**5a**), dppe (**5b**), dppp (**5c**)] as yellow crystalline solids. The NMR spectra (^{31}P , ^{77}Se , ^{195}Pt) (Table 1) are similar to several organochalcogenolates $[\text{Pt}(\text{ER})_2(\text{P-P})]$ reported by us.^[16,21,23,26] These complexes have been assigned a *cis* configuration. Unlike **1**, the $\text{Me}_2\text{NCH}_2\text{CH}_2\text{Se}$ in **5** acts in monodentate fashion i.e., binding through selenium only. This mode of binding can readily be identified from ^1H NMR spectra. The NMe_2 protons in **5** appear at $\delta \approx 2.0$ with the absence of ^{195}Pt couplings whereas in **1** they appear at $\delta \approx 2.7$ with ^{195}Pt couplings. When the reaction is carried out in 1:1 stoichiometry in the presence of NaBPh_4 (Scheme 1), a new series of binuclear complexes, $[\text{Pt}_2(\text{SeCH}_2\text{CH}_2\text{NMe}_2)_2(\text{P-P})_2][\text{BPh}_4]_2$ (**6**) [$\text{P-P} = \text{dppm}$ (**6a**), dppe (**6b**), dppp (**6c**)] could be isolated. Complex **6** can also be prepared, as pale yellow fibrous crystals, by the reaction of **5** with $[\text{Pt}(\text{solvent})_2(\text{P-P})][\text{BPh}_4]_2$. The ^{77}Se NMR spectra exhib-

ited single resonances suggesting that two bridging selenolate ligands are equivalent. The signals are deshielded with increased $^1J(\text{Pt-Se})$ in comparison to the corresponding resonance for **5**. However the $^{31}\text{P}\{^1\text{H}\}$ (Figure 1) and $^{195}\text{Pt}\{^1\text{H}\}$ (Figure 2) spectra showed two sets of resonances, and doublet of doublets, respectively; a pattern indicative of non-equivalence of phosphorus nuclei of the P-P ligand. The spectra of **6a** and **6c** further showed phosphorus coupling, thus each signal appeared as a doublet (Figure 1). The X-ray structures of several mononuclear compounds $[\text{M}(\text{ER})_2(\text{P-P})]$ ($\text{E} = \text{S}$ or Se , $\text{M} = \text{Pd}$ or Pt) have been reported.^[13,23] The structures reveal that in thiolates the two M-S distances are nearly identical,^[13,23] but for selenolates the two M-Se distances differ markedly^[21,23,26] (e.g. $\text{Pt}(\text{Sepy})_2(\text{dppe})$ $\text{Pt-Se} = 2.498, 2.433$ Å).^[26] Similar differences in Pt-E distances in binuclear complexes $[\text{Pt}_2\text{X}_2(\mu\text{-ER})_2(\text{PR}_3)_2]$ ($\text{ER} = \text{SeEt}$, SeCH_2Ph)^[19,27] are reported. The selenolate ligands form an asymmetric Pt_2Se_2 ring^[19,27] whereas the thiolates give a symmetrical Pt_2S_2 fragment.^[28] On chelation of $\text{M}(\text{ER})_2(\text{P-P})$ with another metal centre, binuclear complexes such as $[\text{M}_2(\text{ER})_2(\text{P-P})_2]^{++}$ [11,13] ($\text{M} = \text{Pd}$ or Pt) are formed when $\text{E} = \text{S}$ a symmetrical M_2E_2 bridge forms as shown by the X-ray structure of $[\text{M}_2(\mu\text{-SC}_5\text{H}_9\text{NMe})_2(\text{dppe})_2][\text{BPh}_4]_2$ ^[13] where M-S distances are nearly equivalent. Accordingly all phosphorus nuclei become chemically equivalent and display only one ^{31}P NMR resonance.^[11,13,21,23] In case of binuclear cationic selenolate complexes, as observed for $[\text{Pt}_2\text{Cl}_2(\mu\text{-SeR})_2(\text{PR}_3)_2]$,^[19,27] the M-Se bridge may be asymmetric (**I**) due to different M-Se distances consequently making the

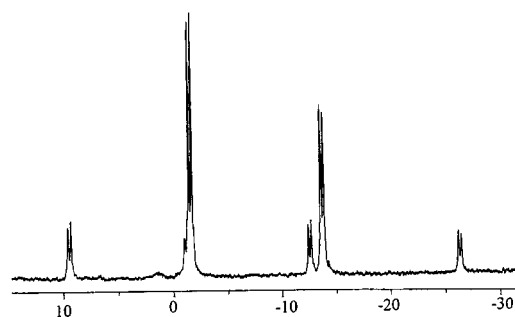


Figure 1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Pt}_2(\text{SeCH}_2\text{CH}_2\text{NMe}_2)_2(\text{dppp})_2][\text{BPh}_4]_2$ (**6c**) in CDCl_3

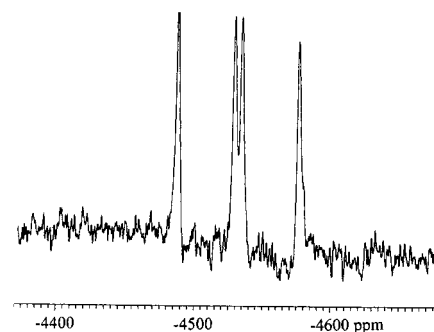
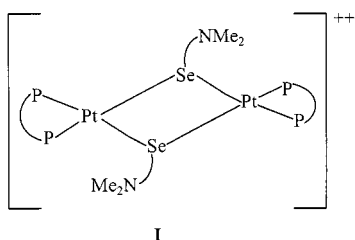
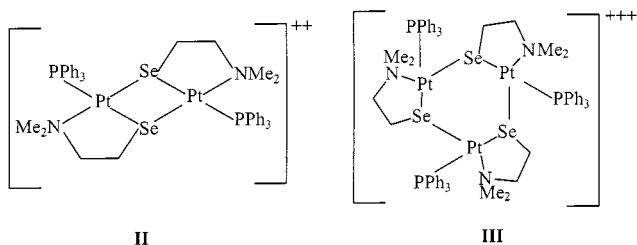


Figure 2. $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectrum of $[\text{Pt}_2(\text{SeCH}_2\text{CH}_2\text{NMe}_2)_2(\text{dppp})_2][\text{BPh}_4]_2$ (**6c**) in CDCl_3

phosphorus nuclei magnetically different. The two inequivalent phosphorus nuclei are coupled together to give doublets in the ^{31}P NMR spectra of **6a** and **6c**. The magnitude of $^2J(\text{P-P})$ couplings are in accordance with the literature values.^[29] The absence of $^2J(\text{P-P})$ in **6b** might be due to different signs of $^3J(\text{P-P})$, $^2J(\text{P-P})$ coupling operating through P-C-C-P and P-Pt-P routes, respectively.^[30] The intensity of two resonances (Figure 1) is significantly different. This can be attributed to the difference in the magnitude of T_1 of two sites, as reported earlier.^[30]



Treatment of **1f** with AgPF_6 affords $[\text{Pt}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PPh}_3)]_n[\text{PF}_6]_n$ (**7**). The ^{31}P , ^{77}Se , and ^{195}Pt spectra exhibited two separate resonances in approximately a 2:1 ratio. The $^1J(\text{Pt-P})$ in ^{31}P and ^{195}Pt NMR spectra are comparable, indicating that both the species have similar configuration. Recently we have reported the structure of $[\{\text{Pd}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)\text{Cl}\}_n]$ which is a trimer ($n = 3$) in which the chelated Se-N ligand bridges another palladium atom through Se .^[8] The observed two signals may be interpreted for dimeric (**II**) and trimeric (**III**) forms in which each platinum is bonded to two Se atoms, one N and one PPh_3 in nearly similar environments.



Absorption Spectra and Electrochemistry

The absorption spectra of the complexes $[\text{PtCl}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PR}_3)]$ in CH_2Cl_2 solution are characterised by a very weak band at 400–430 nm (Figure 3, Table 2). The band is hypsochromically shifted on replacing the phenyl substituents on the PR_3 group by donating alkyl groups. As will be confirmed by TD-DFT calculations (see below) this absorption is due to a ligand (Se)-to-ligand (PR_3) charge transfer (LLCT) transition. The geometry obviously allows only rather poor orbital overlap, resulting in very weak yet well discernible bands (Figure 3). A similar band with $\epsilon = 80 \text{ mol}^{-1}\cdot\text{dm}^3\cdot\text{cm}^{-1}$ at 514 nm has been reported for the palladium analogue $[\text{PdCl}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PPh}_3)]$.^[8] Allowed transitions occur only at higher energies with $\lambda_{\text{max}} < 300 \text{ nm}$, in agreement with theory. The dinuclear species $[\text{Pt}_2\text{Ph}_2(\text{Cl})(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{P}n\text{Bu}_3)_2]$ does not allow a detectable $\text{Se-to-P}n\text{Bu}_3$ transition in the visible or near UV region (Table 2).

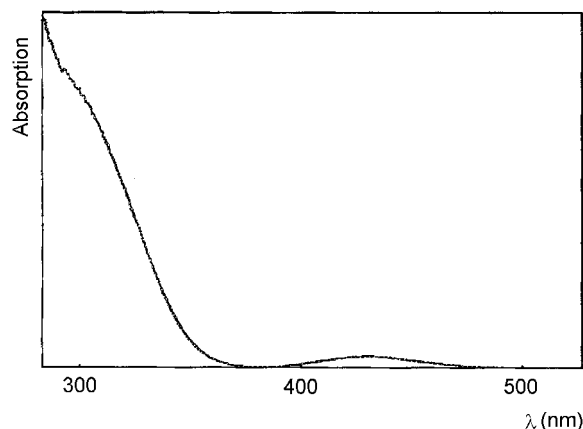


Figure 3. UV/Vis spectrum of $[\text{PtCl}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PPh}_3)]$ (**1f**) in CH_2Cl_2

Table 2. UV/Vis absorption data of some platinum complexes recorded in CH_2Cl_2

Complex	λ_{max} (nm)
$[\text{PtCl}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PEt}_3)]$ (1a)	284, 405
$[\text{PtCl}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PMe}_2\text{Ph})]$ (1d)	283, 405
$[\text{PtCl}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PMePh}_2)]$ (1e)	266 sh, 273 sh, 293 sh, 418
$[\text{PtCl}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PPh}_3)]$ (1f)	268 sh, 275 sh, 300 sh, 430

According to cyclic voltammetry in $\text{CH}_2\text{Cl}_2/0.1 \text{ mol}\cdot\text{dm}^{-3} \text{ Bu}_4\text{NPF}_6$ the Pt^{II} complexes **1** and **3** are oxidised irreversibly. The peak potentials for **1** show little variation (0.83–0.89 V vs. ferrocene/ferrocenium), confirming that it is primarily the selenolate part (HOMO) which loses an electron and not the PR_3^- ligating platinum centre. The bridging selenolate in compound **3** is hard to oxidise as illustrated by the anodic peak potential of 1.13 V for irreversible oxidation.

Electronic Structure Calculations on **1f**

The ADF/BP calculated one-electron scheme of the $[\text{PtCl}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PPh}_3)]$ complex is schematically given in Figure 4. The composition of important molecular

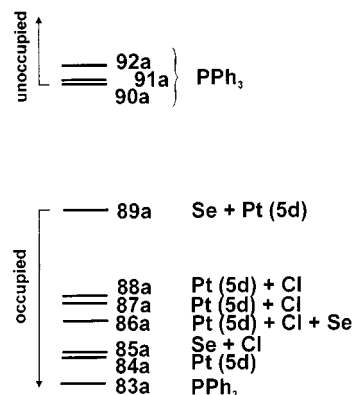


Figure 4. ADF/BP calculated qualitative MO scheme of **1f**

Table 3. ADF/BP calculated one-electron energies and percentage composition of selected highest occupied and lowest unoccupied molecular orbitals of $[\text{PtCl}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PPh}_3)]$ (**1f**) expressed in terms of composing fragments

MO	<i>E</i> [eV]	Prevailing Character	Pt	PPh ₃	Se	Cl	N
Unoccupied –							
92a	–1.87	PPh ₃	3 (d)	90	2	2	
91a	–2.06	PPh ₃	2 (d)	94			
90a	–2.11	d _{Pt} + PPh ₃ + Se	13 (d)	63	9	3	3
Occupied							
89a	–4.05	Se + d _{Pt}	29 (d)	–	58	10	–
88a	–5.37	d _{Pt}	11 (s); 57(d)	1	7	23	–
87a	–5.45	d _{Pt} + Cl	5 (s); 42(d)	3		43	
86a	–5.70	Cl + Se + d _{Pt}	1(p); 19 (d)		25	50	
85a	–6.16	Cl + Se	3(p); 4 (d)	4	46	34	
84a	–6.25	d _{Pt}	78 (d)	10	3	2	
83a	–6.60	PPh ₃	6 (d)	72	10	3	2

orbitals is summarised in Table 3. The highest molecular orbital 89a is formed mainly from a Se *p* orbital with some additional metal contribution. Pt 5*d* and Cl 3*p* orbitals contribute significantly to the next lower lying occupied MOs. The set of the lowest lying unoccupied molecular orbitals, 90a, 91a, and 92a, is to a large extent located on the PPh₃ fragment. The composition of the occupied MOs of the $[\text{PtCl}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PH}_3)]$ model (Table 4) corresponds to those of the PPh₃ complex. The lowest lying molecular orbital is delocalised; PH₃ localised unoccupied MOs lie at a rather high energy. The excitation energies listed in Table 5 were calculated for the $[\text{PtCl}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PH}_3)]$ model with different DFT program configurations. In agreement with the experiments, there is one very weak transition (HOMO→LUMO, oscillator strength $< 10^{-3}$) at low energy, set apart by more than 1 eV from the following singlet transitions (Table 5). The calculated excitation energies of about 2.4 eV (corresponding to ca. 500 nm) are in broad agreement with the 400–430 nm observed for various substituted derivatives (Table 2). This conspicuous absorption must be formulated mainly as ligand (Se)-to-ligand (PR₃) charge transfer, as has been proposed previously for palladium analogues.^[8]

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Crystal Structures of **1f** and **3**

An ORTEP plot of **1f** with the crystallographic numbering scheme is shown in Figure 5, and Table 6 summarises essential data. The geometry around the platinum atom is essentially square planar with the atoms P, Cl, Se, and N defining the coordination sphere. The phosphane ligand is *trans* to the nitrogen atom of the chelating selenolate group as inferred from the NMR spectroscopic data. The five-membered chelate ring (Pt–Se–C–C–N) exists in a puckered conformation with the carbon atoms C(19) and C(20) lying on opposite sides of the mean plane. The structure of **1f** is isomorphous to its palladium analogue, $[\text{PdCl}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PPh}_3)]$ ^[8] and various bond lengths and angles in the two structures are comparable.

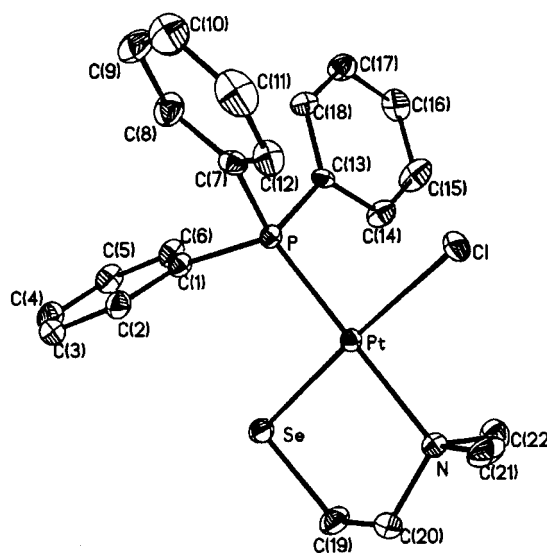


Figure 5. Molecular structure of $[\text{PtCl}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PPh}_3)]$ (**1f**) with crystallographic numbering scheme

Table 4. ADF/BP calculated one-electron energies and percentage composition of selected highest occupied and lowest unoccupied molecular orbitals of model complex $[\text{PtCl}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PH}_3)]$ expressed in terms of composing fragments

MO	<i>E</i> [eV]	Prevailing Character	Pt	PH ₃	Cl	Se
Unoccupied –						
49a	–0.77	PH ₃	17(d)	68		10
48a	–0.83	PH ₃	7(d)	47		30
47a LUMO	–2.23	delocalized	28 (d)	20	11	28
Occupied						
47a HOMO	–4.30	Se + d _{Pt}	28 (d)	2	9	62
46a	–5.58	d _{Pt}	18 (s); 71(d)	–	4	7
45a	–5.71	d _{Pt} + Cl	2 (s); 27(d)	–	61	5
44a	–5.85	Cl + Se + d _{Pt}	1(p); 16 (d)	–	57	24
43a	–6.10	Se + Cl	7 (d)	1	36	52
42a	–6.40	d _{Pt}	85 (d)	11	–	–

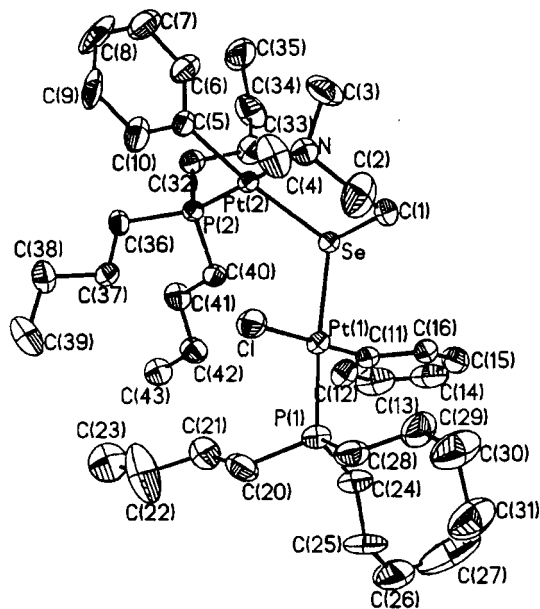
Table 5. Selected calculated lowest TD DFT singlet excitation energies (eV) for $[\text{PtCl}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PH}_3)]$

State	Main character	ADF/BP		G98/B3LYP	
		Transition energy [eV]	Oscillator strength	Transition energy [eV]	Oscillator strength
¹ A ₁	HOMO → LUMO	2.24	0.0004	2.53	0.0006
¹ A ₁	HOMO → LUMO + 1	3.55	0.001	3.71	0.002
¹ A ₁	HOMO – 1 → LUMO	3.58	0.002	3.95	0.005
¹ A ₁	HOMO → LUMO + 2	3.67	0.010	4.08	0.012
¹ A ₁	HOMO – 4 → LUMO	4.71	0.082	5.09	0.190

Table 6. Selected bond lengths [Å] and bond angles [°] with esd's for [PtCl(SeCH₂CH₂NMe₂)(PPh₃)] (**1f**)

Pt–N	2.161 (5)	N–C(20)	1.501 (8)
Pt–P	2.2292 (15)	N–C(21)	1.485 (8)
Pt–Se	2.3773(7)	N–C(22)	1.486 (8)
Pt–Cl	2.3788 (15)	C(19)–C(20)	1.502 (9)
Se–C(19)	1.953 (6)	P–C (av)	1.830
N–Pt–P	174.57 (14)	C(20)–N–C(21)	107.1 (5)
N–Pt–Se	87.02 (14)	C(20)–N–C(22)	109.5 (5)
P–Pt–Se	91.07 (4)	C(21)–N–C(22)	106.6 (5)
N–Pt–Cl	90.61 (15)	Pt–N–C(21)	114.9 (4)
P–Pt–Cl	90.89 (6)	Pt–N–C(22)	107.2 (4)
Se–Pt–Cl	174.92 (4)	Pt–N–C(20)	111.3 (4)
Pd–Se–C(19)	95.9 (2)	N–C(20)–C(19)	112.2 (5)
		Se–C(19)–C(20)	108.9 (4)

The molecular structure of [Pt₂Ph₂(Cl)(SeCH₂CH₂NMe₂)(PnBu₃)₂] (**3**), established by the X-ray diffraction method, is illustrated in Figure 6. Selected bond lengths and bond angles are given in Table 7. The structure consists of two distorted square planar platinum atoms which are held together by a bridging selenolate centre. The two square planes of the platinum atoms are inclined to each other through a Pt(1)–Se–Pt(2) angle of 111.69 (5)°. Each platinum atom is coordinated to four different ligand atoms. The Pt(1) centre is coordinated to Ph, Cl, PBU₃, and the selenium atom, the latter being mutually *trans*. The Pt(2) atom is bound to the chelating Me₂NCH₂CH₂Se ligand and to the other PBU₃ and Ph groups. The phosphane is *trans* to the nitrogen atom whereas Se is *trans* to Ph. The Pt–Se distances in **1f** [2.3788(15) Å] and **3** [2.4793(14) and 2.4562(12) Å] are significantly different, although these distances are in agreement with the standard values. The longer Pt–Se distances in **3** compared with that of **1f** reflect greater *trans* influence of Ph and PBU₃ than the chloride.

Figure 6. ORTEP plot of [Pt₂Ph₂Cl(SeCH₂CH₂NMe₂)(PnBu₃)₂] (**3**) with crystallographic numbering schemeTable 7. Selected bond lengths [Å] and bond angles [°] with esd's for [Pt₂Ph₂(Cl)(SeCH₂CH₂NMe₂)(PnBu₃)₂] (**3**)

Pt(1)–Se	2.4793(14)	Pt(2)–Se	2.4562(12)
Pt(1)–P(1)	2.235(3)	Pt(2)–P(2)	2.227(2)
Pt(1)–Cl	2.432(3)	Pt(2)–N	2.177(9)
Pt(1)–C(11)	2.010(10)	Pt(2)–C(5)	2.039(10)
Se–C(1)	1.931(12)	N–C(2)	1.542(18)
C(11)–Pt(1)–P(1)	92.1(3)	C(5)–Pt(2)–N	90.7(3)
C(11)–Pt(1)–Cl	178.4(3)	C(5)–Pt(2)–P(2)	88.5(3)
P(1)–Pt(1)–Cl	88.20(11)	P(2)–Pt(2)–N	178.9(2)
C(11)–Pt(1)–Se	85.1(3)	C(5)–Pt(2)–Se	174.0(3)
P(1)–Pt(1)–Se	175.23(8)	N–Pt(2)–Se	87.2(2)
Cl–P(1)–Se	94.69(8)	P(2)–Pt(2)–Se	93.64(7)
Pt(1)–Se–Pt(2)	111.69(8)	Pt(2)–N–C(2)	109.2(7)
Pt(1)–Se–C(1)	101.7(4)	Se–C(1)–C(2)	110.7(9)
		Pt(2)–Se–C(1)	95.3(4)

The comparable *trans* influence of PBU₃ and Ph groups is evident from the ¹J(Pt–P) values from NMR spectra. Other distances, Pt–P, Pt–Cl, Pt–N, and Pt–C are well in agreement with those reported in the literature.^[16,21,23,26]

Experimental Section

All the reactions were carried out under a nitrogen atmosphere in dry, distilled analytical grade solvents to prevent oxidation of the oxygen sensitive selenolate ions. The complexes K₂[PtCl₄], *cis*-[PtCl₂(PPh₃)₂], *cis*-[PtCl₂(P–P)], *trans*-[Pt₂Cl₂(μ-Cl)₂(PR₃)₂], and the mixture of *cis*- and *trans*-[Pt₂Ph₂(μ-Cl)₂(PnBu₃)₂] (P–P = dppm, dppe, dppp; PR₃ = PET₃, PnPr₃, PnBu₃, PMe₂Ph, PMePh₂) were prepared by the literature methods.^[31,32,33] Melting points were determined in capillary tubes and are uncorrected. Microanalyses were performed by the Analytical Chemistry Division of B.A.R.C. ¹H, ³¹P{¹H}, ⁷⁷Se{¹H}, and ¹⁹⁵Pt{¹H} NMR spectra were recorded on a Bruker DPX-300 NMR spectrometer operating at 300, 121.49, 57.31, 64.52 MHz, respectively. Chemical shifts are relative to internal chloroform peak (δ = 7.26) for ¹H, external 85% H₃PO₄ for ³¹P, Me₂Se for ⁷⁷Se, and Na₂PtCl₆ for ¹⁹⁵Pt. UV/Vis absorption spectra were recorded on a Bruins Instruments Omega 10 spectrophotometer. Cyclic voltammetry was carried out at 100 mV/s scan rate in dichloromethane/0.1 M Bu₄NPF₆ using a three electrode configuration (glassy carbon working electrode, Pt counter electrode, Ag/AgCl reference) and a PAR 273 potentiostat and function generator. The ferrocene/ferrocenium couple served as internal reference.

Ground state electronic structure calculations on [PtCl(SeCH₂CH₂NMe₂)(PPh₃)] have been done by density-functional theory (DFT) methods using the ADF2000.01^[34,35] and Gaussian 98^[36] program packages. The lowest excited states were calculated by the time dependent DFT (TD-DFT) method (both ADF and G98 programs) for the model system [PtCl(SeCH₂CH₂NMe₂)(PH₃)]. Within the ADF program, Slater type orbital (STO) basis sets of double-ζ quality with polarisation functions within the phenyl rings and triple-ζ for the rest of the system were employed. The inner shells were represented by the frozen core approximation (1s for C, N 2p for Cl, 3p for Se, and 1s–4d for Pt were kept frozen). The following density functionals were used within ADF: The local density approximation (LDA) with VWN parameterisation of electron gas data or the functional including Becke's gradient correction^[37] to the local exchange expression in conjunction

with Perdew's gradient correction^[38] to the LDA expression (ADF/BP). The scalar relativistic (SR) zero order regular approximation (ZORA) was used within the study. Within Gaussian-98 Dunning's polarized valence double- ζ basis sets^[39] were used for C, N, Cl, and H atoms; quasirelativistic effective core pseudopotentials and a corresponding optimized set of basis functions was employed for Pt^[40] and Se.^[41] Becke's three parameter hybrid functional with the Lee, Yang, and Parr correction functional (B3LYP)^[42] was used in Gaussian 98 calculations (G98/B3LYP). The calculation on the model system [PtCl(SeCH₂CH₂NMe₂)(PH₃)] was done with the experimental geometry of the PPh₃ complex with an optimized structure of the PH₃ ligand.

1. Preparation of [PtCl(SeCH₂CH₂NMe₂)(PEt₃)] (1a): To a freshly prepared methanolic solution (5 cm³) of NaSeCH₂CH₂NMe₂ [prepared from (Me₂NCH₂CH₂Se)₂ (99.7 mg, 0.32 mmol) and NaBH₄ (25.4 mg, 0.67 mmol)] was added a dichloromethane solution (20 cm³) of [Pt₂Cl₂(μ -Cl)₂(PEt₃)₂] (247.7 mg, 0.32 mmol). The reaction mixture was stirred at room temperature for 4 h. The solvents were

evaporated under reduced pressure and the residue was extracted with dichloromethane (3 $\times$ 7 cm³), the solution was passed through a Florisil column and the solvent removed in vacuo. The residue was recrystallised from hexane (yield 210 mg, 65%). All other mononuclear complexes [PtCl(SeCH₂CH₂NMe₂)(PR₃)] (PR₃ = PnPr₃, PnBu₃, PMe₂Ph, PMePh₂) were prepared in a similar manner. Pertinent data are summarized in Table 8.

2. Preparation of [PtCl(SeCH₂CH₂NMe₂)(PPh₃)] (1f): Prepared analogously as described in method 5 by using [PtCl₂(PPh₃)₂] (268.8 mg, 0.34 mmol) NaSeCH₂CH₂NMe₂ [prepared from (Me₂NCH₂CH₂Se)₂ (54.4 mg, 0.18 mmol) and NaBH₄ (14.0 mg, 0.37 mmol)]. The residue was washed thoroughly with diethyl ether to remove liberated triphenylphosphane and then recrystallised from CH₂Cl₂/acetone mixture as yellow-orange crystals (yield 158 mg, 72%).

3. Preparation of [PtPh(SeCH₂CH₂NMe₂)(PnBu₃)] (2) and [Pt₂Ph₂Cl(SeCH₂CH₂NMe₂)(PnBu₃)₂] (3): Prepared analogously

Table 8. Physical, analytical and ¹H NMR spectroscopic data for dimethylaminoethaneselenolate complexes of platinum(II)

Complex	Recrystallisation solvent (% yield)	M.p. (^o C)	Analysis: Found (calcd)			¹ H NMR spectroscopic data
			(%) C	H	N	δ
[PtCl(SeCH ₂ CH ₂ NMe ₂)(PEt ₃)] (1a)	hexane (65)	63	23.6 (24.0)	5.3 (5.0)	2.6 (2.8)	1.40 [d, t, 7.6 Hz (t), 17 Hz (d) PCH ₂ Me]; 1.86 [d, q, 7.6 Hz (q), 17 Hz (d) PCH ₂ -]; 2.33 [t, 6.1 Hz, ³ J(Pt-H) = 27 Hz, SeCH ₂]; 2.75 [d, ⁴ J(P-H) = 2.6 Hz, ³ J(Pt-H) = 17 Hz, NMe ₂]; 2.86 [d, t, 1.7 Hz (d) ⁴ J(P-H), J(H-H) = 7 Hz; ³ J(Pt-H) = 36 Hz, NCH ₂]; 1.04 (t, 7.2 Hz, PCH ₂ CH ₂ Me); 1.52–1.67 (m, PCH ₂ CH ₂ -); 1.75–1.87 (m, PCH ₂ -); 2.33 [t, 6.2 Hz, ³ J(Pt-H) = 27 Hz, SeCH ₂]; 2.74 [d, ⁴ J(P-H) = 2.5 Hz, ³ J(Pt-H) = 15 Hz, NMe ₂]; 2.85 [t, d, ⁴ J(P-H) = 1.5, 6 Hz (d), ³ J(Pt-H) = 37 Hz, NCH ₂ -]; 0.85 (t, 7.1 Hz, PCH ₂ CH ₂ Me); 1.30–1.50 (m, PCH ₂ CH ₂ -); 1.72–1.80 (m, PCH ₂ -); 2.24 [t, 6.2 Hz, ³ J(Pt-H) = 27 Hz, SeCH ₂]; 2.67 [d, ⁴ J(P-H) = 2.6 Hz, ³ J(Pt-H) = 14 Hz, NMe ₂]; 2.78 [d, t, ⁴ J(P-H) = 1.5, 5 Hz (t), ³ J(Pt-H) = 36 Hz, NCH ₂ -]
[PtCl(SeCH ₂ CH ₂ NMe ₂)(PnPr ₃)] (1b)	hexane (72)	87	28.3 (28.8)	6.0 (5.8)	2.8 (2.6)	1.80, 1.81 [each d, ² J(P-H) = 11.2 Hz, ³ J(Pt-H) = 40 Hz, PMe ₂]; 2.23 (br, SeCH ₂); 2.70 [d, ³ J(P-H) = 2.2 Hz, NMe ₂]; 2.85 [br, ³ J(Pt-H) = 38 Hz, NCH ₂]; 7.34 (br), 7.67 (br) (Ph) [2.23 [d, J(P-H) = 11.2, ³ J(Pt-H) = 32 Hz, PMe]; 2.21 (SeCH ₂ , merged with PMe resonance) 2.83 [d, ⁴ J(P-H) = 2.8 Hz, ³ J(Pt-H) = 18 Hz, NMe ₂]; 2.99 [d, t, 1.6 Hz (d) ⁴ J(P-H), J(H-H) = 6.1 Hz; ³ J(Pt-H) = 38 Hz, NCH ₂]; 7.38–7.43 (m) (Ph) 2.21 [t, 6.2 Hz ³ J(Pt-H) = 24 Hz, SeCH ₂]; 2.88 [d, ⁴ J(P-H) = 2.8 Hz, ³ J(Pt-H) = 17 Hz, NMe ₂]; 3.08 [d, t, (d) ⁴ J(P-H) = 1.5 Hz, J(H-H) = 6.2 Hz; ³ J(Pt-H) = 42 Hz, NCH ₂]; 7.33–7.49 (m) 7.68–7.49 (m) (Ph) 0.89 (t, 7.2 Hz, PCH ₂ CH ₂ Me); 1.34 (m, PCH ₂ CH ₂ -); 1.50 (m, PCH ₂ CH ₂ -); 2.33 [d, ⁴ J(P-H) = 1.9 Hz, ³ J(Pt-H) = 27 Hz, NMe ₂]; 2.45 (t, 6 Hz, SeCH ₂); 2.99 [t, d, ⁴ J(P-H) = 2.2 Hz; J(H-H) = 5.5 Hz, ³ J(Pt-H) = 38 Hz, NCH ₂ -]; 6.89–7.00 (m), 7.45–7.48 (m) (Ph) 0.90 (m, PCH ₂ CH ₂ Me); 1.26–1.88 (m, PCH ₂ CH ₂ -); 2.01 (s, NMe ₂); 2.20 (br, SeCH ₂); 2.43 (br, NCH ₂); 7.38–7.57 (m, Ph) 1.16 (m, PCH ₂ Me); 1.82–2.16 (m; PCH ₂ -); 2.63 (br, SeCH ₂); 2.79 (br, NMe ₂) 3.02 (br, NCH ₂).
[PtCl(SeCH ₂ CH ₂ NMe ₂)(PnBu ₃)] (1c)	hexane (80)	46	32.2 (32.9)	6.3 (6.4)	2.1 (2.4)	1.64, 1.83, 1.88, 2.04 (each d, 11.5 Hz PMe ₂); 2.55 [d, ⁴ J(P-H) = 2.3 Hz]; 3.00 [d, ⁴ J(P-H) = 2.8 Hz, NMe ₂ 1:1]; 3.58 (br., NCH ₂), 2.64 (br, SeCH ₂), 7.32–7.54(m), 7.76–7.83 (m) (Ph) 1.96 (s, NMe ₂); 2.42 (br, SeCH ₂); 2.59 (br, NCH ₂); 4.35 [t, ² J(P-H) = 10.4 Hz; ³ J(Pt-H) = 44 Hz, PCH ₂ -]; 7.39–7.47 (m), 7.82–7.89 (m) (Ph) 2.03 (s, NMe ₂); 2.15–2.56 (m, NCH ₂ , SeCH ₂ , PCH ₂); 7.51 (br), 7.88–7.96 (m) (Ph) 1.88 (s, NMe ₂); 1.94–2.96 (overlapping resonance due to NCH ₂ , SeCH ₂ , PCH ₂) 7.29–7.82 (m, Ph) 2.47 (br, NMe ₂); 2.74 (br, SeCH ₂); 2.82 (br, NCH ₂); 4.04 [t, ² J(P-H) = 11 Hz PCH ₂ -]; 6.75–6.93 (m), 7.23–7.62 (m) (Ph) 1.80–1.95 (br, PCH ₂); 2.34 (s, J(Pt-H) = 16 Hz NMe ₂); 2.61 (br, SeCH ₂); 3.05 [br, ³ J(Pt-H) = 45 Hz NCH ₂]; 6.77–6.91 (m), 7.18–7.31 (m), 7.37–7.69 (m) (Ph) 1.68 (br, PCH ₂); 2.17 (s, NMe ₂); 2.25 (br, CH ₂ -CH ₂ P), 2.49 (br, SeCH ₂); 3.07 [br, J(Pt-H) = 46 Hz, NCH ₂]; 6.87–7.06 (m); 7.42–7.64 (m) (Ph) 2.79 (s, NMe ₂ + NCH ₂ base of the peak broadened); 2.30 (br, SeCH ₂); 7.34–7.70 (m) Ph.
[PtPh(SeCH ₂ CH ₂ NMe ₂)(PnBu ₃)] (2)	hexane (40)	147	41.6 (42.2)	6.7 (6.8)	1.1 (2.2)	
[Pt ₂ Ph ₂ Cl(SeCH ₂ CH ₂ NMe ₂)(PnBu ₃) ₂] (3)		153	41.6 (42.3)	6.8 (6.6)	1.0 (1.2)	
[Pt ₂ Cl ₃ (SeCH ₂ CH ₂ NMe ₂)(PEt ₃) ₂] (4a)	hexane (80)	187	21.1 (21.7)	4.2 (4.6)	1.7 (1.6)	
[Pt ₂ Cl ₃ (SeCH ₂ CH ₂ NMe ₂)(PMe ₂ Ph) ₂] (4b)	hexane (87)	102	25.7 (26.0)	3.5 (3.5)	1.3 (1.5)	
[Pt(SeCH ₂ CH ₂ NMe ₂) ₂ -(dppm)] (5a)	acetone/hexane (62)	154	44.2 (44.9)	4.8 (4.8)	3.0 (3.2)	
[Pt(SeCH ₂ CH ₂ NMe ₂) ₂ -(dppe)] (5b)	acetone/hexane (60)	184	44.8 (45.6)	4.9 (4.9)	3.0 (3.1)	
[Pt(SeCH ₂ CH ₂ NMe ₂) ₂ -(dppp)] (5c)	acetone/hexane (75)	162	44.7 (46.2)	4.8 (5.1)	2.0 (3.1)	
[Pt ₂ (SeCH ₂ CH ₂ NMe ₂) ₂ -(dppm) ₂][BPh ₄] ₂ (6a)	CH ₂ Cl ₂ /hexane (65)	84	60.6 (60.6)	5.0 (5.0)	1.1 (1.3)	
[Pt ₂ (SeCH ₂ CH ₂ NMe ₂) ₂ -(dppe) ₂][BPh ₄] ₂ (6b)	acetone/hexane (72)	126	60.3 (61.0)	5.2 (5.1)	1.4 (1.3)	
[Pt ₂ (SeCH ₂ CH ₂ NMe ₂) ₂ -(dppp) ₂][BPh ₄] ₂ (6c)	acetone/hexane (60)	195	60.5 (61.3)	5.1 (5.2)	1.1 (1.3)	
[Pt(SeCH ₂ CH ₂ NMe ₂)(PPh ₃) _n][PF ₆] _n (7)						

as described in method 1 from $[\text{Pt}_2\text{Ph}_2(\mu\text{-Cl})_2(\text{P}n\text{Bu}_3)_2]$ (99.5 mg, 0.10 mmol) and $\text{NaSeCH}_2\text{CH}_2\text{NMe}_2$ [prepared from $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{Se})_2$ (32 mg, 0.11 mmol) and NaBH_4 (8.9 mg, 0.23 mmol)]. The ^{31}P and ^{195}Pt NMR spectra of this product exhibited three resonances. The product on recrystallization from hexane gave colourless crystals of $[\text{PtPh}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{P}n\text{Bu}_3)]$ (yield 29 mg, 24%). The supernatant solution on repeated recrystallization from hexane containing $\approx 5\%$ benzene afforded $[\text{Pt}_2\text{Ph}_2(\text{Cl})(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{P}n\text{Bu}_3)_2]$ (54 mg, 48%).

4. Preparation of $[\text{Pt}_2\text{Cl}_3(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PEt}_3)_2]$ (4a): Solid $[\text{PtCl}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PEt}_3)]$ (17.7 mg, 0.04 mmol) was mixed with $[\text{Pt}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{PEt}_3)_2]$ (13.5 mg, 0.02 mmol) in CDCl_3 (0.5 cm^3) in an NMR tube. After a few days the solution was dried in vacuo, the pale yellow product was washed with hexane and dried in vacuo (yield 25.0 mg, 80%).

5. Preparation of $[\text{Pt}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)_2(\text{dppe})]$ (5b): To a stirred methanolic solution (5 cm^3) of $\text{NaSeCH}_2\text{CH}_2\text{NMe}_2$ [prepared from $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{Se})_2$ (92.8 mg, 0.31 mmol) and NaBH_4 (23.8 mg, 0.63 mmol)] solid $[\text{PtCl}_2(\text{dppe})]$ (201.5 mg, 0.30 mmol) was added. To this mixture dry acetone (20 cm^3) was added whereupon a yellow solution formed which was stirred for 3 h at room temperature. The solvents were stripped off under vacuum and the residue was extracted with acetone (3 $\times$ 7 cm^3) and filtered. The filtrate was reduced to a minimum volume (5 cm^3), a few drops of hexane were added to yield yellow crystals of the title complex (yield 163 mg, 60%).

The complexes $[\text{Pt}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)_2(\text{P-P})]$ ($\text{P-P} = \text{dppm}, \text{dppe}$) were prepared in an analogous manner.

6. Preparation of $[\text{Pt}_2(\text{SeCH}_2\text{CH}_2\text{NMe}_2)_2(\text{dppm})_2][\text{BPh}_4]_2$ (6a): a) A dichloromethane suspension of (20 cm^3) of $[\text{PtCl}_2(\text{dppm})]$ (248.9 mg, 0.38 mmol) was added to a stirred methanolic solution (5 cm^3) of $\text{NaSeCH}_2\text{CH}_2\text{NMe}_2$ [prepared from $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{Se})_2$ (59.2 mg, 0.20 mmol) and NaBH_4 (15.5 mg, 0.41 mmol)]. After 1 h of stirring a methanolic solution of NaBPh_4 (133.5 mg, 0.39 mmol)

was added and the whole mixture was stirred for 3 h. Solvents were evaporated in vacuo and the residue was extracted with dichloromethane and passed through a Florisil column. The solvent was evaporated in vacuo, the residue was washed with hexane and recrystallised from a CH_2Cl_2 /hexane mixture (yield 261 mg, 65%). Other cationic complexes $[\text{Pt}_2(\text{SeCH}_2\text{CH}_2\text{NMe}_2)_2(\text{P-P})_2][\text{BPh}_4]_2$ ($\text{P-P} = \text{dppe}, \text{dppp}$) were prepared in a similar way.

b) To a methanolic suspension (8 cm^3) of $[\text{PtCl}_2(\text{dppm})]$ (215.7 mg, 0.33 mmol) a methanolic solution (3 cm^3) of NaBPh_4 (114.2 mg, 0.33 mmol) was added and stirred for 1 h whereupon a pale yellow solution formed. To this a freshly prepared methanolic solution of $\text{NaSeCH}_2\text{CH}_2\text{NMe}_2$ [prepared from $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{Se})_2$ (51.4 mg, 0.17 mmol), NaBH_4 (13.2 mg, 0.35 mmol)] and 20 cm^3 of dichloromethane was added and stirred. After 3 h the solvents were stripped off under vacuum. The residue was extracted with dichloromethane (3 $\times$ 7 cm^3) and passed through a Florisil column. The volume of the solution was reduced to 5 cm^3 . Recrystallisation from CH_2Cl_2 /hexane mixture gave yellow solid (yield 216 mg, 62%).

7. Preparation of $[\text{Pt}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PPh}_3)]_n[\text{PF}_6]_n$ (7): An acetone solution (15 cm^3) of AgPF_6 (51 mg, 0.21 mmol) was added to solid $[\text{PtCl}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PPh}_3)]$ (116 mg, 0.20 mmol) with stirring. Silver chloride immediately precipitated with concomitant colour change from orange to pale yellow. The reactants were stirred at room temperature for 4 h. Precipitated AgCl was filtered through celite and the solvent was evaporated in vacuo. The yellow residue was examined by NMR spectroscopy.

Crystallography: X-ray data of an orange crystal of $[\text{PtCl}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PPh}_3)]$ (**1f**) (0.2 $\times$ 0.2 $\times$ 0.2 mm) and a colourless crystal of $[\text{Pt}_2\text{Ph}_2\text{Cl}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{P}n\text{Bu}_3)_2]$ (**3**) (0.3 $\times$ 0.3 $\times$ 0.3 mm) were collected at 173(2) K on a Siemens P3 diffractometer using graphite monochromated Mo-K_α radiation ($\lambda = 0.71073 \text{ \AA}$), employing the ω -2 θ scan technique. The unit cell parameters (Table 9) were determined from 25 reflections each, measured by random search routine. The intensity data were

Table 9. Crystal data and structure refinement for $[\text{PtCl}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PPh}_3)]$ (**1f**) and $[\text{Pt}_2\text{Ph}_2\text{Cl}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{P}n\text{Bu}_3)_2]$ (**3**)

	1f	3
Empirical formula	$\text{C}_{22}\text{H}_{25}\text{ClINPSePt}$	$\text{C}_{43}\text{H}_{68}\text{ClINP}_2\text{SePt}_2$
Molecular mass	643.90	1165.55
Crystal system,	Monoclinic,	Triclinic,
Space group	$P2_1/n$	$P\bar{1}$
Unit cell dimensions:		
<i>a</i> [$\text{\AA}$]	9.4299(19)	9.3083(19)
<i>b</i> [$\text{\AA}$]	19.972(4)	15.859(3)
<i>c</i> [$\text{\AA}$]	11.704(2)	16.587(3)
α [$^\circ$]		108.96(3)
β [$^\circ$]	95.19(3)	97.55(3)
γ [$^\circ$]		93.32(3)
<i>V</i> [$\text{\AA}^3$]	2175.6(8)	2282.5(8)
<i>Z</i>	4	4
<i>D_c</i> [$\text{Mg}\cdot\text{m}^{-3}$]	1.966	1.924
Absorption coefficient μ [mm^{-1}]	8.326	7.938
<i>F</i> (000)	1232	1300
Range for data collection [$^\circ$]	2.03 to 30.00	1.55 to 30.00
Refinement method	Full-matrix least-squares on $F^2 > 0$	Full-matrix least-squares on $F^2 > 0$
Reflections collected/unique	7797/6351	14091/13328
Data/restraints/parameters	6351/0/244	13328/0/419
Goodness of fit on F^2	0.937	1.092
Final <i>R</i> indices	$R1 = 0.0444$, $wR2 = 0.1151$	$R1 = 0.0357$, $wR2 = 0.0838$
<i>R</i> indices (all data)	$R1 = 0.0574$, $wR2 = 0.1263$	$R1 = 0.0996$, $wR2 = 0.1798$
Largest diff. peak and hole [$\text{e}\cdot\text{\AA}^{-3}$]	2.000 and -5.602	2.340 and -2.075

corrected for Lorentz polarisation and absorption effects. The structures were solved using direct methods, the mononuclear complex proved to be isostructural with the previously reported palladium analogue.^[8] The non-hydrogen atoms were refined anisotropically except for the methyl carbon atoms C(23) and C(43). These two atoms were treated within a disorder model [0.62 and 0.38 for C(23) and C(23A), 0.93 and 0.07 for C(43) and C(43A)]; each of the adjacent methylene carbon atoms C(22) and C(42) was refined using two different sets of hydrogen atoms. Three of the *n*-butyl groups and the phenyl ligands exhibit high standard deviations, presumably due to thermal motion.

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