

Aryl chalcogenolates of palladium(II) and platinum(II): Synthesis and structure

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Complexes of the type $[\text{PtCl}(\text{SeAr})(\text{PPh}_3)_2]$ (I), $[\text{Pt}(\text{SeAr})_2(\text{PPh}_3)_2]$ (II) and $[\text{M}(\text{DPPE})(\text{EAr})_2]$ (III) [$\text{Ar} = \text{Ph}$, $\text{C}_6\text{H}_4\text{OMe-4}$; $\text{M} = \text{Pd}$, Pt ; $\text{DPPE} = 1, 2\text{-bis}(\text{diphenylphosphino})\text{ethane}$; $\text{E} = \text{Se}$, Te] have been synthesized from the reactions between *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ and NaSeAr , and between $[\text{M}(\text{DPPE})\text{Cl}_2]$ and NaEAr (generated *in situ*) in ethnaol-benzene at room temperature. Their structures have been established on the basis of elemental analyses, conductance and molecular weight measurements, and IR, ^1H and ^{31}P NMR spectra. A *trans*-form for I and II and a *cis*-form for III have been assigned. The reaction of III ($\text{M} = \text{Pt}$; $\text{Ar} = \text{Ph}$) with $[\text{Pd}(\text{PhCN})_2\text{Cl}_2]$ has led to the formation of an interesting class of hetero binuclear complexes $[\text{DPPE}]\text{Pt}(\mu\text{-EPH})_2\text{PdCl}_2]$ (IV) with phenyl chalcogen bridging.

Sodium organyl chalcogenolate, NaER ($\text{E} = \text{S}$, Se , Te ; $\text{R} = \text{alkyl or aryl}$) is an effective reagent for incorporating RE^- ligand in the coordination sphere of certain metal ions. The coordination chemistry of RS^- has been extensively explored^{1,2}. However, the interaction of RSe^- and RTe^- with d^8 metal ions like $\text{Pd}(\text{II})$ and $\text{Pt}(\text{II})$ has not been so well studied³⁻⁵. In continuation of our previous work on coordination chemistry⁶⁻¹⁰ of $\text{Pd}(\text{II})$ and $\text{Pt}(\text{II})$ ions, we undertook the present study. Our aim was to (a) find whether organyl chalcogenolates could form complexes of novel structures with palladium and platinum and (b) compare the donor tendencies of S , Se and Te in chalcogenolates towards $\text{Pd}(\text{II})$ and $\text{Pt}(\text{II})$.

Materials and Methods

cis- $[\text{PtCl}_2(\text{PPh}_3)_2]$ (Strem Chemicals) and $[\text{Pd}(\text{PhCN})_2\text{Cl}_2]$ (Aldrich) were used as such. $[\text{Pd}(\text{DPPE})\text{Cl}_2]$ and $[\text{Pt}(\text{DPPE})\text{Cl}_2]$ were prepared by published methods^{11,12}. Sodium aryl chalcogenolates, NaEAr , were generated *in situ* by NaBH_4 reduction of the corresponding diaryl dichalcogenides, Ar_2E_2 , in ethanol^{13,14}.

IR spectra were recorded in the solid state as CsI pellets on a Nicolet 5 DX FT instrument. ^1H - and ^{31}P - $\{^1\text{H}\}$ NMR spectra were recorded in CDCl_3 solution on a Bruker AM 500 MHz FT instrument using TMS and H_3PO_4 as internal and external references, respectively. Conductance was measured in CH_3CN using a highly sensitive Pye conductance bridge (Model No. 11700) and molecular weights were determined in CHCl_3 using a Knauer vapour pressure osmometer (Model No. 11.00). Elemental analyses were performed on a Perkin-Elmer 240 C analyser.

Solvents were dried and distilled before use. All the reactions were carried out under an atmosphere of dry oxygen-free nitrogen.

Preparation of $[\text{PtCl}(\text{SeAr})(\text{PPh}_3)_2]$ (I) ($\text{Ar} = \text{Ph}$ and $\text{C}_6\text{H}_4\text{OMe-4}$)

A suspension of *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ (1 mmol) in benzene (30 ml) was added to the NaSeAr (1 mmol) solution, all at one go. The mixture was stirred continuously for 6 h and then filtered (celite) to remove the NaCl formed. The clear solution thus obtained was evaporated to dryness under reduced pressure. It was dissolved in the minimum amount of chloroform and poured into a mixture of petroleum ether and ether (1:1, v/v; 200 ml) under rapid stirring. The product then separated out in the form of microscopic crystals. It was dried *in vacuo*.

Preparation of $[\text{Pt}(\text{SeAr})_2(\text{PPh}_3)_2]$ (II) ($\text{Ar} = \text{Ph}$ and $\text{C}_6\text{H}_4\text{OMe-4}$)

These complexes were prepared in a way similar to that mentioned above except that *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ and NaSeAr were taken in 1:2 molar ratio.

Preparation of $[\text{M}(\text{DPPE})(\text{EAr})_2]$ (III) ($\text{M} = \text{Pd}$, $\text{Ar} = \text{Ph}$; $\text{M} = \text{Pt}$, $\text{Ar} = \text{Ph}$ and $\text{C}_6\text{H}_4\text{OMe-4}$)

A benzene suspension of $\text{M}(\text{DPPE})\text{Cl}_2$ (1 mmol) was added to the ethanolic solution of NaEAr ($\text{E} = \text{Se}$, Te) (2 mmol). Stirring was continued for 6 h during which period $\text{M}(\text{DPPE})\text{Cl}_2$ dissolved to give a clear solution. It was filtered through celite to remove the NaCl formed and any unreacted Pd or Pt complex. The clear filtrate thus obtained was evaporated to dryness. It was redissolved in the minimum amount of

Table 1—Physical and analytical data of complexes

Complex	Colour (yield, %)	m.p. (°C)	Found (Calc.), %				Molecular weight ^a
			C	H	Cl	Se/Te	
[PtCl(SePh)(PPh ₃) ₂]	Yellow (58)	151 (dec.)	55.4 (55.3)	3.8 (3.8)	4.2 (3.9)	9.2 (8.6)	926 (910)
[PtCl(SeC ₆ H ₄ OMe-4)(PPh ₃) ₂]	Yellow (63)	145 (dec.)	54.7 (54.8)	3.9 (3.9)	4.0 (3.7)	8.7 (8.4)	915 (940)
[Pt(SePh) ₂ (PPh ₃) ₂]	Orange (65)	134 (dec.)	55.9 (55.8)	3.8 (3.8)		15.6 (15.3)	1051 (1031)
[Pt(SeC ₆ H ₄ OMe-4) ₂ (PPh ₃) ₂]	Orange (70)	131 (dec.)	55.1 (54.9)	4.1 (4.0)		14.8 (14.4)	1079 (1091)
[Pd(DPPE)(SePh) ₂]	Reddish	186	56.3	4.2		19.7	836
	Brown (71)		(55.8)	(4.1)		(19.3)	(816)
[Pd(DPPE)(TePh) ₂]	Brown (72)	133	50.1 (49.8)	3.6 (3.7)		28.4 (27.9)	927 (914)
[Pt(DPPE)(TePh) ₂]	Orange (57)	175	45.5 (45.4)	3.4 (3.3)		25.8 (25.4)	1036 (1002)
[Pt(DPPE)(TeC ₆ H ₄ OMe-4) ₂]	Orange (55)	196	45.4 (45.1)	3.8 (3.5)		24.5 (24.0)	1086 (1062)
[Pt(DPPE)(SePh) ₂]	Yellow (61)	205	50.5 (50.3)	3.7 (3.7)		17.7 (17.4)	927 (905)
[Pt(DPPE)(SeC ₆ H ₄ OMe-4) ₂]	Yellow (60)	192	50.0 (49.7)	4.0 (3.9)		16.8 (16.3)	978 (965)
[Pt(DPPE)(μ-TePh) ₂ PdCl ₂]	Brown (80)	246 (dec.)	38.8 (38.6)	2.9 (2.8)	6.4 (6.0)	22.0 (21.6)	1210 (1180)
[Pt(DPPE)(μ-SePh) ₂ PdCl ₂]	Brown (70)	267 (dec.)	42.4 (42.1)	3.2 (3.1)	6.8 (6.5)	15.1 (14.5)	1105 (1083)

^aMolecular weights were determined in CHCl₃.

CHCl₃ and mixed with an appropriate amount of diethyl ether until turbidity appeared. On cooling it overnight, a crystalline material separated out. It was filtered, washed with ether and dried *in vacuo*.

Preparation of [(DPPE)Pt(μ-EPh)₂PdCl₂] (IV)

Pt(DPPE)(EPh)₂ (1 mmol) and Pd(PhCN)₂Cl₂ (1 mmol) were mixed in benzene (30 ml) and the solution was stirred for 6 h at room temperature. Concentration of the solution at reduced pressure and addition of diethyl ether to the resulting solution gave a reddish brown material. It was washed with ether and dried *in vacuo*.

Results and Discussion

The yield, colour, m.p., analytical and molecular weight data of all the isolated complexes have been incorporated in Table 1.

The reaction of NaSeAr (generated *in situ*) with *cis*-[PtCl₂(PPh₃)₂] in ethanol-benzene in 1:1 and 2:1 molar ratios at room temperature resulted in the formation of complexes of the types [PtCl(SeAr)(PPh₃)₂]

(I) and [Pt(SeAr)₂(PPh₃)₂] (II), similar to their Te analogues⁶. Addition of excess of NaSeAr to Pt(II) solution yielded the compound with stoichiometry corresponding to II only. All the mono selenol complexes (I) were yellow while bis-selenol complexes (II) were orange in colour. These complexes were soluble in common organic solvents except petroleum ether and diethyl ether. The molar conductance values for complexes I and II in CH₃CN were fairly low (6-17 ohm⁻¹ cm² mol⁻¹) as compared to the values reported¹⁵ for 1:1 electrolytes (120-160 ohm⁻¹ cm² mol⁻¹) suggesting their non-electrolytic nature. Molecular weight determinations in CHCl₃ established their monomeric nature in solution. Elemental analyses agreed well with their formulations.

The IR spectra showed one ν(Pt-Cl) band in I and none in II (Table 2). The observed ν(Pt-Cl) values are characteristic of terminal chlorine *trans* to Se ligands¹⁶.

The ¹H NMR spectra of the complexes I and II (Table 2) showed all the expected peaks in the proper intensity ratio. The data, which agreed with the ear-

Table 2— ^1H NMR^a, ^{31}P - $\{^1\text{H}\}$ NMR^b and IR^c spectral data of complexes

Complex	δ Aromatic H (ppm)	δ CH ₂ (DPPE) (ppm)	δ CH ₃ (ppm)	δ P (ppm)	^1J (Pt-P) (Hz)	(M-Cl) (cm ⁻¹)
PtCl(SePh)(PPh ₃) ₂	6.23-7.69 (m)			15.37	2827	297
PtCl(SeC ₆ H ₄ OMe-4)(PPh ₃) ₂	6.27-7.64 (m)		3.67 (s)	15.55	2875	318
Pt(SePh) ₂ (PPh ₃) ₂	6.31-7.65 (m)			13.88	3040	
Pt(SeC ₆ H ₄ OMe-4) ₂ (PPh ₃) ₂	6.15-7.59 (m)		3.72 (s)	13.51	3010	
Pd(DPPE)(SePh) ₂	6.50-7.62 (m)	$J^{2.08(d)}_{\text{PH} = 21 \text{ Hz}}$		48.12		
Pd(DPPE)(TePh) ₂	6.42-7.87 (m)	$J^{2.36(d)}_{\text{PH} = 21 \text{ Hz}}$		43.73		
Pt(DPPE)(SePh) ₂	6.58-7.81 (m)	$J^{2.06(d)}_{\text{PH} = 19 \text{ Hz}}$		42.21	2957	
Pt(DPPE)(TePh) ₂	6.56-7.66 (m)	$J^{1.98(d)}_{\text{PH} = 19 \text{ Hz}}$		41.56	2890	
Pt(DPPE)(SeC ₆ H ₄ OMe-4) ₂	6.17-7.69 (m)	$J^{2.01(d)}_{\text{PH} = 19 \text{ Hz}}$	3.62 (s)	41.98	2960	
Pt(DPPE)(TeC ₆ H ₄ OMe-4) ₂	6.14-7.68 (m)	$J^{1.96(d)}_{\text{PH} = 19 \text{ Hz}}$	3.63 (s)	41.14	2884	
Pt(DPPE)(SePh) ₂ PdCl ₂	7.26-7.95 (m)	$J^{2.33(d)}_{\text{PH} = 18 \text{ Hz}}$		36.94	3620	313, 290
Pt(DPPE)(TePh) ₂ PdCl ₂	7.25-8.05 (m)	$J^{2.34(d)}_{\text{PH} = 18 \text{ Hz}}$		36.91	3619	313, 292

^aRecorded in CDCl₃. ^bRecorded in CDCl₃, H₃PO₄ as external reference. ^cRecorded in the solid state as CsI pellets. s = singlet, d = doublet, m = multiplet.

lier reports^{6,10}, established equivalence of both the aryl groups in the complex II.

The ^{31}P - $\{^1\text{H}\}$ NMR spectra of both the complexes and II (Table 2) displayed a single ^{31}P resonance consistent with the presence of only one type of phosphorus atom in the solution. Further, the ^{31}P resonances were associated with platinum satellites (approximately 1:4:1 triplet structure) (Fig. 1). The coupling constant, $^1J(\text{Pt-P})$ for complexes I and II lied in the range 2827-3040 Hz which is characteristic of *trans*-Ph₃P-Pt-PPh₃ system. Thus, starting from *cis*-[PtCl₂(PPh₃)₂] the materials obtained on addition of NaSeAr are the *trans*-[PtCl(SeAr)(PPh₃)₂] and *trans*-[Pt(SeAr)₂(PPh₃)₂] which are similar to those obtained in the case of the Te analogues⁶. Although no mechanistic studies have been carried out on this system, it seems probable that the *cis*-starting material yields the *trans*-products via a two stage mechanism involving a five coordinate transition intermediate followed by rearrangement of the ligands.

It is interesting to note that the reaction between *cis*-[PtCl₂(PPh₃)₂] and NaEAr (E = Se, Te) at the room temperature resulted only in the formation of a monomeric species. However, PdCl₂(PPh₃)₂ is reported to form with ArTe⁻ a dimeric and with ArSe⁻, a monomeric product^{7,10}. The similar monomeric

thiol complexes have also been reported from the reaction between PdCl₂(PR'₃)₂ (PR'₃ = PEt₃ or 1/2 DPPE) and RS⁻ (ref. 11). Thus, a marked distinction is observed in the behaviour of thiols and selenols on one side and tellurols on the other side.

The observations suggest that among chalcogenolates the donor tendency of Te, being larger in size, is higher towards Pd(II) and Pt(II) relative to that towards Se and S. Further, this tendency is more in the case of Pd(II) as compared to that in the case of Pt(II). Thus, the sequence, Te > Se > S is followed for favoured donation to Pd(II) and Pt(II).

Reactions between M(DPPE)Cl₂ and NaEAr in 1:2 or higher molar ratios in ethanol-benzene at room temperature yielded the chelated complexes [M(DPPE)(EAr)₂] (III). They were found to be crystalline solids, fairly soluble in organic solvents except in petroleum ether and diethyl ether. The elemental analyses of these complexes and their molecular weight data in CHCl₃ (Table 2) were consistent with the above formulation. Conductance measurements in CH₃CN indicated their non-electrolytic nature. IR spectra indicated the absence of $\nu(\text{M-Cl})$ bands in all the complexes.

The ^1H NMR spectra of complexes III (Table 2) showed all the expected peaks in the proper intensity ratio. A doublet ($^2J_{\text{PH}} = 18-21 \text{ Hz}$) was present in

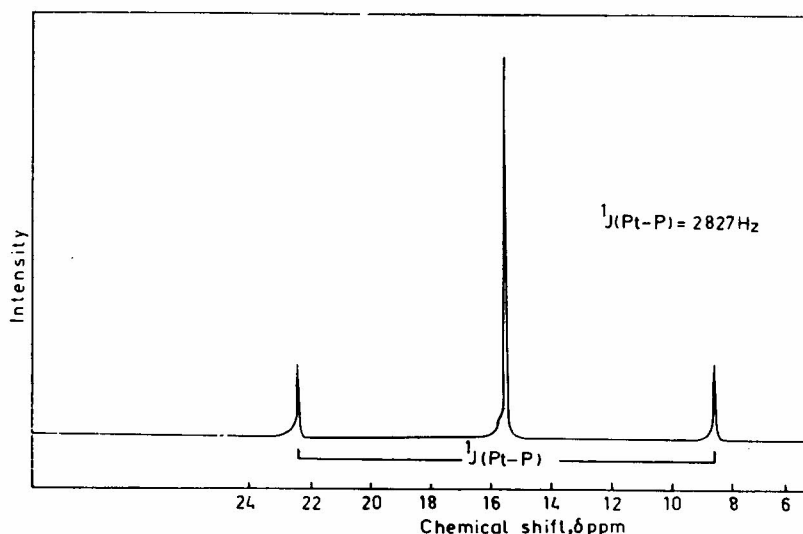


Fig. 1— ^{31}P NMR spectrum of *trans*-[PtCl(SePh)(PPh₃)₂] in CDCl_3 at 202.5 MHz

each case at δ 1.9–2.3 ppm due to the methylene backbone of DPPE.

The ^{31}P - $\{^1\text{H}\}$ NMR spectra of complexes III (Table 2) comprised a single ^{31}P resonance indicating the equivalence of the two phosphorus atoms in the complexes. The ^{31}P resonance in the complexes III ($\text{M} = \text{Pt}$) was associated with ^{195}Pt satellites (approximately 1:4:1 triplet structure). The coupling constant $^1J(\text{Pt-P})$ observed in the range 2884–2960 Hz is characteristic of P *trans* to Se or Te ligands¹⁷. Thus, complexes III have essentially a *cis* structure similar to their S-analogues¹⁸.

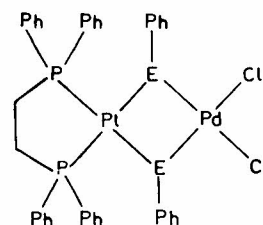
The reaction of complex III ($\text{M} = \text{Pt}$, $\text{Ar} = \text{Ph}$) with $\text{Pd}(\text{PhCN})_2\text{Cl}_2$ in benzene at room temperature lead to the formation of a hetero binuclear complex [(DPPE)Pt(μ -EPh)₂PdCl₂] (IV) with phenyl chalcogen bridging. The characterization data are given in Table 1. Conductance measurements in CH_3CN indicated their non-electrolytic nature. Elemental analyses and molecular weight measurements in CHCl_3 were consistent with the above formulation.

The IR spectra (Table 2) showed two $\nu(\text{Pd}-\text{Cl})$ bands in the region $313\text{--}290\text{ cm}^{-1}$ indicating the presence of terminal chloride ligands. The observed $\nu(\text{Pd}-\text{Cl})$ values are typical of Cl *trans* to Se¹⁶ and Te¹⁹ ligands.

In the ^1H NMR spectra of complexes IV (Table 2) the phenyl protons have been found to be considerably deshielded (~ 0.7 ppm) in comparison to those of complexes I, II and III, suggesting that the phenyl chalcogen groups form bridges between Pd and Pt atoms.

The ^{31}P NMR spectra of complexes IV (Table 2) consisted of a single ^{31}P resonance associated with

platinum satellites (approximately 1:4:1 triplet structure). This clearly indicates the equivalence of the two phosphorus atoms in the complexes. The observed $^1J(\text{Pt-P})$ values (3619–3620 Hz; Table 2) are higher than that expected for P *trans* to Se or Te. This is probably because of the bridging nature of PhE that the interaction between Pt and E is relatively weak and as a consequence of it, the Pt–P bonds become stronger. This is supported by the fact that these values are in good agreement with those for P *trans* to Cl, which is a weak ligand (the $^1J(\text{Pt-P})$ for *cis*-[PtCl₂(PPh₃)₂] is 3679 Hz (PPh₃ *trans* to Cl)²⁰. Hence, a hetero binuclear structure with phenyl chalcogen bridging, similar to that of its S-analogues²¹, is reasonable for complex IV (structure-I).



(Structure I)

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References

- 1 Dance I G, *Polyhedron*, 5 (1986) 1037.
- 2 Blower P J & Dilworth J R, *Coord Chem Rev*, 76 (1987) 121.

- 3 Chia L Y & McWhinnie W R, *J organomet Chem*, 148 (1978) 165.
- 4 Gardner S A, Trotter P J & Gysling H J, *J organomet Chem*, 212 (1981) 35.
- 5 Gardner S A & Gysling H J, *J organomet Chem*, 197 (1980) 111.
- 6 Khandelwal B L, Kundu K & Gupta S K, *Inorg chim Acta*, 148 (1988) 255.
- 7 Khandelwal B L, Kundu K & Gupta S K, *Inorg chim Acta*, 154(1988) 183.
- 8 Kundu K & Gupta S K, *J Bangladesh chem Soc*, 1 (1988) 135.
- 9 Khandelwal B L & Gupta S K, *Inorg chim Acta*, 161 (1989) 207.
- 10 Khandelwal B L & Gupta S K, *Inorg chim Acta*, 166 (1989) 199.
- 11 Hayter R J & Humiec F S, *J inorg nucl Chem*, 26 (1964) 807.
- 12 Rauchfuss T B, Shu J S & Roundhill D M, *Inorg Chem*, 15 (1976) 2096.
- 13 Sharpless K B & Lauer R F, *J Am chem Soc*, 95 (1973) 2697.
- 14 Clive D L J, Chittattu G J, Farina V, Kiel W A, Menchen S M, Russell C G, Singh A, Wong C K & Curtis N J, *J Am chem Soc*, 102 (1980) 4438.
- 15 Geary W J, *Coord Chem Rev*, 7 (1971) 81.
- 16 Gulliver D J, Hope E G, Levason W, Murray S G & Marshall G L, *J chem Soc, Dalton Trans*, (1985) 1265,
- 17 Giolando D M, Rauchfuss T B & Rheingold A L, *Inorg Chem*, 26 (1987) 1636.
- 18 Braterman P S, Wilson V A & Joshi K K, *J organomet Chem*, 31 (1971) 123.
- 19 Gysling H J, Zumbulyadis N & Robertson J A, *J organomet Chem*, 209 (1981) C41.
- 20 Eaborn C, Pidcock A & Steele B R, *J chem Soc, Dalton Trans*, (1976) 767.
- 21 Zanella R, Ros R & Graziani M, *Inorg Chem*, 12 (1973) 2736.