CHAPTER 1

Introduction


1.1 Introduction

Platinum group metals are a cluster of six elements, viz. ruthenium, rhodium, palladium, osmium, iridium and platinum, which occupy 5th and 6th periods of Groups 8, 9 and 10 of the periodic Table. Among them palladium and platinum are the most widely studied elements. A recent survey by Gavin [1] is a testimony to the growing interest in the chemistry of palladium and platinum with an increase of 51 (Pd) and 89 (Pt) % non-patent literature during a decade (1998-2008). In fact the chemistry of both these elements has played a pivotal role in the development and progress of coordination and organometallic chemistry with several firsts to their credit [2, 3]. Soon after their discovery (platinum in 1735 and palladium in 1803 by Wollaston) several inorganic compounds were prepared. The chemistry of these elements developed during the nineteenth century; the important being the Zeise’s salt (K[PtCl3(CH2=CH2)], the first organometallic compound) in 1827 [4]; cis PtCl2(NH3)2 in mid 1850s (now used as antitumor drug) [5] and [PtCl2(CO)]2 (the first metal carbonyl) in 1868. The twentieth century witnessed further acceleration in the progress of their chemistry, notable being isolation of [PtMe3I]4 (the first alkyl compound of transition metals) in 1907, discovery of trans effect in platinum complexes in 1920s [6] and applications in homogenous catalysis from the mid century (e.g. Wacker process [7, 8]).

Both palladium and platinum are silvery white noble metals and are malleable and ductile. They are resistant to chemical attack and highly resistant to wear and tarnish. Both the metals dissolve in aqua-regia (HNO3:3HCl) forming H2MCl4. On heating, elemental Pt can also combine with B, Si, Ge, Pb, S, Se, and Te under reducing conditions resulting in the formation of several solid compounds. Among them, PtTe acts as superconductor below 4K [9]. The most remarkable property of metallic palladium is its ability to absorb hydrogen, which is greater than
any other metal (up to 900 times its own volume). The absorption process is reversible and highly selective for H\textsubscript{2} and D\textsubscript{2}. This property provides a method to purify H\textsubscript{2} on industrial scale just by passing the impure H\textsubscript{2} through a palladium membrane at controlled temperature [10].

Some physical and chemical properties of palladium and platinum are summarized in Table 1.

| Table 1: Some properties of palladium and platinum |
|---------------------------------|------------|-------------|
| **Properties**                  | **Palladium** | **Platinum** |
| Atomic number/ atomic weight    | 46/106.4    | 78/195.1    |
| Ground state electronic configuration | [Kr]4d\textsuperscript{10}5s\textsuperscript{0} | [Xe]5d\textsuperscript{9}6s\textsuperscript{1} |
| Abundance in earth’s crust (by weight) (ppm) | 0.015 | 0.01 |
| Melting point (°C)              | 1554        | 1733.5      |
| Boiling point (°C)              | 3980        | 4170        |
| Lattice structure               | f. c. c.    | f. c. c.    |
| Density (g cm\textsuperscript{-3}) | 11.99     | 21.41       |
| Pauling’s electronegativity     | 2.2         | 2.2         |
| Radius (Å): Atomic M(0) Covalent | 1.375      | 1.387       |
| M(II) Covalent                  | 1.28        | 1.29        |
| Ionic (II)                      | 0.86        | 0.80        |
| Ionization potentials (eV)      |             |             |
| M\textsuperscript{°} → M\textsuperscript{+}; M → M\textsuperscript{+2} | 8.33; 27.75 | 9.0; 27.56  |
| M\textsuperscript{°} → M\textsuperscript{+3}; M → M\textsuperscript{+4} | 60.67; 109.47 | 56.06; 97.16 |
| M\textsuperscript{+} → M\textsuperscript{+2}; M\textsuperscript{+2} → M\textsuperscript{+3} | 19.42; 32.19 | 18.56; 28.50 |
| M\textsuperscript{+3} → M\textsuperscript{+4}; M\textsuperscript{+4} → M\textsuperscript{+5} | 48.8; 66.0 | 41.10; 55.00 |
| Oxidation potential (eV)        |             |             |
| M\textsuperscript{°} → M\textsuperscript{2+} + 2e | −0.92       | −1.2        |
| M\textsuperscript{II} → M\textsuperscript{4+} + 2e | −1.26       | −0.77       |
| Naturally occurring isotopes (% abundance, spin (I)) | 1\textsuperscript{02}Pd (1.0, 0) | 1\textsuperscript{90}Pt (0.01, 0) |
|                               | 1\textsuperscript{04}Pd (11.1, 0) | 1\textsuperscript{92}Pt (0.8, 0) |
|                               | 1\textsuperscript{05}Pd (22.2, 5/2) | 1\textsuperscript{94}Pt (32.9, 0) |
|                               | 1\textsuperscript{06}Pd (27.3, 0) | 1\textsuperscript{95}Pt (33.8, 1/2) |
|                               | 1\textsuperscript{08}Pd (26.5, 0) | 1\textsuperscript{96}Pt (25.3, 0) |
|                               | 1\textsuperscript{10}Pd (11.7, 0) | 1\textsuperscript{98}Pt (7.2, 0) |
The chemistry of palladium and platinum in general is very similar and the similarity can extend even to size and bond lengths in their complexes. However, the most distinctive difference is in their reactivity, the palladium complexes being more labile (reactive than the corresponding platinum analogs). Thus palladium complexes are frequently used in catalytic reactions whereas the platinum derivatives provide an insight about mechanistic aspects (Scheme 1). Like other transition elements, palladium and platinum exhibit variable oxidation states due to the presence of vacant d orbitals. The most common oxidation state is +2 where both the metals form square-planar complexes predominantly, although other geometries (Table 2), e.g. penta coordinated, (e.g. [PtMeCl(AsMe$_3$)$_2$(CF$_3$C≡CCF$_3$)] [11]), tetrahedral are also encountered [12]. The higher coordination complexes can only be stabilized either by the strong π acceptor ligands such as SnCl$_3^-$, NO$^+$. Complexes in zero valent oxidation state adopt geometries ranging from linear (e.g. [Pt(PPh$_3$)$_2$]), planar (e.g. [Pt(PPh$_3$)$_3$] to tetrahedral (e.g. [Pt(PF$_3$)$_4$]). The complexes in low oxidation state are stabilized by strong π-acceptor ligands, such as phosphine, phosphite, arsine, isocyanide, nitric oxide, carbon monoxide. The complexes in oxidation states +1 and +3 are not numerous and the chemistry of these complexes is evolving [13, 14]. These complexes in general are dimeric with a metal –metal bond and consequently diamagnetic, although they have d$^9$ (+1) and d$^7$ (+3) configurations respectively. Nevertheless a paramagnetic (µ = 2.57 BM) purple blue monomeric platinum(III) anion, [Pt(C$_6$Cl$_5$)$_4$]$^-$ [15] has been reported which has an unpaired electron. Tetravalent palladium and platinum complexes are now fairly well investigated and in general adopt regular to distorted octahedral configuration [16, 17]. The palladium(IV) complexes are less stable than the corresponding platinum(IV) derivatives and are readily
reduced to palladium(II). Only platinum shows +5 (e.g. PtF₅) and +6 (e.g. PtF₆) oxidation states, but these are very reactive and highly unstable.

**Table 2**: Stereochemistry of platinum and palladium complexes in various oxidation states and coordination numbers of the metal ion

<table>
<thead>
<tr>
<th>Oxidation state</th>
<th>C. No.</th>
<th>Geometry</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2</td>
<td>Linear</td>
<td>[Pt(PPh₃)₂], K₂[Pd(C=CR)₂][2]</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>Trigonal planar</td>
<td>[Pd(PPh₃)₃], [Pt(SO₂)(PCy₃)₂]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Distorted planar</td>
<td>[PtX(PPh₃)₂] (X = O₂, C₂H₄, CS₂)[2]</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>Tetrahedral</td>
<td>[Pt(PF₃)₄], [Pt(CO)(PPh₃)]</td>
</tr>
<tr>
<td>I</td>
<td>4</td>
<td>Square planar</td>
<td>[M₂X₂(μ-dppm)₂] [18]</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>Trigonal bipyramidal</td>
<td>[Pt₃(SnCl₃)₂(C₈H₁₂)₂][19]</td>
</tr>
<tr>
<td>II</td>
<td>3</td>
<td>T-shaped</td>
<td>[Pd(Br)(Ph)(P'tBu₃)] [20]</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>Tetrahedral</td>
<td>[Pd(EDM)₂]I₂ (EDM = N, N’ ethylene dimorpholine)</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>Square planar</td>
<td>All authenticated four coordinated complexes</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>Trigonal bipyramidal</td>
<td>[Pt(SnCl₃)₃]³⁻, [Pd(QAs)I]⁺</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Square pyramidal</td>
<td>[Pd(Me₄[14]aneP₄)Br₂·6H₂O,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Distorted square-pyramid</td>
<td>[PtMeCl(AsMe₃)₂(CF₃C≡CCF₃)][11]</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>Octahedral</td>
<td>[Pt(η⁵-C₅H₅)Me₃]</td>
</tr>
<tr>
<td>III</td>
<td>4</td>
<td>Square planar</td>
<td>[Pt(C₆Cl₃)₄]⁺ [15]</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>Octahedral</td>
<td>K₂[Pt₂(SO₄)₄(H₂O)₂][22]</td>
</tr>
<tr>
<td>IV</td>
<td>6</td>
<td>Octahedral</td>
<td>[PtL₆]²⁻; L = X, SCN; [PtMe₃]I</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>Piano-stool</td>
<td>[Pt(η⁵-C₅H₅)Me₃]</td>
</tr>
<tr>
<td>V</td>
<td>6</td>
<td>Octahedral</td>
<td>[PtF₆]⁻</td>
</tr>
<tr>
<td>VI</td>
<td>6</td>
<td>Octahedral</td>
<td>[PtF₆]</td>
</tr>
</tbody>
</table>
1.2 A brief coverage on palladium and platinum complexes

The chemistry of palladium and platinum has been covered in several books, monographs and review articles [2, 3, 22-30]. One of the most important classes of reactions in palladium and platinum compounds is oxidative addition reaction where the formal oxidation state of coordinatively unsaturated complex in relatively low oxidation state is increased by two units (loss of two electrons) along with its coordination number. The reverse order of this mechanistic path is categorized as a reductive elimination. In general, the mechanism of an oxidative addition reaction proceeds via three pathways depending on the nature of substrate which are as follows:

(I) Concerted mechanism (generally for non-polar substrate)

(II) Nucleophilic displacement (generally for polar substrate)

(III) Radical mechanism (both polar and nonpolar)
Gonzales, et al. have presented a possible mechanism of an oxidative addition reaction of diaryl dichalcogenides to platinum(0) and palladium(0) precursors (Scheme 2) [31].

\[
\begin{align*}
\text{ER} &- \text{ER} \\
\text{R'}_3\text{P} - \text{M} &\quad \text{PR'}_3
\end{align*}
\]

**Reactants**

\[
\begin{align*}
\text{ER} &- \text{ER} \\
\text{R'}_3\text{P} - \text{M} &\quad \text{PR'}_3
\end{align*}
\]

**Intermediates**

\[
\begin{align*}
\text{ER} &- \text{ER} \\
\text{R'}_3\text{P} - \text{M} &\quad \text{PR'}_3
\end{align*}
\]

**Transition State**

\[
\begin{align*}
\text{ER} &- \text{ER} \\
\text{R'}_3\text{P} - \text{M} &\quad \text{PR'}_3
\end{align*}
\]

**Dimer**

\[
\begin{align*}
\text{ER} &- \text{ER} \\
\text{R'}_3\text{P} - \text{M} &\quad \text{PR'}_3
\end{align*}
\]

**Product 1**

\[
\begin{align*}
\text{ER} &- \text{ER} \\
\text{R'}_3\text{P} - \text{M} &\quad \text{PR'}_3
\end{align*}
\]

**Product**

\[
\begin{align*}
\text{ER} &- \text{ER} \\
\text{R'}_3\text{P} - \text{M} &\quad \text{PR'}_3
\end{align*}
\]

**Scheme 2**: Mechanistic path of an oxidative addition reaction

Platinum and palladium(II) complexes have been extensively employed to study substitution reactions in square planar complexes. The substitution reactions of platinum(II) complexes generally proceed at a slow rate. On the other hand palladium complexes react about \(10^5\) times faster than platinum complexes. Substitution of ligand by another one may precede by two possible ways, viz. (i) nucleophilic substitution (ii) electrophilic substitution. Ligand substitution reaction of square planar complex occurs with stereospecific mode (retention of configuration). The rate and mode of substitution is primarily governed by trans effect of non labile ligand in square planar complexes [2]. In this point of view several definitions have been
proposed and finally a conference on trans effect held in Russia defined it as “In compounds with square planar structure, the rate of substitution of an atom or molecule linked to central atom is determined by nature of substituent at the opposite end of diagonal. Thus stability of bond between this (central atom) and any substituent is little effected by character of neighboring atom or molecules, but is greatly influenced by those more distant, in trans position, on diagonal of the square” [32]. The approximate order of decreasing trans effect is [32, 33]: CO > CN⁻ > C₂H₄ > PR₃ > H > CH₃ > SC(NH₂)₂ > C₆H₅ > NO₂⁻ > I > SCN⁻ > Br > Cl > py > NH₃ > OH⁻ > H₂O.

The square planar complexes of palladium(II) and platinum(II) exhibit cis-trans-isomerism. Palladium(II) complexes generally form only one isomer since they are labile enough to yield only thermodynamically stable isomer under the chosen condition whereas both the isomers can be isolated for platinum. The trans isomer is thermodynamically more stable due to increase in entropy which accompanies isomerization of cis to trans isomer. However, heat of formation of cis isomer is more when π-bonding ligand is present because in cis configuration ligands do not share back-donation of electron density from the same metal d-orbital.

Platinum group metals can bind to a variety of ligands and form complexes with different nuclearity. Chemistry of platinum group metal complexes with the ligands containing donor atoms such as carbon, nitrogen, phosphorus, sulfur and selenium and chlorine relevant to present work is briefly described below:

**Phosphine complexes**

Phosphine ligands have played a crucial role in the progress of platinum and palladium organometallic chemistry due to their ability to form stable complexes with both metals. Phosphorus forms not only strong σ bonds but also capable of accepting back donation of electron density from metal through π bonds possibly due to the empty d-orbitals of phosphorus.
The π electron accepting nature of phosphine ligands is also useful to stabilize other heavier chalcogen atom (Se, Te) attached to metal centre.

One of the factors governing the nuclearity (low or high) of the resultant products is the steric demand of the ligand. The "natural bite angle" (βn) of a chelating ligand is defined as the preferred chelation angle determined only by ligand backbone constraints and not by metal valence angles [34]. It was defined with respect to metal phosphine complexes. The P–M–P angle found in transition metal complexes is a compromise between the ligand’s preferred bite angle and the one preferred by the metal centre [35-37]. Ligand bite angle is determined either through single crystal X-ray diffraction or alternatively through molecular modelling studies.

Two different effects, both related to the effect of bite angle in catalytic reactions are observed [38]. The first one, called steric bite angle effect is related to the steric interactions (ligand–ligand or ligand–substrate) generated when the bite angle is modified by changing the backbone and keeping the substituents at the phosphorus donor atom the same. The resulting steric interactions modified the activity and selectivity of the catalytic system. The second one, the electronic bite angle effect is associated with electronic changes in the catalytic centre when changing the bite angle [39]. It can be described as an orbital effect, because the bite angle determines metal hybridisation and as a consequence metal orbital energies and reactivity.

Mono-nuclear dihalide complexes of the composition, [MX2(PR3)2] (X = Cl, Br, I) are formed via intermediate ionic complexes, ([Pt(PR3)4][PtX4]) when solutions of [MX4]2− are treated with two equivalents of tertiary phosphine. The platinum complexes exist in cis and trans forms which can be separated by fractional recrystallization whereas only the trans isomer is isolated for palladium. The mechanism of cis-trans isomerization generally involves consecutive displacement of X with PR3. The process is accelerated by addition of PR3 [40]. The trans-
[MCl₂(PR₃)₂] reacts with alcoholic potassium hydroxide to give hydrido-platinum(II) complex \( \text{trans-}[\text{Pt}(\text{H})(\text{Cl})(\text{PPh}_3)_2] \) [41], whereas cis-\([\text{PtCl}_2(\text{PPh}_3)_2]\) under the same reaction conditions with excess of triphenyl phosphine leads to the formation of zerovalent complexes \([\text{Pt}(\text{PPh}_3)_n]\), where \( n = 3, 4 \) [42]. However, in case of tertiary phosphine complexes of palladium(II) an excess of strong alkali decomposes the former to palladium metal [43].

Palladium(II) and platinum(II) precursors (e.g., \( \text{K}_2[\text{PtCl}_4], \text{Na}_2[\text{PdCl}_4], [\text{PdCl}_2(\text{PhCN})_2] \)) reacts with chelating phosphine ligands to form complexes of the type, \( \text{cis-}[\text{MX}_2\{\text{Ph}_2\text{P(CH}_2)_n\text{PPh}_2\}]_n \). The resulting platinum(II) complexes are either monomeric (when \( n = 1 \) or 2), dimeric (when \( n = 3 \)) or trimeric (when \( n = 4 \)) depending on alkyl group chain length of the chelating phosphine, \( \text{Ph}_2\text{P(CH}_2)_n\text{PPh}_2 \) [44]. The chloro bridged complexes, \([\text{M}_2\text{Cl}_2(\mu-\text{Cl})_2(\text{PR}_3)_2]\), are prepared by heating the mononuclear complex \( \text{MCl}_2(\text{PR}_3)_2 \) with \( \text{MCl}_2 \) either in the absence [45] or in the presence [46-48] of an appropriate high boiling solvent. Jain et al. employed this method for the preparation of hetero-bimetallic complexes \([\text{MM'}\text{Cl}_2(\mu-\text{Cl})_2(\text{PR}_3)_2]\) [49]. The chloro bridged complexes are often isolated as sym- \( \text{trans} \) isomers whereas its analogous organometallic derivatives, \([\text{M}_2\text{R}_2(\mu-\text{Cl})_2(\text{PR}_3)_2]\) are isolated as a mixture of \( \text{cis} \) and \( \text{trans} \) isomers [50-52]. The isomerization is rapid for palladium complexes at room temperature.

### 1.3 Organochalcogen ligands

Chalcogen family comprises of elements of Group 16, viz. oxygen, sulfur, selenium, tellurium, radioactive polonium and synthetic element ununhexium. The compounds of a chalcogen with a more electropositive element are referred as chalcogenides and the latter term is generally reserved for sulfides, selenides and tellurides rather than oxides. Chemistry of thio and seleno ligand is well explored while due to higher reactivity, air sensitivity and diffusive sets of
orbitals make tellurium complexes highly unstable and uncharted. Tellurium chemistry has attracted considerable interest in recent years [53-58].

Metalloid nature of tellurium makes it to act as both Lewis acid as well as Lewis base, depending on reacting substrate [59-62]. Recently, extensive work has been done on various organo-selenium and -tellurium ligand system by Singh and his group. They elucidated that internally chelated organo-selenium and -tellurium compounds show interactions between chalcogen atom and other hetero atoms such as N or O [63-66]. These interactions play an important role not only in the catalytic antioxidant activity of these compounds but also in their application as reagents in synthetic organic chemistry [67-71]. In asymmetric synthesis, these interactions play a crucial role in chirality transfer [72, 73]. The application of intramolecular coordination has been extended to the synthesis of novel organochalcogen ligands containing both ‘hard’ and ‘soft’ donor atoms [73]. Various organoselenium compounds developed by different groups as antioxidants are shown in Scheme 3.

![Scheme 3: Organoselenium compound as antioxidants](image)

\[
\text{(I)} \quad \text{R} = \text{H, Me, Et, Pr} \\
\text{R'} = \text{Me, Ey, Pr} \\
\text{R, R'} = \text{Me or C-H}_x
\]

\[
\text{(II)}
\]

\[
\text{(III)}
\]

\[
\text{(IV)} \quad \left( \text{HOOC} - \text{Se} \right)_2
\]

\[
\text{(V)} \quad \text{HO} - \text{OH}
\]
In midst of several oragoselenium and tellurium ligand, hemilabile organochalcogenolate ligands have been a subject of considerable interest due to their rich coordination chemistry. The coordination potentiality of heterocyclic chalcogenonones (thiones, selenones, telluronones) especially those possessing α-N-hetero atom as well as their corresponding anions, referred to as chalcogenolates, are immense [74, 75]. There is indeed a considerable versatility in the coordination modes of these molecules which may include monodentate binding through E (I) or through N(II), bridging through a single E (III), bridging through both E and N (IV) or chelating via the E-to-N backbone (VI) (Scheme 4). All these modes either alone or in combinations (V, VII) have been observed or assigned on the basis of spectroscopic and/or crystallographic evidence of both homo- and hetero-leptic metal complexes.

**Scheme 4**: Versatile coordination modes in pyridylchalcogen ligand

**Hydrochalcogenide** (H$_2$E, REH, HE$^-$)

Complexes of palladium and platinum containing H$_2$E are rare because H$_2$E react with compounds of divalent metals to form precipitate of metal sulfides/ selenides [76].

**Chalcogenides** (E$^{2-}$, E$_n$$^{2-}$)

The chemistry of sulfide (S$^{2-}$) is much more developed than selenide (Se$^{2-}$) and telluride (Te$^{2-}$) ligands [77]. In most of the cases, E$^{2-}$ acts as bridging ligand and the increasing order of chalcogen tendency to act as a bridging ligand is S < Se << Te which is due to the diffusive nature of the orbital on moving from S to Te. Hence, the two sets of electron lone pair would be available easily for further reaction and thus the resulting in palladium and platinum clusters or
polymers. For instance the clusters of the type, $[M_3(\mu-E)_2(dppe)_3]^{2+}$ ($M = Pd, Pt; E = S, Se, Te$) [79] and $[Pd_5(\mu-Te)_4(dppe)_4]^{2+}$ [80] were synthesized (Table 3) by the reaction of Pd(NO$_3$)$_2$ with P$^\infty$P, NaEH and NaBPh$_4$ in acetonitrile solution. The chemistry of polychalcogenide ion has been reviewed by Ansari and Ibers [81].

**Chalcogenolates (RE$^-$)**

The chemistry of platinum group metal thio- and selenolate complexes is well developed [82, 83]. The platinum group chalcogenolate complexes on keeping for re-crystallization in halogenated solvents yielded polymers or clusters. For instance, a substitution reaction between Pd(II) phosphine precursors and sodium tellurolate yielded a mononuclear complex, which on stirring up to 6 h is converted in to trinuclear complexes $[Pd_3(\mu-Te)_2(dppe)_3]^{2+}$. To avoid polymerization internally functionalized ligands have been introduced such as 3-dimethylamino-1-propane thiolate [84, 85], 2-chalcogenopyridinates [86-87], phosphorus-sulfur donor ligands [88-90]. Jain and coworkers have developed an extensive chemistry based on Me$_2$NCH$_2$CH$_2$E$^-$ and Me$_2$NCH$_2$CH$_2$CH$_2$E$^-$ (E = S, Se, Te) ligands [91-99].

**Chalcenoethers (R$_2$E, RR$'$E, RE(CH$_2$)$_n$ER)**

A number of review articles dealing with mono-, bi- and poly- and hybrid seleno- and telluro-ethers have been published [100-104]. Cyclic complexes like $[Pd_2Cl_2(\mu$-MeSe)$_2$][(MeSe(C$_4$H$_3$O)$_2$)CMe$_2$], $[Pd_2Cl_4([24]$aneSe$_6)]$(BF$_4$)$_2$ and $[Pd([16]$aneSe$_4)]$(BF$_4$)$_2$ [105-108] have been reported which are synthesized by the addition of MCl$_2$ ($M = Pd$ or Pt), cyclic diselenoether [8]$aneSe_2$ and TlPF$_6$ in acetonitrile solution. Platinum(IV) complexes of the type, $[[PtMe_3I]_2${4-MeOC$_6$H$_4$Te$_2$CH$_2$}], $[PtMe_3I(PhTeCH$_2$TePh)]$ and $[PtMe_3I(PhTeCH$_2$TePh)$_2$] [109] have been synthesized. These complexes contain bridging, chelating and monodentate
ditelluro ether ligands, respectively. A series of platinum complexes $[\text{PtMe}_3X\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{ER}\}]$ (ER = SBu$^t$, SC$_6$H$_4$Me, SPh, SePh, TePh; X = Cl, Br, I) have also been synthesized by Jain, et.al. [110, 111].

**Diorgano-dichalcogenides ($R_2E_2$)**

The coordination chemistry of several diorgano-disulfides and –diselenides are of considerable interest for quite some time [112]. Oxidative addition of these ligands to platinum(0) complexes such as $[\text{Pt}(\text{PPh}_3)_4]$ or $[\text{Pt}(\text{PPh}_3)_2(\text{olefin})]$ yields mononuclear $[\text{Pt}(\text{ER})_2(\text{PPh}_3)_2]$ [113-117] while similar reactions with palladium(0) derivatives (e.g., $[\text{Pd}(\text{PPh}_3)_4]$, $\text{Pd}_2(\text{dba})_3/\text{PR}'_3$) result in the formation of dinuclear complexes $[\text{Pd}_2(\mu-\text{ER})_2(\text{ER})_2(\text{PR}'_3)_2]$ (E = S or Se) [112, 115, 117, 118]. In contrast to disulfides and diselenides, several complexes have been isolated in case of diorgano ditellurides [117, 119, 120].

Addition of E–H (Scheme 5) and E–E (Scheme 6) bond to alkynes is an important reactions in organic synthesis employed for the preparation of a variety of allyl and vinyl chalcogenides which find numerous applications. Non-catalytic addition yields a mixture of Z- and E- isomers, thus posing problem for their separation and purification. However the catalytic process not only yields one isomeric form, but also proceeds with 100% atom efficiency. Palladium(0) phosphine complexes have been successfully employed as catalyst. The active catalytic species is believed to be a Pd(II) chalcogenolate with a cis configuration. The reactions proceeds cleanly with E = S, Se, but with E = Te, a complex mixture of unidentified products is formed.
Scheme 5

Catalytic

E = S or Se

Δ or hv

R\equiv CH + Ar-E-E-Ar

Z-isomer

E-isomer

Scheme 6

hv (base)

non-catalytic

R\equiv CH + Ar-EH

Markovnikov-type addition

E = S or Se
**Table 3:** Palladium(II) and platinum(II) complexes of various chalcogen ligands

<table>
<thead>
<tr>
<th>Ligand</th>
<th>S</th>
<th>Se</th>
<th>Te</th>
</tr>
</thead>
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<td>[Pt(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;H(SeH)]</td>
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1.4 Application of platinum group metal chalcogen complexes

1.4.1 Anticancer Drugs

The interest in platinum-based anti tumour drugs has its origin in the 1960s, with Rosenberg’s path-breaking discovery of the inhibition of cell division by cis-diamminedichloroplatinum (\(\text{cis-}[\text{PtCl}_2(\text{NH}_3)_2]\)) and cis-diamminetetrachloroplatinum (\(\text{cis-}[\text{PtCl}_4(\text{NH}_3)_2]\)) (Scheme 7) [121]. Further, it was identified that Pt compounds are only the prime cause for the inhibition of cancer cells [121, 122] and found possible application in cancer treatment [121, 123-126].

The success of \(\text{cis-}\)platin paved the way for the second and third generation platinum(II) drugs, carboplatin and oxaliplatin while platinum(IV) (Scheme 7) complex satraplatin has undergone for phase III trial recently and is awaiting FDA approval [127]. Despite severe toxicity like nephrotoxicity, neurotoxicity and emetogenesis, platinum drugs continue to play a crucial role in the treatment of cancer and are used in chemotherapeutic treatment of cancer patient throughout the world [128, 129]. The approved platinum compounds share some common structural features such as presence of two NLG (non leaving groups, typically nitrogen ligands) and two leaving groups, e.g. halides or carboxylates) in the \(\text{cis}\) position [130]. Such type of configuration in principle allows, bidentate configuration to adjacent nucleobases of the DNA double helix. In most of the cases, cytotoxic platinum complexes are considered as prodrugs and their activation is normal prerequisite for biological activity which is generally attained through release of one or more labile ligands.

The above observations have prompted scientists to establish the precise structure - activity -relationship for the anticancer platinum compounds that would be useful for the design of new active molecules. In this context, recently, Weigand, et. al. [131] have synthesized new
series of platinum complexes with cis-PtP_2S_2 pharmacophores (where P_2 refers to two monodentate or one bidentate phosphine ligand and S_2 is dithiolato ligand) which displayed significant anti proliferative properties specifically against A2780 human ovarian carcinoma cells.

Scheme 7: Schematic presentation of various anticancer drugs of different generation

1.4.2 Homogenous Catalysis

Both palladium and platinum complexes find extensive applications in homogenous catalysis [132-134]. They catalyse a variety of reactions such as oxidation of alkene and carbonyl group, amination, cyclisation and alkylation through transmetallation, etc. All these reactions are catalysed by various palladium complexes in Pd(0) and Pd(II) oxidation state. Depending upon the oxidation state of palladium, these reactions can be classified as presented in Scheme 8.
Cross coupling reactions

An important class of palladium catalysed reaction is C-C cross coupling reactions. The basic reaction was initially published by Miyaura and Suzuki in 1979 [135] using alkenyl boronates and alkenyl halides, but the ‘classic’ reaction of phenyl boronic acid and aryl halides was reported in 1981 [136].

Scheme 8: Schematic representation of palladium catalysed various organic reactions

This chemistry has been greatly extended and elaborated over the years [137]. In general catalytic cycle for the cross-coupling reaction of organometallics, involves oxidative addition-transmetalation-reductive elimination sequences. Although each step involves further knotty processes including ligand exchanges, there is no doubt about the presence of several boronic acid intermediate products. It is significant that the great majority of cross-coupling reactions are catalyzed by palladium(0) [138]. Understanding the properties of the Pd intermediates in the catalytic cycle has allowed the reactions to be applied to a wider range of substrates with
improved selectivity under milder conditions. Various palladium catalysed C-C coupling reactions are depicted in scheme 9.

**Scheme 9**: Palladium catalyzed C-C coupling reactions

**Oxidation of ketone**

Brunner and co-workers synthesized the trinuclear complex \([Pt_2Rh(\mu-3-S)\{(−)-diop\}_2(COD)]Cl\) (diop = \((4R,5R)-(−)-O\)-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)-butane; COD = cycloocta-1,5-diene) by the treatment of \([Rh(COD)Cl_2]\) with chiral “ligand” \([Pt_2(\mu-S)_2\{(−)-diop\}_2]\) (Scheme 10) [139]. The tri-nuclear complex was used
as a catalyst in the hydrosilylation of acetophenone with diphenylsilane and in the hydrogenation of ketopantolactone. Reaction with diphenylsilane in the presence of rhodium(I) catalyst is a well-known method for the reduction of prochiral ketones to the corresponding alcohols [140]. Addition of a Si-H bond to the carbonyl function of acetophenone affords the silylalkyl ether, the acidic hydrolysis of which leads to the chiral alcohol 1-phenylethanol. With the catalyst/substrate
ratio of 1:1000, the complex [Pt₂Rh(μ₃-S){(-)-diop}₂(COD)]Cl shows moderate catalytic activity giving the product 1-phenylethanol in 74-76% yield as a racemic mixture. In the hydrogenation of ketopantolactone reaction, the compound [Pt₂Rh(μ₃-S){(-)-diop}₂(COD)][Cl] gives a product yield of 14%-16% with a considerably higher enantioselectivity of 58-59% (Scheme 11).

![Scheme 11](image)

**Selective Alkylation**

Another platinum catalyst [Pt₂(μ-SMe₂)₂Me₄] [141] which is inspired by Crespo and Martinez [142], promotes stiochiometric C-F activation of a series of aryl imines. The Pt-F species could undergo transmetallation with an appropriate organometallic reagent and the subsequent reductive elimination would provide the functionalized product and regenerate the Pt(II) catalyst. The first example of Pt-catalyzed C-F cross-coupling was developed by Love and co-workers [143]. A series of polyfluoroaryl imines undergo selective C-F cross-coupling in the presence of Me₂Zn and obtain yield from 70% to 99%. The reaction is selective for ortho C-F activation with weaker aryl C-Br bonds (Scheme 12).
1.4.3 Luminiscent properties

The diplatinum(II) complex K₄[Pt₂(µ-P₂O₅H₂)₄], which is often referred to as "platinum pop", is prepared from K₂PtCl₄ and phosphorous acid [22, 144]. The Pt₂ complex has electronic absorption bands at 367 (log ε 4.54) and 435 nm (log ε 2.04) that are attributable to singlet and triplet (dσ* pσ) transitions, respectively [145, 146]. An unusual feature of the complex is that aqueous solutions show an intense green emission at 514 nm at ambient temperature. This phosphorescence at 514 nm (T ≈ 9 ps) from a triplet excited state is accompanied by a shorter lived fluorescence (8-40 ps) at 407 nm. Depending on the photo-luminescence property, two applications of Pt₂ have been suggested. One is in the trace detection of platinum. A second possible use is in the fabrication of luminescent solar concentrators [147].

Owing to good photoluminescence property of Pt₂ complexes, the luminescence studies of platinum-chalcogen complexes have also attracted considerable interested. Yam and co-workers [148, 149] had synthesized platinum binuclear complex [Pt₂(µ-S)₂(dppy)₄] (dppy = Ph₂Ppy). The electronic absorption of the latter complex shows low-energy band at 350-425 nm.
region, and long-lived excitation luminescence at ~ 630 nm at 77K. Compared to [PtCl₂(dppy)$_2$], [Pt$_2$(µ-S)$_2$(dppy)$_4$] has an additional good σ-donating sulfido moiety, which may lead to ligand-to-metal charge transfer (LMCT) character from the newly emergent low-energy emitting state.

The heterometallic complexes from [Pt$_2$(µ-S)$_2$(dppy)$_4$] also show interesting luminescent properties. With additional supporting ligands from the nitrogen of dppy, [Pt$_2$(µ-S)$_2$(dppy)$_4$] reacts with Group 11 transition metal complexes, resulting in a series of interesting dimetallic and trimetallic products [148]. The chemistry also extends to the selenium analogue, [Pt$_2$(µ-Se)$_2$(dppy)$_4$] [150], leading to similar results to [Pt$_2$(µ-S)$_2$(dppy)$_4$] (Scheme 13)

![Scheme 13]

Scheme 13
Luminescence data of the products indicates that the origin of the low-energy transitions does not lie in dppy intraligand (IL) nor in metal-to-ligand charge transfer (Pt → dppy, MLCT), but is based on the sulfido moiety to platinum charge transfer (LMCT). The additional band at 560 nm suggests that it could arise from M-S or M-Pt charge transfer. An assignment of a ligand-to-ligand charge transfer (LLCT) [X2 → dppy] transition could also give rise to the observed trend. In conclusion, the emission is likely to be LMCT in majority, with some involvement of a LLCT character.

1.4.4 Metallophilic ligand

The metalloligands, [Pt2(µ-S)2(P-P)2] [P-P = 2PPh3, 2dppy, dppp, dppf, 2PMe2Ph] show powerful Lewis basicity towards p-, d- and f- block, hard and soft metals, as well as late and early transition metals. Therefore, they are among the best known building blocks of homo-, hetero- and inter-metallic sulfide aggregates [148, 150-158]. The first homometallic aggregate, [Pt3(µ3-S)2(PMe2Ph)]Cl2, could be isolated from derivatization of the complex [Pt2(µ-S)2(PMe2Ph)2] only after the synthesis of a series of heterometallic aggregates of general formula [{Pt2(µ-S)2(PPh3)4}xMLy]n+ by Mingos and co-workers which is based on the concept of Lewis acid-base reactions with a variety of transition metal fragments. Synthetic utility of [Pt2(µ-S)2(P-P)2] can be ascribed to the high nucleophilicity and adjustable orientations of the sulfide lone pairs, making it a powerful Lewis base that is capable of supporting a wide range of coordination geometries of the heterometals. Furthermore, the sulfido ligand is inherently capable of forming relatively strong bonds with most of the transition metals. The nuclearity of these aggregates and the coordination modes of their sulfur centers are determined largely by the local geometry of the metal (scheme 14). Many geometries have been identified, such as linear, [156, 159-160],
angular [161], T-shaped [159], Y-shaped [162], tetrahedral [163-170], square planar [157, 163, 164], square pyramidal, distorted trigonal prismatic [171], trigonal bipyrimidal [172], hexagonal bipyrimidal, “piano stool” [173] and others [148, 149]. The metal center usually anchors on both sulfide centers and only one of them leading to the formation of \(\{\text{Pt}_2\text{S}_2\text{M'}\} \) or \(\{\text{Pt}_2\text{S}_2\text{M'}_2\} \) cores. The metal centers in these aggregates include the p-block and almost the entire range of the d-block elements, as well as an actinide element. The Lewis basic \(\{\text{Pt}_2(\mu-S)_2\} \) core can combine with most Lewis acidic metal complexes to give mixed-metal materials as well as multinuclear homo-platinum complexes [169, 174].

Scheme 14
1.5 Scope of Work

The above discussion of palladium and platinum chemistry clearly reflects that there are various active areas of research and their chemistry has many promising trends for further research. The chemistry of palladium and platinum complexes with tellurium ligands is evolving. The reactions of metal(0) with tellurium compounds, which would have relevance in catalysis and in material science, would be of interest. To understand the reactivity pattern of organochalcogen, it would be appropriate to cover all the three chalcogen (S, Se, Te) ligands. Since the reactions with simple organotellurium ligands often lead to the formation of a mixture of uncharacterizable products, a hemilabile ligand, such as pyridyl/pyrimidyl based, would assist in stabilizing the complex through M–N coordination in solution. Thus with this strategy reactions of M(0) and M(II) with various N-heterocyclic chalcogen ligands have been investigated.

With this view a detailed study of palladium and platinum complexes with various N-heterocyclic chalcogen ligands has been carried out. All the complexes prepared during the present investigation have been characterized by elemental analyses, IR, NMR ({}^{1}H, {}^{13}C, {}^{31}P, {}^{77}Se, {}^{125}Te, {}^{195}Pt) spectroscopy. For clarity, the present work is sub-divided as follows:

- Chemistry of pyridyl and 3-methyl-2-pyridyltellurolate complexes of platinum.
- Chemistry of pyridyl and 3-methyl-2-pyridylthiolate, selenolate and tellurolate complexes of palladium.
- Chemistry of pyrimidylselenolate and tellurolate complexes of palladium and platinum.
- Chemistry of nicotinamide based organoselenolate complexes of palladium and platinum.
- Chemistry of arylchalcogenolate complexes of palladium and platinum.