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Palladium(II) and Platinum(II) Complexes with Aryl Selenols and Diaryl Diselenides: A Comparative Approach with Tellurium and Sulfur Analogues

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Abstract

Sodium aryl selenols, NaSeAr (Ar = phenyl and *p*-anisyl), react with Na_2PdCl_4/K_2PtCl_4 in aqueous ethanol in 1:1 and 1:2 molar ratios to form polymeric complexes $[MCl(SeAr)]_n$ (I) and $[M(SeAr)_2]_n$ (II) (M = Pd or Pt) at room temperature. Chemical and far IR spectral evidences support alternating chloride and selenol bridges in **I** and only selenol bridges in **II**. Reactivity of Pd(II) complexes has been further investigated. While the reaction of **I** (M = Pd; Ar = Ph) with PPh_3 in stoichiometric amount results in splitting of chloride bridges and formation of a selenol bridged dimeric complex $[PdCl(SePh)(PPh_3)]_2$ (III), with excess of PPh_3 or with a stoichiometric amount of DPPE, simultaneous cleavage of both chloride and selenol bridges leads to the formation of monomeric compounds $[PdCl(SeAr)(PPh_3)_2]$ (IV) and [PdCl(SePh)(DPPE)] (V). Complex **II** (M = Pd) also undergoes bridge splitting reactions with excess of PPh_3 to yield a monomeric compound $[Pd(SeAr)_2(PPh_3)_2]$ (VI). Complex **IV** and **VI** could also be prepared from the reactions between $Pd(PPh_3)_2Cl_2$ and NaSeAr in alcohol at room temperature.

The reaction of diaryl diselenides, Ar_2Se_2, with $Pd(PhCN)_2Cl_2$ in benzene or with Na_2PdCl_4 in alcohol affords a dimeric complex $[PdCl_2(Se_2Ar_2)]_2$ (VII). No product could, however, be isolated by the reactions of Ar_2Se_2 (or Ph_2S_2) with $PtCl_4^{2-}$. The complex **VII** on refluxing with MeOH/EtOH undergoes cleavage of the Se–Se bond to form polymeric complex **I**. However, the reaction of complex **VII** with PPh_3 liberated free diselenides. The characterization of all the complexes has been made on the basis of elemental analysis, IR and ^1H NMR, conductivity and molecular weight measurements where possible.

Introduction

The ligational behaviour of thiols and tellurols and their precursors with palladium(II) and platinum(II) derivatives has been extensively discussed in earlier reports [1–14]. The analogous chemistry of selenol and their precursor diselenides with Pt(II) and Pd(II) has not been reported so far [15, 16] and this has stemmed our interest in them. The present work reports the synthesis of new polymeric selenol complexes of palladium(II) and platinum(II) and bridge-splitting reactions of palladium(II) polymers. The selenols are generally obtained *in situ* by reductive cleavage of the Se–Se bond of diselenide and, therefore, it was also thought worthwhile to study the complexation of their precursor diselenides. This adds to the few known examples where diselenide coordinates with transition metals keeping the Se–Se bond intact [17–25]. Moreover, the aim was also to compare the ligational behaviour of tellurols, selenols and thiols along with their precursors towards palladium(II) and platinum(II) derivatives.

Experimental

Reactions were carried out in three necked round bottom flask of the appropriate size equipped with an inlet for dry nitrogen gas under which the reactions were conducted. The purification and characterization of the products were carried out in air. Solvents were dried and distilled before use. Melting points were recorded in open capillary tubes and are uncorrected. IR spectra were recorded in the solid state as CsI pellets on a Nicolet 5DX FT instrument. ^1H NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 solutions on a Jeol FX 100 FT instrument with TMS as an internal standard. Conductance measurements were made in DMF using a high sensitive PYE Conductance bridge (model no. 11700) and molecular weights were determined in chloroform using a Knauer Vapour Pressure Osmometer (model no. 11.00). Elemental analyses were performed on a Perkin-Elmer 240 C analyser.

$Pd(PhCN)_2Cl_2$, Na_2PdCl_4, K_2PtCl_4 (Aldrich Chemicals) and Ph_2S_2, DPPE (1,2-bis(diphenyl phosphino ethane) (Fluka chemicals) were commercially available. Diaryl diselenides, Ar_2Se_2 (Ar = phenyl and *p*-anisyl), were prepared following the literature

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method [26, 27]. Sodium aryl selenols, NaSeAr, were generated *in situ* by $NaBH_4$ reduction of Ar_2Se_2 in alcohol.

Preparation of $[PdCl(SeAr)]_n$ (I) (Ar = phenyl and p-anisyl)

An alcoholic solution of Na_2PdCl_4 (1 mmol) was treated with NaSeAr (1 mmol), generated *in situ* in alcohol by $NaBH_4$ reduction of Ar_2Se_2 (0.5 mmol), and the mixture was stirred for 6 h. The wine-red solid separated on centrifugation, was washed with water, alcohol and ether and dried *in vacuo*.

Preparation of $[Pd(SeAr)_2]_n$ (II) (Ar = phenyl and p-anisyl)

These were prepared in a similar way to **I** except that Na_2PdCl_4 and NaSeAr were taken in a 1:2 molar ratio.

Preparation of $[PtCl(SeAr)]_n$ (Ar = phenyl and p-anisyl)

An alcoholic solution of NaSeAr (1 mmol) generated *in situ* was mixed with an aqueous solution of K_2PtCl_4 (1 mmol) and kept for 2 days when a finely powdered brown compound was obtained. It was filtered, washed with water, alcohol and ether and dried *in vacuo*.

Preparation of $[Pt(SeAr)_2]_n$ (Ar = phenyl and p-anisyl)

These were prepared in a similar way to $[PtCl(SeAr)]_n$ from the reactions between K_2PtCl_4 and NaSeAr in a 1:2 molar ratio.

Preparation of $[PdCl(SePh)(PPh_3)]_2$ (III)

$[PdCl(SePh)]_n$ (300 mg, 1.0 mmol) suspended in 40 cm^3 of $CHCl_3$ was treated with a stoichiometric amount of PPh_3 and the mixture was kept under vigorous stirring for 6 h at room temperature. The clear solution thus obtained was treated with a large volume of ether–petroleum ether (1:1) mixture when a yellow solid separated out. It was washed with the same mixture and dried *in vacuo*.

Preparation of $[PdCl(SeAr)(PPh_3)_2]$ (IV) (Ar = phenyl and p-anisyl)

Method A

$[PdCl(SeAr)]_n$ (250 mg, 0.83 mmol) was treated with an excess of PPh_3 in $CHCl_3$ (40 cm^3) and the solution was stirred vigorously for 6 h. The clear solution thus obtained was concentrated under low pressure and then treated with ether–petroleum ether (1:1) mixture when a yellow solid separated out. It was washed with the same mixture and dried *in vacuo*.

Method B

To an alcoholic solution of NaSeAr (1 mmol) was added solid $Pd(PPh_3)_2Cl_2$ (1 mmol) and the clear solution obtained after mixing for sometime was stirred overnight. The yellowish suspension thus obtained was centrifuged. It was washed with water, alcohol and ether and its purity was checked by TLC.

Preparation of $[PdCl(SePh)(DPPE)]$ (V)

$[PdCl(SePh)]_n$ (200 mg, 0.67 mmol) suspended in 40 cm^3 of CH_2Cl_2 was treated with a stoichiometric amount of DPPE (1:1 ratio) and the mixture was stirred for 6 h. To the clear solution thus obtained was added a large volume of diethyl ether and a light brown product was isolated. It was washed thoroughly with ether and dried *in vacuo*.

Preparation of $[Pd(SeAr)_2(PPh_3)_2]$ (VI) (Ar = phenyl and p-anisyl)

These complexes were prepared exactly as $[PdCl(SeAr)(PPh_3)_2]$ (**IV**) following the methods A and B from the reactions between $[Pd(SeAr)_2]_n$ and PPh_3(excess) or $Pd(PPh_3)_2Cl_2$ and NaSeAr in a 1:2.5 molar ratio at room temperature.

Preparation of $[PdCl_2(Se_2Ar_2)]_2$ (VII) (Ar = phenyl and p-anisyl)

Method A

Solid Se_2Ar_2 (1 mmol) was added to a clear solution of $Pd(PhCN)_2Cl_2$ (1 mmol) in benzene at room temperature. The orange suspension which appeared immediately after addition was stirred for 4 h. The orange solid was filtered, washed with benzene and ether and dried *in vacuo*. The reactants with a higher diselenide concentration also yielded the same product.

Method B

A clear solution of Se_2Ar_2 (1 mmol) in ethanol was slowly added to another clear solution of Na_2PdCl_4 (1 mmol) in the same solvent and the mixture was stirred for 2 h. The material separated on keeping, was washed with ice-cold water, cold alcohol and ether and dried *in vacuo*.

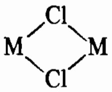
Complex **VII** on refluxing with MeOH/EtOH gave mostly the polymeric complex $[PdCl(SeAr)]_n$ (**I**) which was isolated pure after successive washings with MeOH/EtOH and chloroform.

Reaction between $[PdCl_2(Se_2(C_6H_4OMe\text{-}4)_2)]_2$ and PPh_3

An excess of PPh_3 in diethyl ether (50 cm^3) was added to $[PdCl_2(Se_2(C_6H_4OMe\text{-}4)_2)]_2$ (100 mg) and the suspension stirred for 1 h at room temperature. The ether solution had turned yellow by this time. It was filtered to remove $Pd(PPh_3)_2Cl_2$ and the clear filtrate thus obtained was evaporated to dryness to give a yellow solid. ^1H NMR of this in $CDCl_3$ showed it to be a mixture of $Se_2(C_6H_4OMe\text{-}4)_2$ and PPh_3. Diselenide was also detected *in situ* from a reaction mixture of the two in $CDCl_3$ by ^1H NMR.

Results and Discussion

The yield, colour, decomposition temperature, analytical and molecular data of all the isolated complexes are incorporated in Table 1 and infrared data in Table 2. Tetrachlorometallate anions, MCl_4^{2-} (M = Pd and Pt), react with aryl selenols, $ArSe^-$, in 1:1 and 1:2 molar ratios to form complexes $[MCl(SeAr)]_n$ (**I**) and $[M(SeAr)_2]_n$ (**II**) in aqueous ethanol at room temperature. Similar S and Te analogues of Pd(II) and Pt(II) have been reported earlier [1–5, 12–14]. Complexes **I** and **II** are insoluble in most of the common organic solvents. Their elemental analyses correspond to the empirical formulae [MCl(SeAr)] and $[M(SeAr)_2]$. The IR spectrum of **I** in the solid state as CsI pellets exhibits bands in the range 299–246 cm^{-1} which are typical of M–Cl (M = Pd and Pt) bridging stretching frequencies [28]. The occurrence of more than two ν(M–Cl) bands in the complex may be due to either ^{37}Cl isotope effect or non-planarity of



units. A polymeric chain structure having alternate chloride and selenol bridges (Fig. 1) is tentatively

TABLE 1. Characterization data of palladium(II) and platinum(II) complexes

Complex	Yield (%)	Colour	Decomposition temperature (°C)	Analysis[a] (%)				Molecular[b] weight
				C	H	Cl	Se	
$[PdCl(SePh)]_n$	75	wine-red	186	24.2 (24.1)	1.7 (1.7)	12.2 (11.9)	26.1 (26.5)	
$[PdCl(SeC_6H_4OMe\text{-}4)]_n$	71	wine-red	159	25.6 (25.2)	2.1 (2.2)	10.8 (11.2)	24.0 (24.5)	
$[Pd(SePh)_2]_n$	80	wine-red	180	34.7 (34.4)	2.2 (2.3)		38.3 (38.7)	
$[Pd(SeC_6H_4OMe\text{-}4)_2]_n$	80	wine-red	174	35.6 (35.1)	2.9 (2.9)		33.4 (32.9)	
$[PtCl(SePh)]_n$	72	dark brown	185	19.1 (18.6)	1.4 (1.3)	9.5 (9.1)	20.7 (20.4)	
$[PtCl(SeC_6H_4OMe\text{-}4)]_n$	76	dark brown	190	19.7 (20.1)	1.7 (1.6)	8.3 (8.5)	19.3 (18.9)	
$[Pt(SePh)_2]_n$	73	dark brown	167	29.0 (28.4)	2.0 (1.9)		31.6 (31.1)	
$[Pt(SeC_6H_4OMe\text{-}4)_2]_n$	70	dark brown	170	29.1 (29.6)	2.4 (2.4)		28.3 (27.8)	
$[PdCl(SePh)(PPh_3)]_2$	65	pale yellow	238	51.8 (51.4)	3.6 (3.5)	6.8 (6.3)	14.8 (14.1)	1080 (1120)
$[PdCl(SePh)(PPh_3)_2]$	67	yellow	215	61.5 (61.3)	4.3 (4.2)	4.7 (4.3)	10.2 (9.6)	850 (822)
$[PdCl(SeC_6H_4OMe\text{-}4)(PPh_3)_2]$	75	brown	225	60.0 (60.5)	4.4 (4.3)	4.6 (4.1)	9.7 (9.2)	811 (852)
[PdCl(SePh)(DPPE)]	60	light brown	207	55.6 (55.1)	4.2 (4.1)	5.6 (5.1)	11.8 (11.3)	705 (696)
$[Pd(SePh)_2(PPh_3)_2]$	70	yellow	210	60.5 (61.1)	4.4 (4.2)		17.0 (16.7)	910 (942)
$[Pd(SeC_6H_4OMe\text{-}4)_2(PPh_3)_2]$	62	brown	220	60.2 (59.8)	4.4 (4.4)		15.9 (15.7)	987 (1002)
$[PdCl_2(Se_2Ph_2)]_2$	84	orange	221	29.7 (29.4)	2.1 (2.0)	14.7 (14.3)	31.7 (32.2)	1018 (979)
$[PdCl_2(Se_2(C_6H_4OMe\text{-}4)_2]_2$	69	orange	184	30.2 (30.5)	2.4 (2.5)	12.2 (12.9)	28.1 (28.7)	1048 (1099)

[a] Calculated values are given in parentheses. [b] Molecular weights were determined in $CHCl_3$.

TABLE 2. Metal–chlorine stretching frequencies

Complex	ν(M–Cl) [a] (cm^{-1}) (M = Pd and Pt)
$[PdCl(SePh)]_n$	291m, 282s, 269m, 247ms
$[PdCl(SeC_6H_4OMe\text{-}4)]_n$	290m, 279s, 226sh, 253w
$[PtCl(SePh)]_n$	293ms, 266w, 253s, 246s
$[PtCl(SeC_6H_4OMe\text{-}4)]_n$	299w, 289m, 268ms, 248s
$[PdCl(SePh)(PPh_3)]_2$	314ms
$[PdCl(SePh)(PPh_3)_2]$	357s
$[PdCl(SeC_6H_3OMe\text{-}4)(PPh_3)_2]$	358s
$[PdCl(SePh)(DPPE)]$	290s
$[PdCl_2(Se_2Ph_2)]_2$	353s, 304ms
$[PdCl_2(Se_2(C_6H_4OMe\text{-}4)]_2$	354s, 326m

[a] Recorded in the solid state as CsI pellets; s = strong, m = medium, sh = shoulder, w = weak.

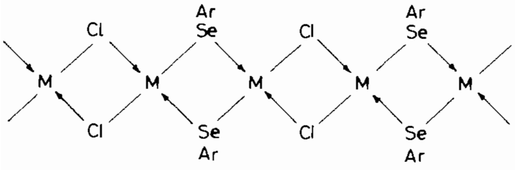
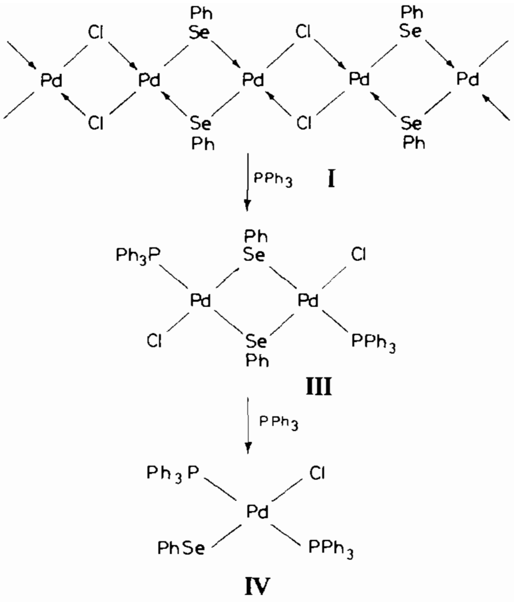


Fig. 1. Proposed structure for complex $[MCl(SeAr)]_n$ (I).

suggested for **I**. The complexes $[PdCl(EAr)]_n$ (E = S and Te) as reported earlier [5, 13] also have alternating chloride and aryl chalcogen bridges.

It is observed that the reactions between $PtCl_4^{2-}$ and $ArSe^-$ are relatively much slower as compared to the reactions between $PdCl_4^{2-}$ and $ArSe^-$ (see 'Experimental'). This is in agreement with the relatively smaller tendency of platinum with respect to palladium to form polymeric units. The sequence Ni > Pd > Pt followed for favoured polymerization with thiols [29], seems to be analogous with selenols and tellurols.

Complex **I** with PPh_3 in a 1:1 molar ratio affords a dimeric complex $[PdCl(SePh)(PPh_3)]_2$ (**III**) consistent with molecular weight measurement. Elemental analysis corresponds to the empirical formula $[PdCl(SePh)(PPh_3)]$. The IR spectrum showing the ν(Pd–Cl) vibration at 314 cm^{-1} is suggestive of the presence of a terminal chloride rather than a bridging one. A dimeric structure with selenol bridging and PPh_3 in the *trans* position is assumed as the most possible one, similar to its S and Te analogues. The reaction of **I** with excess of PPh_3 gives *trans*-$[PdCl(SeAr)(PPh_3)_2]$ (**IV**) which has been characterized by elemental analysis, IR (ν(Pd–Cl) (Ar = Ph, 357 cm^{-1}; Ar = *p*-anisyl, 358 cm^{-1} typical for a terminal chloride ligand [30]), ^{1}H NMR ($CDCl_3$, 25 °C, δ 7.94–6.25 ppm (m, aromatic, H), 3.74 ppm (s, 3H, OCH_3)), molecular weight in $CHCl_3$ and conductivity measurement in DMF (indicating its non-electrolytic nature).



Scheme 1. Suggested mechanism for the formation of complex IV from complex I and PPh_3(excess).

Hence the formation of *trans*-$[PdCl(SeAr)(PPh_3)_2]$ (**IV**) from the reaction between **I** and excess of PPh_3 may be explained by Scheme 1 in which it is evident that PPh_3 first splits the chloride bridges to give selenol bridged dimer **III**, which then with more PPh_3 yields the monomeric complex **IV** by cleavage of the selenol bridges. A similar type of mechanism is discussed in the case of S and Te analogues [5, 13].

Further evidence for simultaneous cleavage of chloride and selenol bridges has also been observed when **I** reacts with DPPE in a 1:1 molar ratio in CH_2Cl_2 and results in a chelated complex $[PdCl(SePh)(DPPE)]$ (**V**) (Fig. 2) similar to the S and Te analogues. The elemental analysis corresponds to the stoichiometry and the IR spectrum exhibits ν(Pd–Cl) at 290 cm^{-1} consistent with a Cl *trans* to phosphine [31]. The conductivity measurement in DMF shows its non-electrolytic nature and the molecular weight in $CHCl_3$ is consistent with the above formulation.

Complex **II**, like thiol and tellurol bridged Pd(II) and Pt(II) complexes [32, 33], undergoes bridge splitting reactions with excess of PPh_3 to form monomeric compounds $[Pd(SeAr)_2(PPh_3)_2]$ (**VI**) which have been characterized by elemental analysis, ^{1}H NMR ($CDCl_3$, 25 °C, δ 7.81–6.45 ppm (m, Aromatic H), 3.75 ppm (s, 3H, OCH_3) and molecular weight measurement in $CHCl_3$. A polymeric chain structure with aryl selenol bridges may be most reasonably assigned to complex **II** (Fig. 3).

Complexes **IV** and **VI** are also obtained from the reactions between $Pd(PPh_3)_2Cl_2$ and $ArSe^-$ in ethanol at room temperature. This seems to be analogous

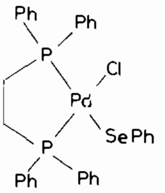


Fig. 2. Suggested structure for complex V.

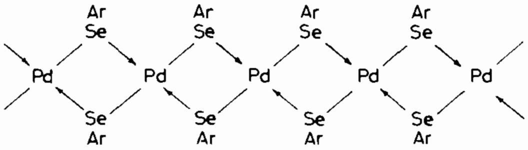


Fig. 3. Suggested structure for complex **II**.

with monomeric thiol complexes obtained from the reactions between $Pd(PR_3)_2Cl_2$ ($PR_3 = PEt_3$ or $\frac{1}{2}$DPPE) and SR^- [4] or between $[Pd(PPh_3)_2(N_3)_2]$ and RSSR [8]. However, the reactions between $Pd(PPh_3)_2Cl_2$ and $ArTe^-$ or between $[Pd(TeAr)_2]_n$ and PPh_3 always furnished a dimeric product [13]. This reveals the fact that Te, being larger in size, has a greater affinity for coordination with Pd(II) derivatives relative to Se and S ligands.

The diaryl diselenide Ar_2Se_2 (Ar = phenyl and *p*-anisyl) reacts with $Pd(PhCN)_2Cl_2$ in benzene or with Na_2PdCl_4 in alcohol to form a dimeric complex $[PdCl_2(Ar_2Se_2)]_2$ (VII) consistent with the molecular weight measurement. Elemental analysis corresponds to the empirical formula $[PdCl_2(Ar_2Se_2)]$. The IR spectrum shows two ν(Pd–Cl) bands in the region 354–304 cm^{-1} (Table 2) which favour the *cis* configuration of the complex. The possibility of any ionic structure has been eliminated by their conductance measurements in DMF which show their non-electrolytic nature. Complex **VII** shows the absence of ν(Ph–CN) bands which favours the facile replacement of benzonitrile in the initial palladium compound. The presence of the diselenide ligands is confirmed by its reaction with PPh_3 in diethyl ether which gave the free diselenide. The ^1H NMR spectrum of complex **VII** ($Ar = C_6H_4OCH_3$-4) shows equivalence of an aryl group in the complex (DMSO d^6, 25 °C, δ 7.59–6.88 ppm (m, Aromatic H), 3.76 ppm (s, 3H, OCH_3)). Thus a dimeric structure with two $PdCl_2$ moieties bridged by two molecules of diselenide similar to the S and Te analogues [5, 13] is reasonably proposed for complexes **VII** (Fig. 4). Complex **VII** on refluxing with MeOH/EtOH undergoes cleavage of the Se–Se bond to form polymeric complexes $[PdCl(SeAr)]_n$ in good yield. The behaviour of **VII** is thus similar to disulphide [5] and ditelluride [13] bridged complexes.

Interestingly, diphenyl disulphide and diaryl diselenide (Ar = phenyl and *p*-anisyl) are unreactive towards $PtCl_4^{2-}$. It may be noted that the diaryl ditelluride is known to react with $PtCl_4^{2-}$ to form a monomeric species $[PtCl_2(Te_2Ar_2)_2]$ [12]. In another observation, the disulphide and diselenide seemed to be ineffective in the displacement of bridging chlorine atoms from *trans*-$[Pd_2Cl_2(\mu\text{-}Cl)_2(PPh_3)_2]$, which the ditelluride does to form the bridged complex $Pd_2Cl_4(\mu\text{-}Te_2Ar_2)(PPh_3)_2]$ [14].

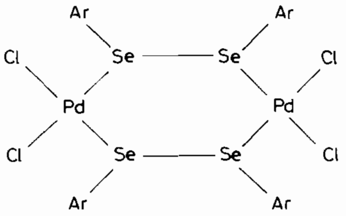


Fig. 4. Proposed structure for complex **VII**.

These observations strongly suggest that amongst dichalcogenides the donor tendency of Te relative to S and Se is higher towards Pd(II) and Pt(II) derivatives. Further, this tendency is greatly enhanced towards Pd(II) in comparison to Pt(II) derivatives. Thus the sequence Te, Se ~ S is followed for favoured donation to Pd(II) and Pt(II).

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