ORGANOMETALLIC CHEMISTRY OF PLATINUM GROUP METAL CHALCOGENOLATES: SYNTHESIS, STRUCTURE AND SPECTROSCOPY

By

Rohit Singh Chauhan

BHABHA ATOMIC RESEARCH CENTRE

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Date:

Guide: Dr. V. K. Jain 8/2/2013

Date: 8/2/2013

Co-guide Dr. S. Kannan 8/2/13

Date: 8/02/2013

Member 1: Dr. S. K. Ghosh Ghosh

Date: 08/02/2013

Member 2: Dr. (Smt.) S. Banerjee Sharmila Banerjee

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DECLARATION

I, hereby declare that the investigations presented in thisThesis has been carried out by me. The work is original and has not been submitted earlier in whole or part for a degree / diploma to this or any other Institution / University.

Rohit Singh

(Rohit Singh Chauhan)

Dedicated to…………

My Mother

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Rohit Singh Chauhan

Abbreviations

PPh_3 = Triphenylphosphine

OAc = Acetate

dppm = bis(diphenylphosphino)methane

dppe = 1,2-bis(diphenylphosphino)ethane

dppp = 1,3-bis(diphenylphosphino)propane

E = sulfur, selenium, tellurium

X = Halogen

Mes = mesityl (2, 4, 6-trimethylphenyl)

Ph = Phenyl

py = Pyridyl

pym = Pyrimidyl

Th = thienyl (C_4H_3S)

Epy = pyridine-2-chalcogenolate

p-tol = 4-MeC_6H_4

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2.1. Materials and methods

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Synopsis

Organometallic chemistry of platinum group metal chalcogenolates: synthesis, structure and spectroscopy

The chemistry of platinum group metal complexes played a pivotal role in the advancement of organometallic and coordination chemistry [1, 2]. The interest in these complexes has grown with the advent of covalency concept which made it possible for the depiction of square planar geometry in palladium and platinum derivatives that in turn opened up the prospects of cis-trans isomerism followed by the discovery of trans effect [3]. The interest in these complexes has further accelerated with their applications in homogenous catalysis for the synthesis of organic compounds. For instance, Wacker process has been commercially used for the preparation of acetaldehyde by homogenous catalytic oxidation of ethylene in the presence of $PdCl_2$ and copper chloride as a co-catalyst [4, 5]. The role of platinum complexes like cisplatin, carboplatin as an anticancer drug is well known. The chemistry of platinum group metal complexes is of topical interest encompassing areas like catalysis, biology and materials science. Advancements in characterization techniques, like NMR and single crystal X-ray crystallography, have further boosted up the progress of work.

The chemistry of platinum group metal chalcogenolate complexes has been an active area of research for the past several decades. The sustained interest in these complexes can be attributed to their role as molecular tectons for the synthesis of high nuclearity complexes [6], precursors for low temperature synthesis of metal chalcogenides [7-8], catalysis in organic synthesis [9-10] and in biology.

The present dissertation is aimed to study oxidative addition reactions of various organochalcogen ligands to zero valent palladium and platinum phosphine precursors. The thesis is divided into four chapters, *viz.*, introduction, experimental, results and discussion and summary and conclusions, followed by references.

Chapter 1: Introduction

This chapter deals with a general introduction to the chemistry of palladium and platinum complexes with an emphasis on their phosphine precursors followed by a brief account on different types of organometallic reactions, e.g. oxidative addition reaction, exchange reaction, *etc.* Further, a short discussion on applications of platinum group metal chalcogenolate complexes in catalytic reactions and in materials science is included. A brief overview on complex chemistry of Se and Te ligands is also given which is followed by the scope and plan of the present work. Relevant literature references are given in bibliography at the end of the thesis.

Chapter 2: Experimental

In this chapter, materials and methods used during the present study are described followed by discussion on analytical and instrumental techniques, *e.g.* IR, UV-vis, NMR, elemental analysis, XPS, mass spectroscopy and X-ray crystallography used during the course of the present investigation. The synthesis of various organochalcogen ligands is discussed, followed by their reactions with palladium and platinum phosphine complexes.

Chapter 3: Results and discussion

The chapter deals with the results obtained during the present investigation and include significant discussion on these findings. The chapter is divided in to five sections. All the complexes have been characterized by elemental analysis, NMR (^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$, $^{77}Se\{^{1}H\}$, $^{125}Te\{^{1}H\}$ and $^{195}Pt\{^{1}H\}$) spectroscopy. In some cases, compounds have also been characterized by IR, UV-vis absorption and mass spectroscopy. The molecular structures of some representative complexes have been established by single crystal X-ray diffraction analyses.

The first **section 3.1** is divided in to two sub-sections. The section 3.1.1 covers the chemistry of non-chelated phosphine compounds of platinum with bis(2-pyridyl)ditellurides (scheme 1). Oxidative addition reactions of [Pt(PPh$_3$)$_4$] with {TeC$_5$H$_3$(3-R)N}$_2$ (R = H or Me) gave expected complexes, [Pt{TeC$_5$H$_3$(3-R)N}$_2$(PPh$_3$)$_2$] together with a small amount of a crystalline serendipitous products, [Pt{TeC$_5$H$_3$(3-R)N}$_2$Te(PPh$_3$)], containing bare tellurium (Te^0) coordinated to platinum(II). The above complexes can also be obtained by the reaction of [PtCl$_2$(PR'$_3$)$_2$] (PR'$_3$ = PPh$_3$ or PPh$_2$(2-py)) with two equivalents of NaTe-C$_5$H$_3$RN. The molecular structures of [Pt(C$_5$H$_4$N)$_2$Te(PPh$_3$)] (Figure 1) and [Pt{TeC$_5$H$_3$(3-Me)N}$_2$Te(PPh$_3$)] were unambiguously established by single crystal X-ray diffraction.

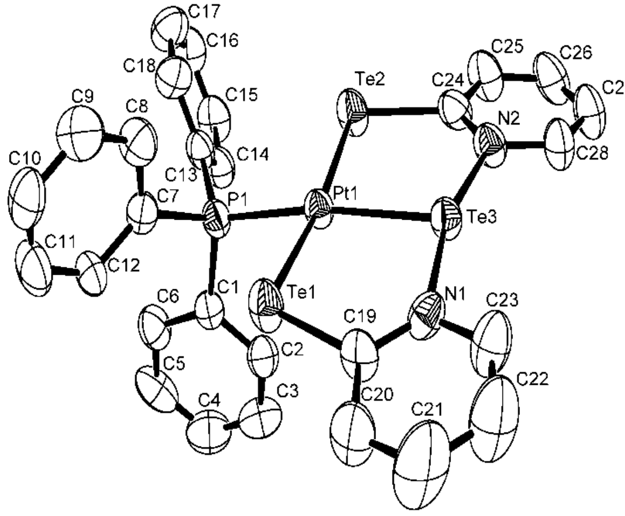
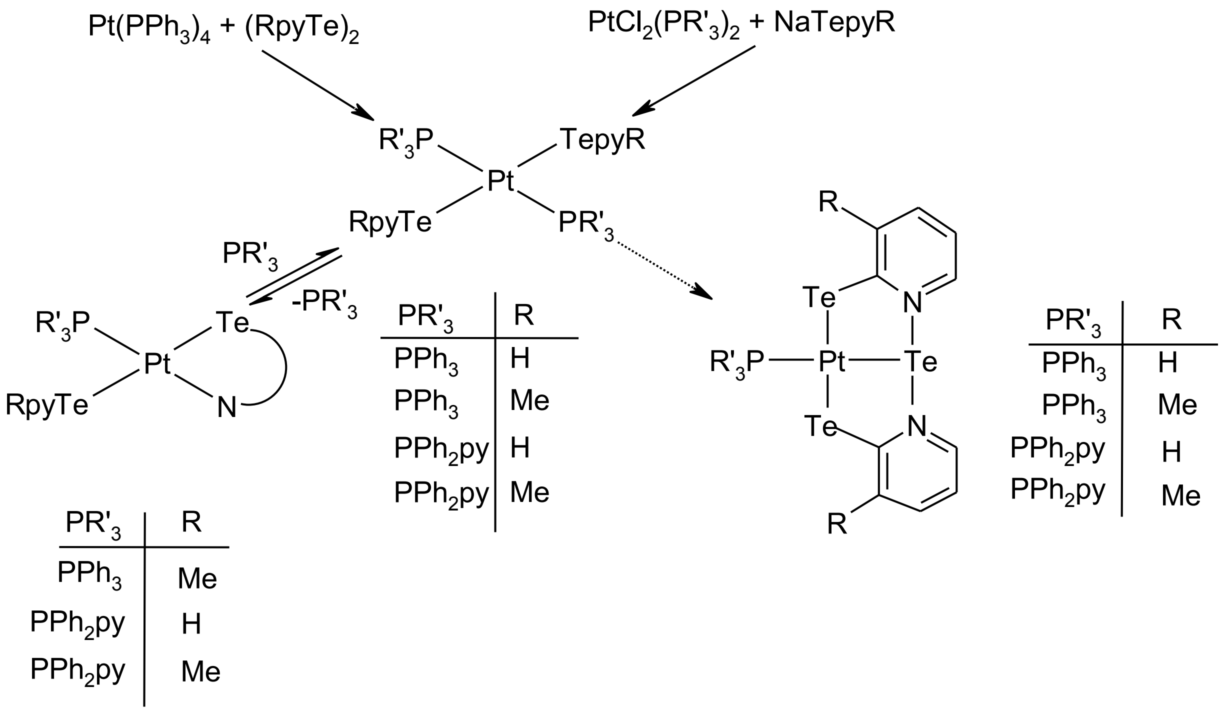
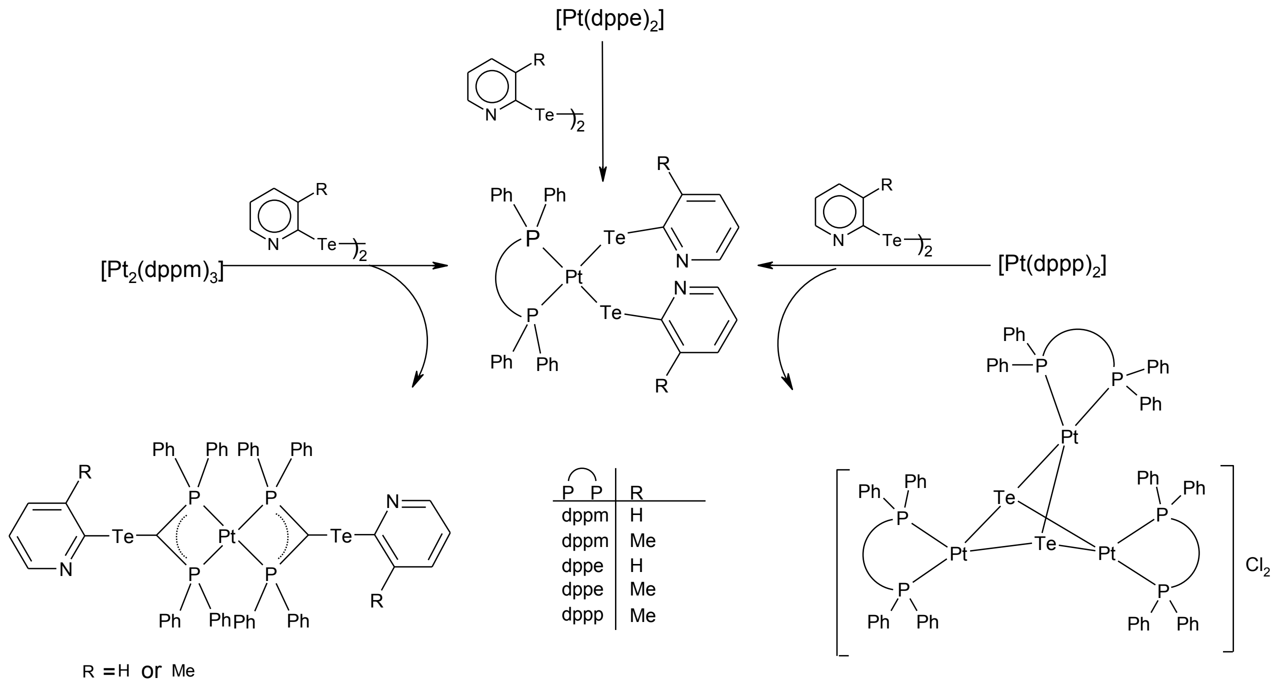


Figure 1: The molecular structure of [Pt(TeC$_5$H$_4$N)$_2$Te(PPh$_3$)].

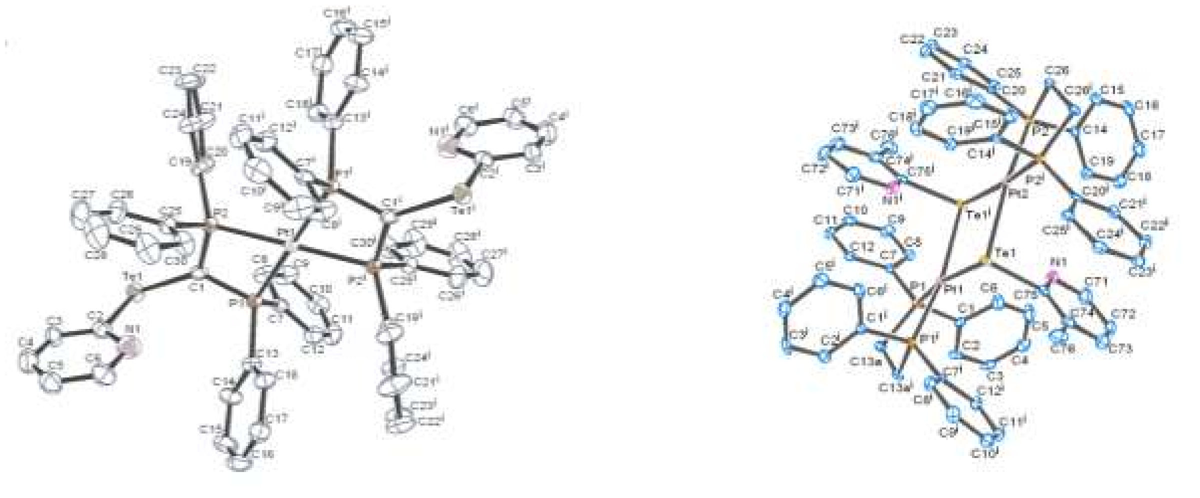


Scheme 1

The section **3.1.2** deals with oxidative addition and substitution reactions of platinum complexes containing chelating phosphine ligand with pyridyltellurolate ligands (Scheme 2). Various serendipitous products such as **[**$Pt\{PPh_2C(TeC_5H_3(3\text{-}R)N)PPh_2\}_2]$, $[Pt_2\{TeC_5H_3(3\text{-}Me)N\}_2(dppe)_2][BPh_4]_2$ and $[Pt_3Te_2(dppp)_3]^{2+}$ have been isolated depending on the nature of chelating phosphine and substituent in pyridyl ring. The complex $[Pt_3Te_2(dppp)_3]^{2+}$ has been analyzed through relativistic density functional calculations. The molecular structures of $[Pt\{Ph_2PC(TeC_5H_4N)PPh_3\}_2]$ and centrosymmertic complex $[Pt_2\{TeC_5H_3(3\text{-}Me)N\}_2(dppe)_2][BPh_4]_2$ (Figure 2) were determined by X-ray diffraction analyses.



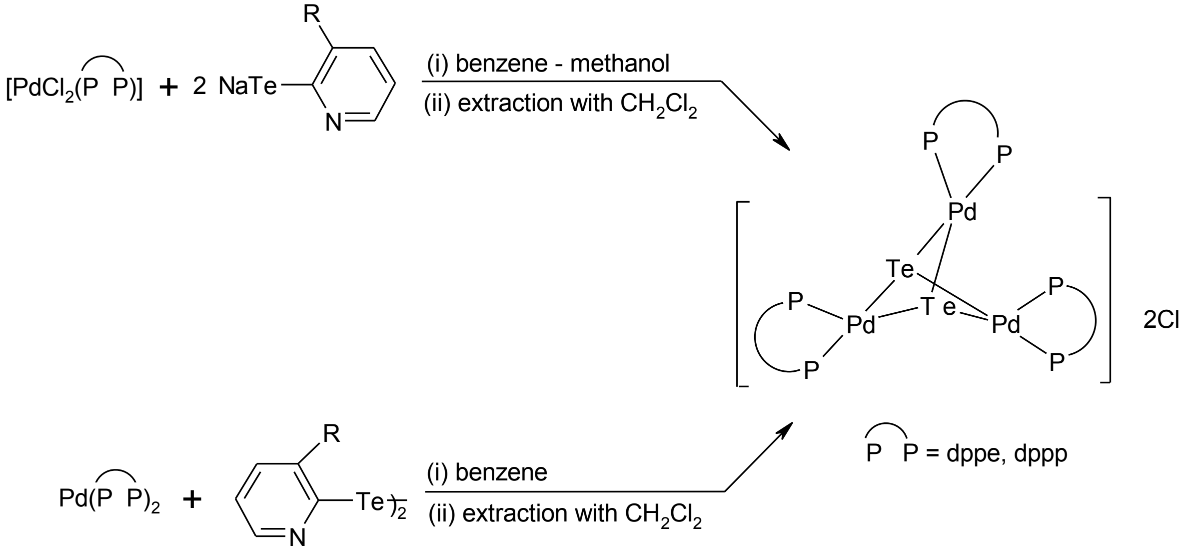
Scheme 2



a **b**

Figure 2: The crystal structures of a) [Pt{$Ph_2PC(TeC_5H_4N)PPh_3$}$_2$] and b) [Pt_2{TeC_5H_3(3-Me)N}$_2$(dppe)$_2$][BPh_4]$_2$.

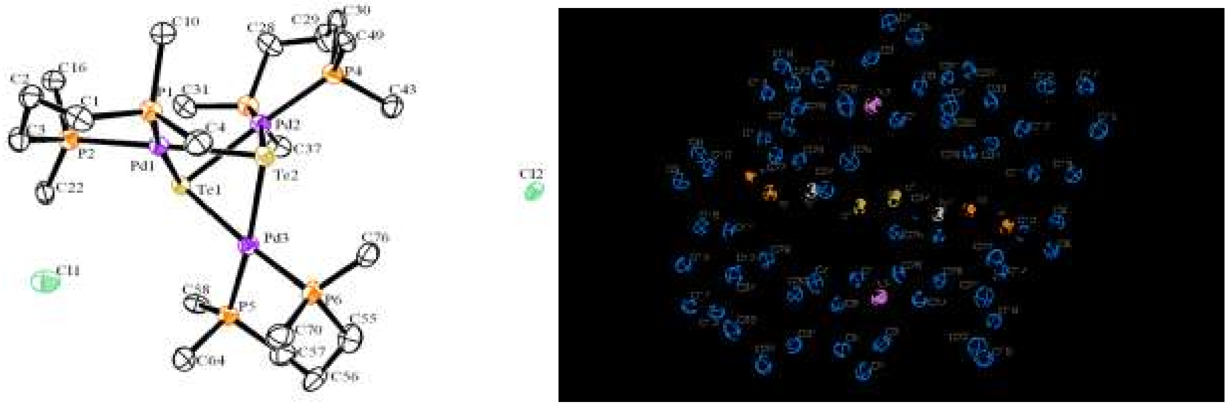
The section **3.2** describes the reactions of 2-chalcogenopyridine ligands with palladium(0) and palladium(II) precursors. These reactions afforded a variety of complexes depending on the nature of chalcogen atom, palladium precursor and the reaction conditions. The treatment of [$PdCl_2$(dppe)] with lead salts of 2-pyridinechalcogenolate gave mononuclear palladium complexes, [Pd{EC_5H_3(3-R)N}$_2$(dppe)] (E = S, Se, Te) as yellow-to-orange powder. Similar substitution reactions between [$PdCl_2$(dppe)] and $NaTeC_5H_3$(3-R)N, prepared by reductive cleavage of Te–Te bond of dipyridyl ditellurides by $NaBH_4$ in methanol, followed by extraction with CH_2Cl_2 gave a tellurido-bridged trinuclear palladium(II) complex, [Pd_3(μ-Te)$_2$(dppe)$_3$]Cl_2 (Scheme 3) as a red crystalline solid which was isolated in good yield. The latter complex can also be obtained by treatment of palladium(0) precursor, [Pd(dppe)$_2$] with dipyridyl ditellurides (Scheme 3). Interestingly, the corresponding reactions of dipyridyl diselenides with [Pd(dppe)$_2$] afforded oxidative addition products, [Pd{SeC_5H_3(3-R)N}$_2$(dppe)] (R = H or Me).



Scheme 3

Treatment of [$Pd(PPh_3)_4$] with dipyridyl ditellurides readily gave oxidative addition products, *trans*-[Pd{TeC_5H_3(3-R)N}$_2$(PPh_3)$_2$] (R = H or Me). The latter complex, when left in

$CDCl_3$ solution, afforded green crystals of a new derivative, $[PdCl\{Te(Cl)_2C_5H_3(3\text{-}Me)N\}(PPh_3)]$. The molecular structures of $[Pd_2\{\mu\text{-}TeC_5H_3(3\text{-}Me)N\}_2(dppp)_2]Cl_2.3H_2O$, $[Pd_3(\mu\text{-}Te)_2(dppp)_3]Cl_2.3CHCl_3$ (Figure 3) and $[PdCl\{2\text{-}Te(Cl)_2C_5H_3(3\text{-}Me)N\}(PPh_3)]$ were established by X-ray diffraction analyses.



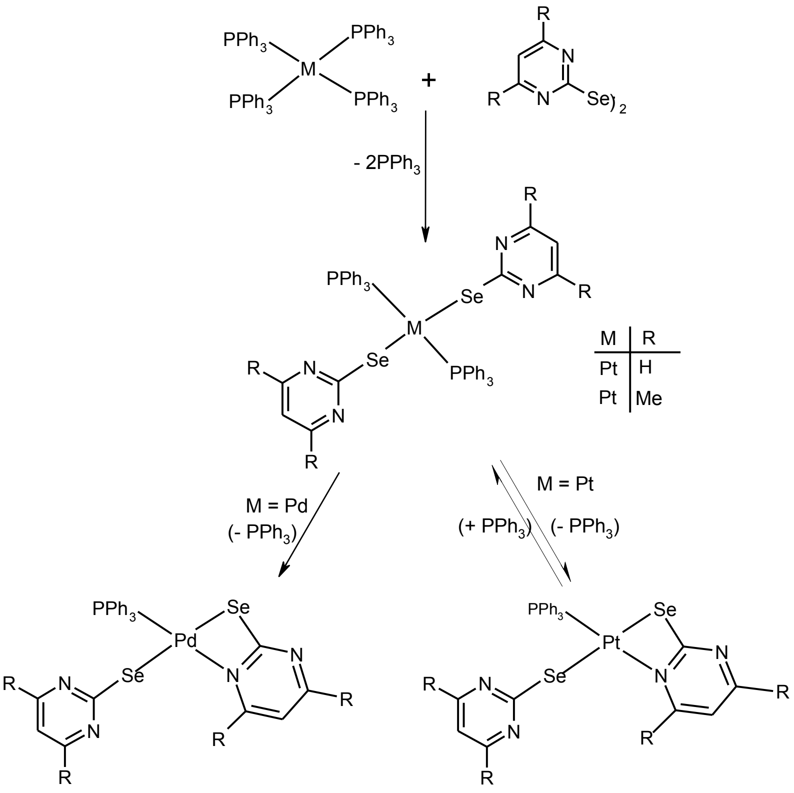
a **b**

Figure 3: The molecular structures of a) $[Pd_3(\mu\text{-}Te)_2(dppe)_3]Cl_2]$ and b) $[Pd_2\{\mu\text{-}TeC_5H_3(3\text{-}Me)N\}_2(dppp)_2]Cl_2$.

The section **3.3** deals with the oxidative addition reactions of dipyrimidyl diselenides, $\{SeC_4H(4,6\text{-}R)_2N_2\}_2$, with $[M(PPh_3)_4]$ (M = Pt or Pd). In these reactions complexes of composition, $[Pt\{SeC_4H(4,6\text{-}R)_2N_2\}_2(PPh_3)_2]$ and $[Pd\{SeC_4H(4,6\text{-}R)_2N_2\}\{\eta^2\text{-}SeC_4H(4,6\text{-}R)_2N_2\}(PPh_3)]$ (R = H or Me) were isolated. The former when left in solution dissociated to $[Pt\{SeC_4H(4,6\text{-}R)_2N_2\}\{\eta^2\text{-}SeC_4H(4,6\text{-}R)_2N_2\}(PPh_3)]$ and PPh_3 (Scheme 4). Treatment of $[PtCl_2(P^\frown P)]$ ($P^\frown P$ = dppe or dppp) with $NaEC_4H(4,6\text{-}R)_2N_2$ (for E/R = Se/H/Me or Te/Me) gave mono-nuclear complexes, $[Pt\{EC_4H(4,6\text{-}R)_2N_2\}_2(P^\frown P)]$ (R = H or Me, $P^\frown P$ = dppe or dppp) which on recrystallization in dichloromethane/$CDCl_3$ solution resulted in tri-nuclear chalcogenido-bridged complexes, $[Pt_3(\mu\text{-}E)_2(P^\frown P)_3].2Cl$ (E = Se or Te). The substitution reactions between $[PdCl_2(P^\frown P)]$ ($P^\frown P$ = dppe or dppp) and $NaEC_4H(4,6\text{-}R)_2N_2$ (E = Se or Te; R = H or Me) afforded chalcogenido-bridged tri-nuclear complexes, $[Pd_3(\mu\text{-}E)_2(P^\frown P)_3]2Cl$ ($P^\frown P$ = dppe or dppp).

The section **3.4** deals with oxidative addition reactions of nicotinyl based organoselenium compounds, $[2\text{-}NC_5H_3(3\text{-}COR)Se]_2$ (R = NH_2, NHPh, or NHpym (pym = pyrimidine)), with $[M(PPh_3)_4]$ (M = Pd, Pt) in benzene which yielded complexes of the type, $[M\{\eta^2\text{-}SeC_5H_3(3\text{-}COR)N\}\{SeC_5H_3(3\text{-}COR)N\}(PPh_3)]$ (M = Pt, Pd; R = NH_2, NHPh, or NHpym) while the similar reactions of $[M(PPh_3)_4]$ with $[2\text{-}NC_5H_3(3\text{-}CONHPh)SeI]$ initially gave the expected oxidative addition product, $[M(I)\{SeC_5H_3(3\text{-}CONHPh)N\}(PPh_3)_2]$ which loses a molecule of PPh_3 to give $[M(I)\{\eta^2\text{-}SeC_5H_3(3\text{-}CONHPh)N\}(PPh_3)]$. Both the complexes on prolong standing in dichloromethane gave several products such as $[Pt(I)_2(PPh_3)_2]$, $[Pt(I)\{C_5H_3(3\text{-}CONH_2)N\}(PPh_3)_2]$, $[M(I)(Ph)(PPh_3)_2]$ and $[2\text{-}NC_5H_3(3\text{-}CO)Se\text{-}NH]$ (Scheme 5). The molecular structures of $[Pt\{\eta^2\text{-}SeC_5H_3(3\text{-}CONH_2)N\}\{SeC_5H_3(3\text{-}CONH_2)N\}(PPh_3)]$, $[Pd\{\eta^2\text{-}SeC_5H_3(3\text{-}CONHPh)N\}\{SeC_5H_3(3\text{-}CONHPh)N\}(PPh_3)]$ (Figure 4) and $[Pt(I)(Ph)(PPh_3)_2]$, were established unambiguously by X-ray diffraction analyses.

The section **3.5** describes Substitution reactions between $[MCl_2(P^\frown P)]$ (M = Pt, Pd ; $P^\frown P$ = dppm, dppe, dppp) and various sodium arylchalcogenolates. These reactions yielded mononuclear complexes of composition, $[M\{2\text{-}EAr\}_2(P^\frown P)]$ (Ar = phenyl, tolyl, mesityl ; E = S,



Scheme 4

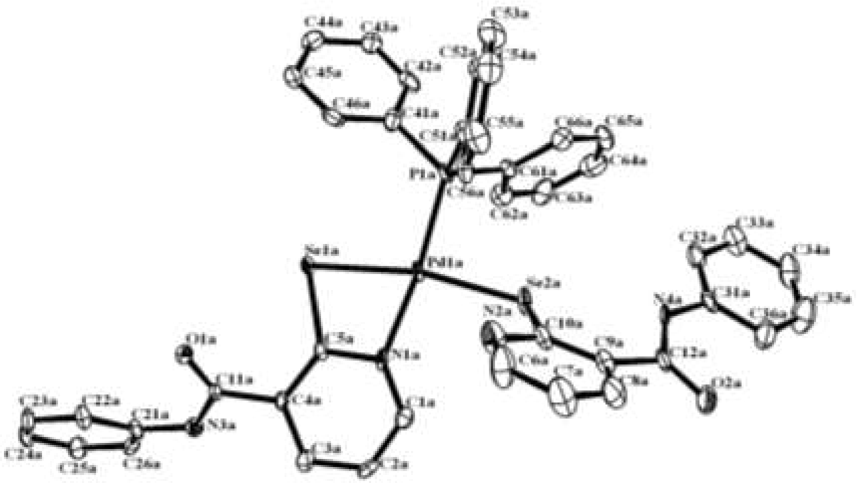
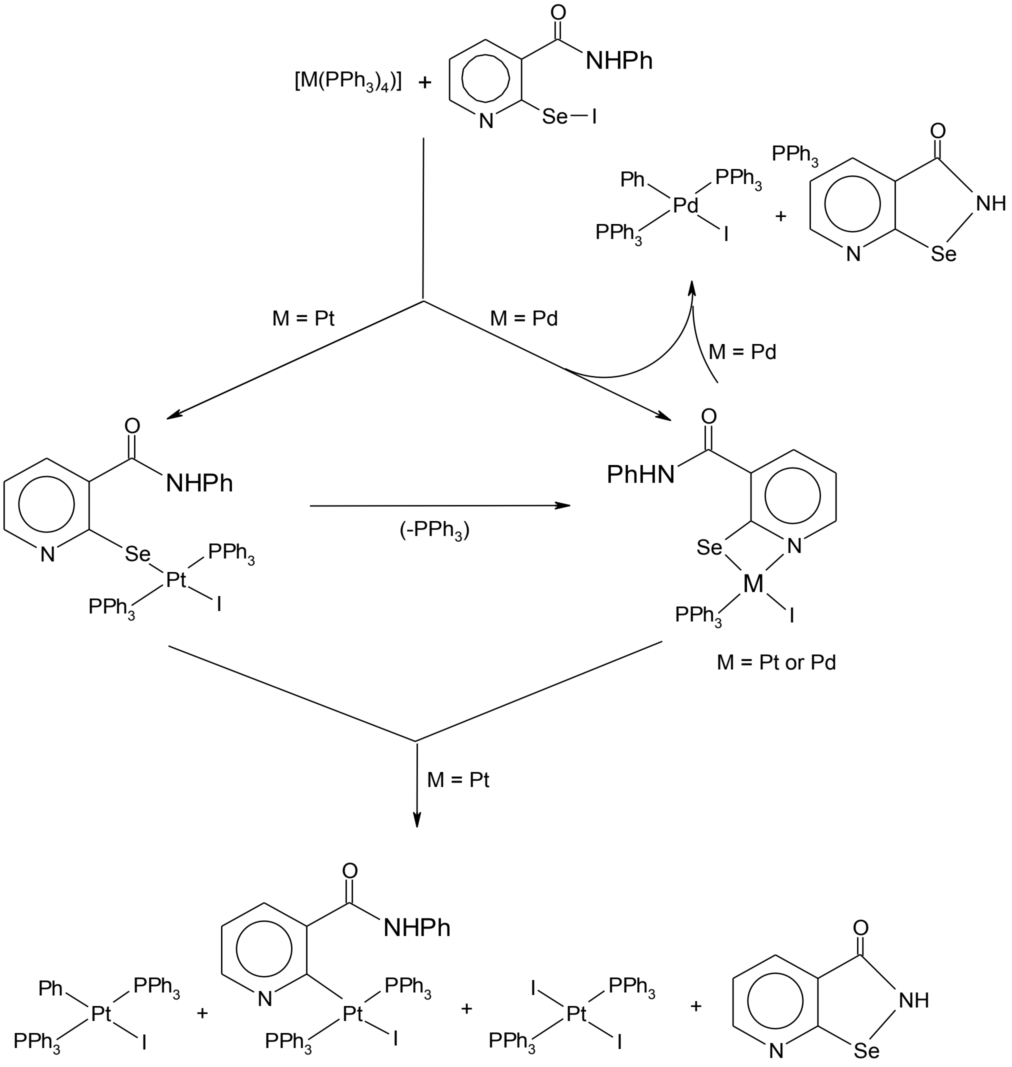


Figure 4: Crystal structure of $[Pd\{\eta^2\text{-}SeC_5H_3(3\text{-}CONHPh)N\}\{SeC_5H_3(3\text{-}CONHPh)N\}(PPh_3)]$.

Se or Te). A comparative study of NMR data has been made to examine bonding and structural features based on the nature of chelated phosphine ligand, chalcogen atom and aryl substituents. The molecular structures of [Pt(SeMes)$_2$(dppp)].C$_6$H$_6$ (Figure 5), [Pt(TeMes)$_2$(dppp)].2C$_6$H$_6$, [Pt(SeC$_5$H$_3$N$_2$)$_2$(dppm)], [Pt{SeC$_5$H(4,6-Me)N$_2$}$_2$(dppm)], and [Pd(SeMes)$_2$(dppe)].CHCl$_3$ were established by single crystal X-ray diffraction analyses.



Scheme 5

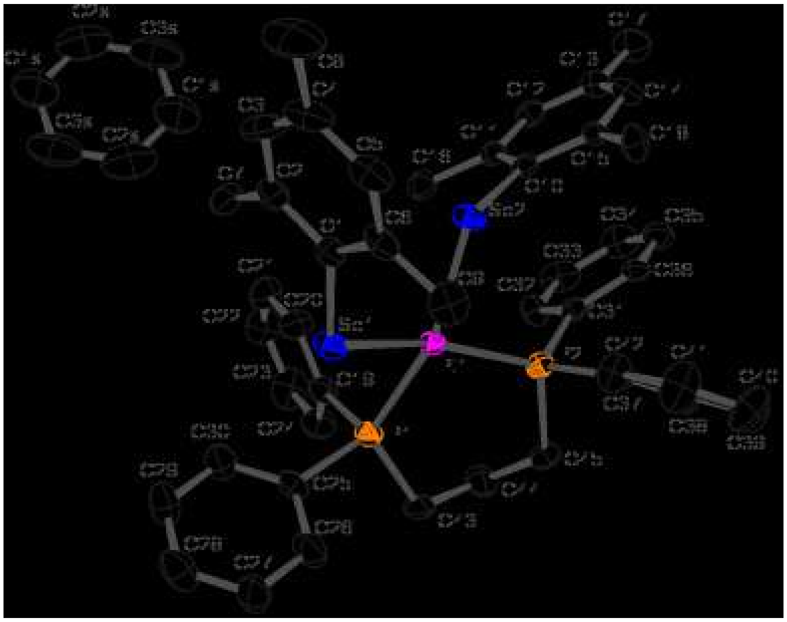


Figure 5: Crystal structure of $[Pt(SeMes)_2(dppp)].C_6H_6$.

Chapter 4: Summary and conclusions

This chapter contains summary and conclusions of the present investigation. The chemistry of 2-chalcogenpyridines with palladium and -platinum phosphine precursors yield a variety of complexes depending on the nature of the phosphine ligand and the chalcogen atom. The reactivity of tellurium ligands is markedly different from those of sulfur/ selenium lignads. The tellurium ligands undergo Te-C bond cleavage leading to the formation of tellurido-bridged derivatives. Literature references for all the chapters are provided at the end.

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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 ($K[PtCl_3(CH_2{=}CH_2)]$, the first organometallic compound) in 1827 [4]; cis $PtCl_2(NH_3)_2$ in mid 1850s (now used as antitumor drug) [5] and $[PtCl_2(CO)]_2$ (the first metal carbonyl) in 1868. The twentieth century witnessed further acceleration in the progress of their chemistry, notable being isolation of $[PtMe_3I]_4$ (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 (HNO_3:3HCl) forming H_2MCl_4. 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_2 and D_2. This property provides a method to purify H_2 on industrial scale just by passing the impure H_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

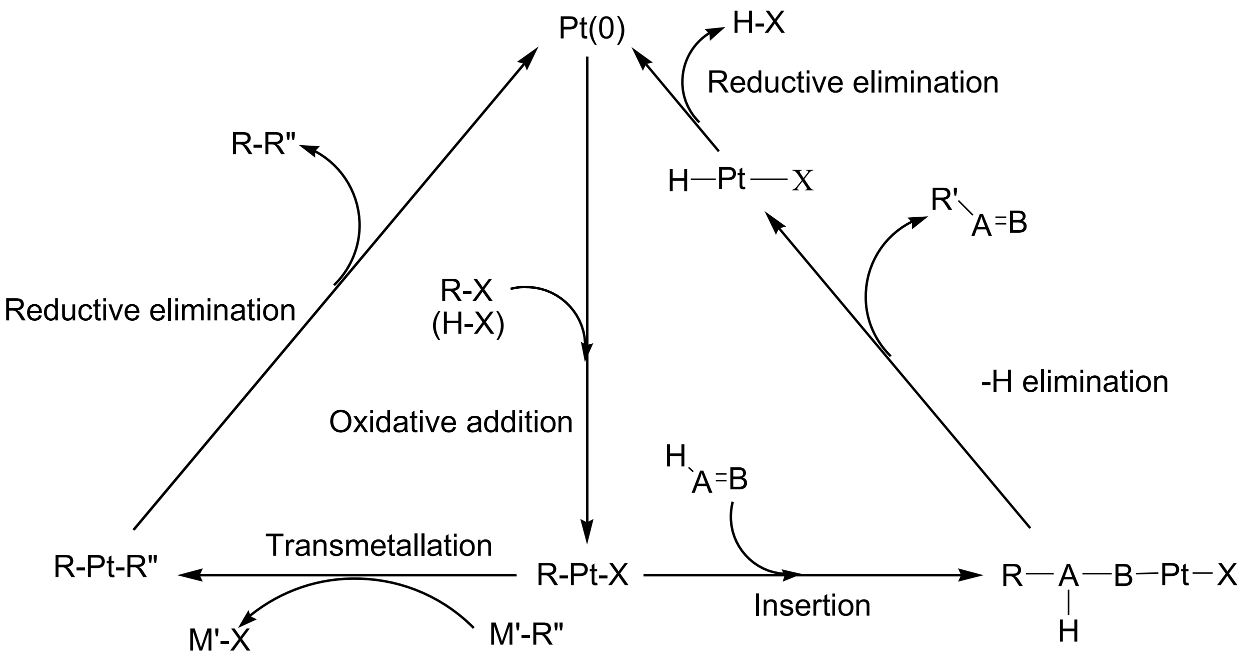
Properties		Palladium	Platinum
Atomic number/ atomic weight		46/106.4	78/195.1
Ground state electronic configuration		$[Kr]4d^{10}5s^0$	$[Xe]5d^9 6s^1$
Abundance in earth's crust (by weight) (ppm)		0.015	0.01
Melting point (°C)		1554	1733.5
Boiling point (°C)		3980	4170
Lattice structure		f. c. c.	f. c. c.
Density (g cm^{-3})		11.99	21.41
Pauling's electronegativity		2.2	2.2
Radius (Å):	Atomic	1.375	1.387
	M(0) Covalent	-	1.31
	M(II) Covalent	1.28	1.29
	Ionic (II)	0.86	0.80
Ionization potentials (eV)			
$M^\circ \rightarrow M^+$; $M \rightarrow M^{+2}$		8.33; 27.75	9.0; 27.56
$M^\circ \rightarrow M^{+3}$; $M \rightarrow M^{+4}$		60.67; 109.47	56.06; 97.16
$M^+ \rightarrow M^{+2}$; $M^{+2} \rightarrow M^{+3}$		19.42; 32.19	18.56; 28.50
$M^{+3} \rightarrow M^{+4}$; $M^{+4} \rightarrow M^{+5}$		48.8; 66.0	41.10; 55.00
Oxidation potential (eV)			
M° Ý M^{2+} + 2e		−0.92	−1.2
M^{II} Ý M^{4+} + 2e		−1.26	−0.77
Naturally occurring isotopes		^{102}Pd (1.0, 0)	^{190}Pt (0.01, 0)
(% abundance, spin (I),		^{104}Pd (11.1, 0)	^{192}Pt (0.8, 0)
		^{105}Pd (22.2, 5/2)	^{194}Pt (32.9, 0)
		^{106}Pd (27.3, 0)	**^{195}Pt (33.8, 1/2)**
		^{108}Pd (26.5, 0)	^{196}Pt (25.3, 0)
		^{110}Pd (11.7, 0)	^{198}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. $[PtMeCl(AsMe_3)_2(CF_3C{\equiv}CCF_3)]$ [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, $[Pt(C_6Cl_5)_4]^-$ [15] has been reported which has an unpaired electron. Tetravalent palladium and platinum complexes are now faily 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. PtF_5) and +6 (e.g. PtF_6) 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

Oxidation state	C. No.	Geometry	Examples
0	2	Linear	$[Pt(PPh_3)_2]$, $K_2[Pd(C{=}CR)_2]$[2]
	3	Trigonal planar	$[Pd(PPh_3)_3]$, $[Pt(SO_2)(PCy_3)_2]$
		Distorted planar	$[PtX(PPh_3)_2]$ ($X = O_2, C_2H_4, CS_2$)[2]
	4	Tetrahedral	$[Pt(PF_3)_4]$, $[Pt(CO)(PPh_3)_3]$
I	4	Square planar	$[M_2X_2(\mu\text{-dppm})_2]$ [18]
	5	Trigonal bipyramidal	$[Pt_3(SnCl_3)_2(C_8H_{12})_3]$[19]
II	3	T-shaped	$[Pd(Br)(Ph)(P^tBu_3)]$ [20]
	4	Tetrahedral	$[Pd(EDM)_2]I_2$ (EDM = N, N' ethylene dimorpholine)
	4	Square planar	All authenticated four coordinated complexes
	5	Trigonal bipyramidal	$[Pt(SnCl_3)_5]^{3-}$, $[Pd(QAs)I]^+$ $[Pd(Me_4[14]aneP_4]Br_2\cdot 6H_2O$,
		Square pyramidal	$[PtMeCl(AsMe_3)_2(CF_3C{\equiv}CCF_3)]$[11] $[Pt(Me_4[14]aneP_4]Br_2\cdot 4H_2O$ [21]
		Distorted square-pyramid	$[Pd(PPI)_3Br_2]$
	6	Octahedral	$[Pd(diars)_2I_2]$
III	4	Square planar	$[Pt(C_6Cl_5)_4]^-$ [15]
	6	Octahedral	$K_2[Pt_2(SO_4)_4(H_2O)_2]$[22]
IV	6	Octahedral	$[PtL_6]^{2-}$; L = X, SCN; $[PtMe_3I]_4$
	8	Piano-stool	$[Pt(\eta^5\text{-}C_5H_5)Me_3]$
V	6	Octahedral	$[PtF_6]^-$
VI	6	Octahedral	$[PtF_6]$



Scheme 1: Representation of various steps involved in catalytic reactions

1.2 A brief coverage on palladium and platinum complexes

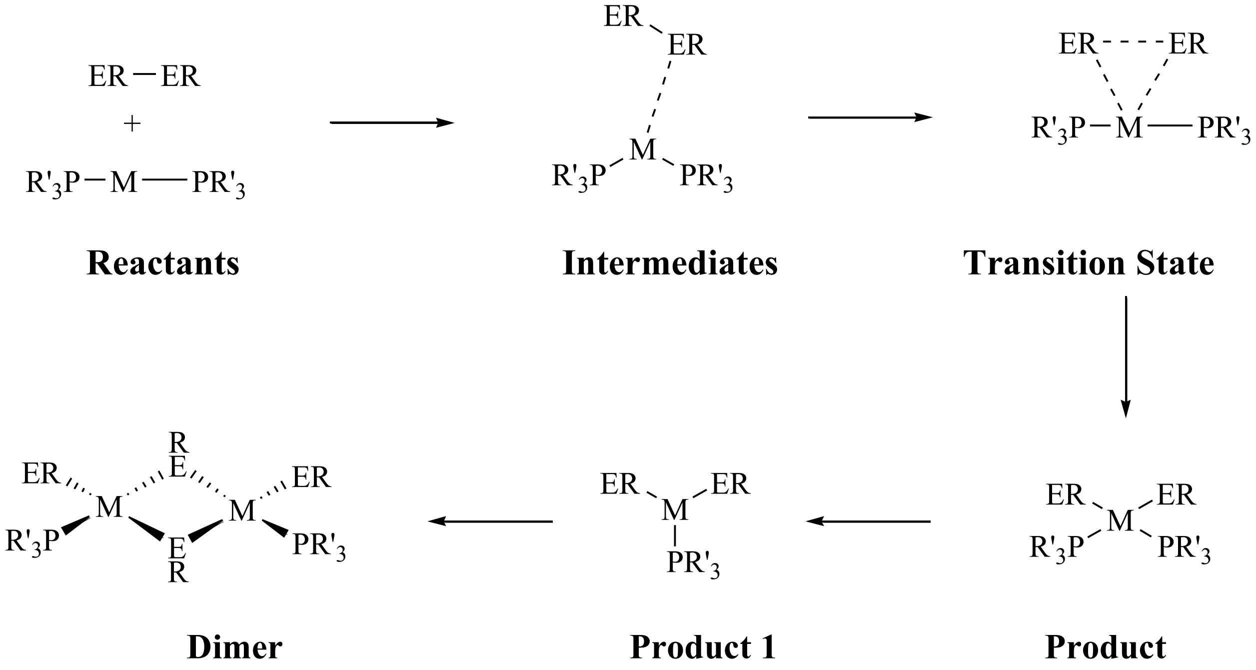
The chemistry of palladium and platinum has been covered in several books, monographs and review articles [2, 3, 22-30]. One of the most important classes of reactions in palladium and platinum compounds is oxidative addition reaction where the formal oxidation state of coordinatively unsaturated complex 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].



M = Pd and Pt E = S, Se and Te

R' and R = alkyl or aryl

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]: $CO > CN^- > C_2H_4 > PR_3 > H^- > CH_3^- > SC(NH_2)_2 > C_6H_5^- > NO_2^- > I^- > SCN^- > Br^- > Cl^- > py > NH_3 > OH^- > H_2O$.

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, $[MX_2(PR_3)_2]$ (X = Cl, Br, I) are formed via intermediate ionic complexes, ($[Pt(PR_3)_4][PtX_4]$) when solutions of $[MX_4]^{2-}$ 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 PR_3. The process is accelerated by addition of PR_3 [40]. The *trans*-

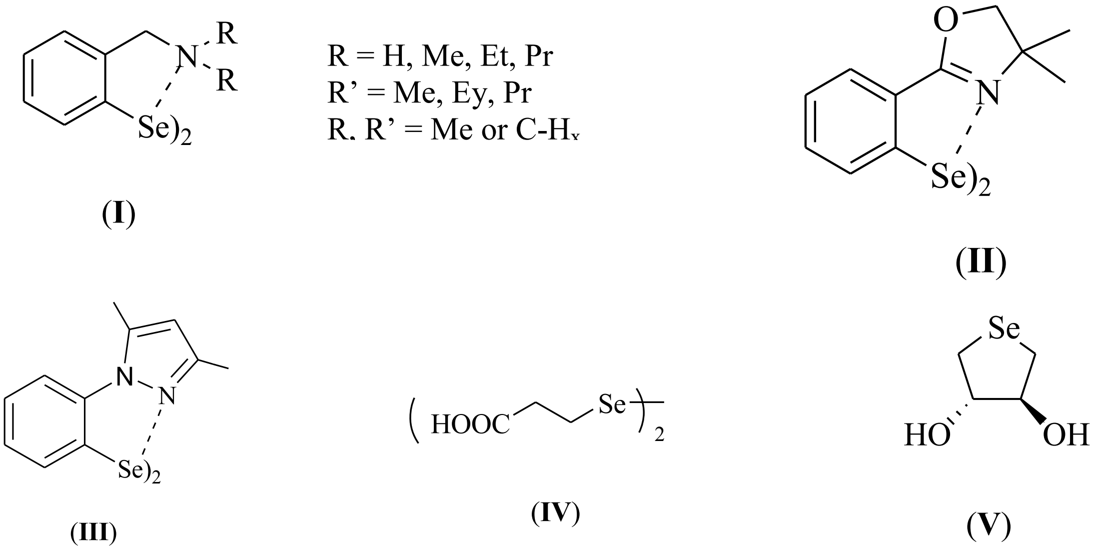
$[MCl_2(PR_3)_2]$ reacts with alcoholic potassium hydroxide to give hydirdo-platinum(II) complex *trans*-$[Pt(H)(Cl)(PPh_3)_2]$ [41], whereas cis-$[PtCl_2(PPh_3)_2]$ under the same reaction conditions with excess of triphenyl phosphine leads to the formation of zerovalent complexes $[Pt(PPh_3)_n]$, where 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., $K_2[PtCl_4]$, $Na_2[PdCl_4]$, $[PdCl_2(PhCN)_2]$) reacts with chelating phosphine ligands to form complexes of the type, *cis*-$[MX_2\{Ph_2P(CH_2)_nPPh_2\}]_m$. 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, $Ph_2P(CH_2)_nPPh_2$ [44]. The chloro bridged complexes, $[M_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$, are prepared by heating the mononuclear complex $MCl_2(PR_3)_2$ with 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 $[MM'Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ [49]. The chloro bridged complexes are often isolated as sym- *trans* isomers whereas its analogous organometallic derivatives, $[M_2R_2(\mu\text{-}Cl)_2(PR_3)_2]$ are isolated as a mixture of *cis* and *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 raher 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.

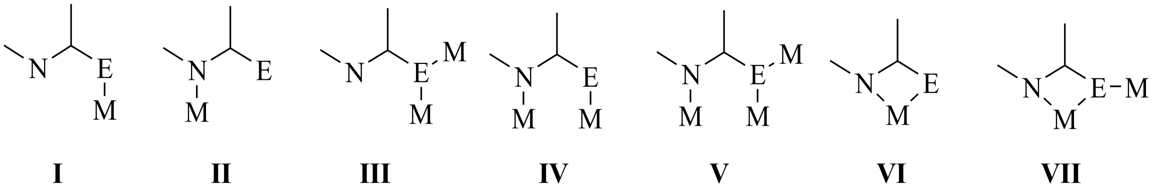


R = H, Me, Et, Pr
R’ = Me, Ey, Pr
R. R’ = Me or C-H$_x$

(I) **(II)** **(III)** **(IV)** **(V)**

Scheme 3: Organoselenium compound as antioxidants

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, tellurones) 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_2E, REH, HE^-)

Complexes of palladium and platinum containing H_2E are rare because H_2E 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, $[M_3(\mu\text{-}E)_2(dppp)_3]^{2+}$ (M = Pd, Pt; E = S, Se, Te) [79] and $[Pd_5(\mu\text{-}Te)_4(dppe)_4]^{2+}$ [80] were synthesized (Table 3) by the reaction of $Pd(NO_3)_2$ with P⌒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 $[Pd_3(\mu\text{-}Te)_2(dppp)_3]^{2+}$. 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 $Me_2NCH_2CH_2E^-$ and $Me_2NCH_2CH_2CH_2E^-$ (E= S, Se, Te) ligands [91-99].

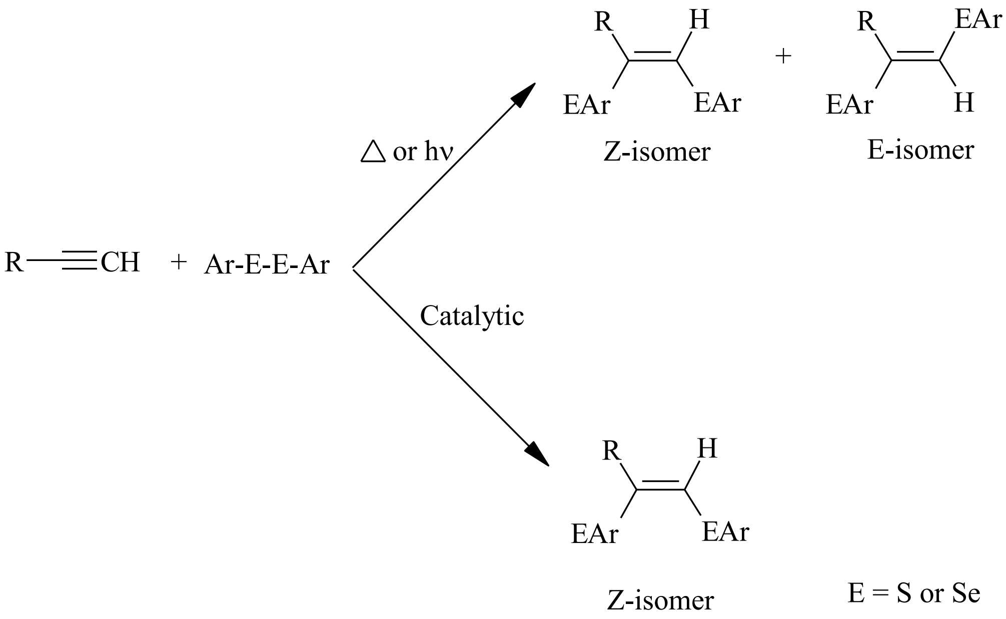
Chalcogenoethers (R_2E, $RR'E$, $RE(CH_2)_nER$)

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 $[Pd_2Cl_2(\mu\text{-}MeSe)_2[(MeSe(C_4H_3O)\}_2CMe_2]$, $[Pd_2Cl_4([24]aneSe_6)](BF_4)_2$ 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, $[\{PtMe_3I\}_2\{4\text{-}MeOC_6H_4Te)_2CH_2\}]$, $[PtMe_3I(PhTeCH_2TePh)]$ and $[PtMe_3I(PhTeCH_2TePh)_2]$ [109] have been synthesized. These complexes contain bridging, chelating and monodentate ditelluro ether ligands, respectively. A series of platinum complexes $[PtMe_3X\{Me_2NCH_2CH_2ER\}]$ (ER = SBu^t, SC_6H_4Me, SPh, SePh, TePh; X = Cl, Br, I) have also been synthesized by Jain, et.al. [110, 111].

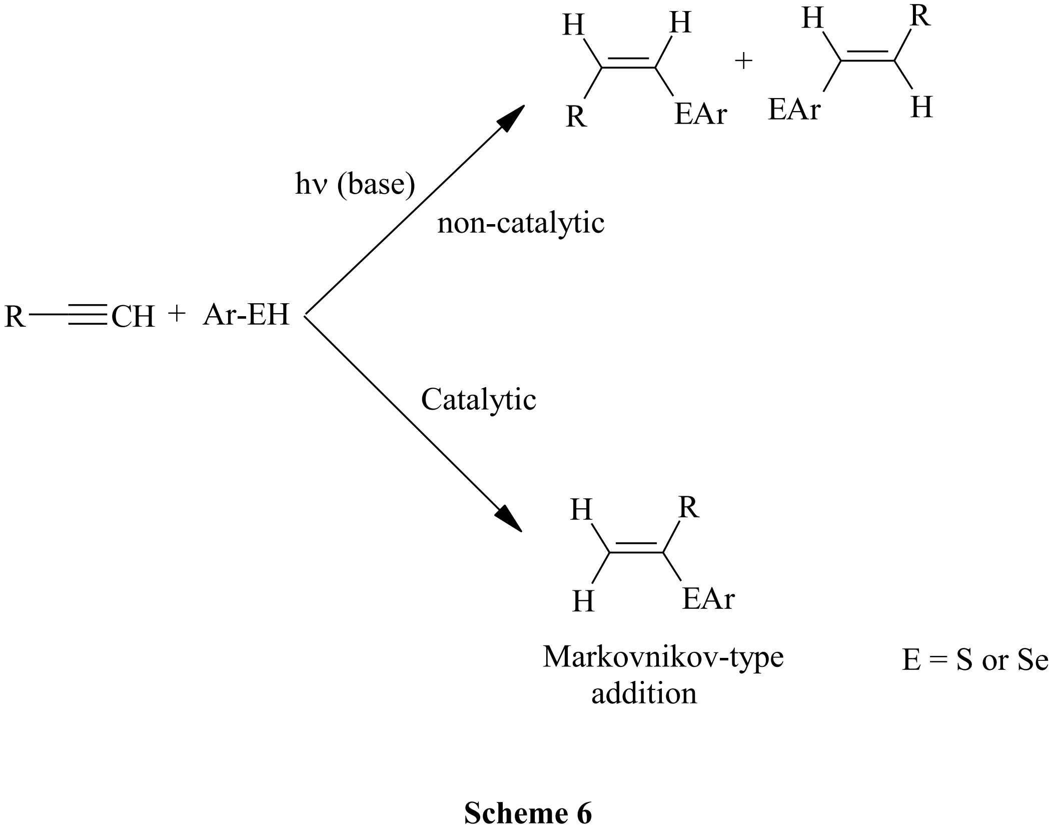
Diorgano-dichalcogenides (R_2E_2)

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 $[Pt(PPh_3)_4]$ or $[Pt(PPh_3)_2(olefin)]$ yields mononuclear $[Pt(ER)_2(PPh_3)_2]$ [113-117] while similar reactions with palladium(0) derivatives (e.g., $[Pd(PPh_3)_4]$, $Pd_2(dba)_3/PR'_3$) result in the formation of dinuclear complexes $[Pd_2(\mu\text{-}ER)_2(ER)_2(PR'_3)_2]$ (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



Scheme 6

Table 3: Palladium(II) and platinum(II) complexes of various chalcogen ligands

Ligand	**S**	**Se**	**Te**
HE^-	$[Pt(PPh_3)_2H(SH)]$	$[Pt(PPh_3)_2H(SeH)]$	–
E^{2-}	$[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ $[Pd_2Pt(\mu_3\text{-}S)_2\text{-}(dppe)_3][BPh_4]$ $[Pt_2(\mu\text{-}S)_2(PMe_2Ph)_4]$	$[Pd_3(\mu_3\text{-}Se)_2\text{-}(dppp)_3][OTf]_2$	$[Pt_3(\mu_3\text{-}Te)_2(dppp)_3]^{2+}$ $[Pd_3(\mu\text{-}Te)_2(dppe)_3]Cl_2$ $[Pd_2(\mu\text{-}Te)_2(PEt_3)_4]$
E_n^{2-}	$K_4[Pt_4S_{22}]\cdot 4H_2O$ $[Pt(\eta^2\text{-}S_4)(PPh_3)_2]$ $[Pt(\eta^2\text{-}S_5)_3]^{2-}$	$[PtSe_4(dppe)]$ $K[PdCu(Se_2)(Se_3)]$ $[Cs_2PdSe_8]$	$[PPh_4]_4[Pt_4Te_4(Te_3)_6]$ $[PPh_4]_4[Pd(Te_4)_2]$
RE^-	$[Pt(SPh)_2(dppm)]$ $[PdCl(SCH_2CH_2\text{-}NMe_2)(PMePh_2)]$.	$[Pt(SePh)_2(dppm)]$	$[Pd(TeC_5H_4N)_2(PPh_3)]$
R_2E	*trans*-$[PdCl_2(Et_2S)_2]$	$[PdCl_2(Me_2Se)_2]$	$[PtCl_2$(telluro-cyclopentane)$]$
RER'	$[PdCl_2(PhSCH_2CH_2\text{-}NMe_2)_2]$	$[PtCl_2\{MeSe(C4H_3S)\}2]$	*Cis*-$[PdCl_2\{MeTe\text{-}(C4H_3O)\}_2]$
$RE(CH_2)_nER$	$[PtCl_2(\eta^1\text{-}PhSCH_2SPh)_2]$	$[PtMe_2\{MeSeCH_2\text{-}CH_2SeMe\}]$ $[PdCl_2(\eta^1\text{-}PhSeCH_2SPh)_2]$	$[PtCl_2\{(4\text{-}MeOC_6H_4Te)_2\text{-}CH_2\}]$ $[Pd\{(4\text{-}MeOC_6H_4Te)_2\text{-}CH_2\}dppe]^{2+}$
REER	$[Pd_2Cl_4(Ph_2S_2)_2]$	–	–

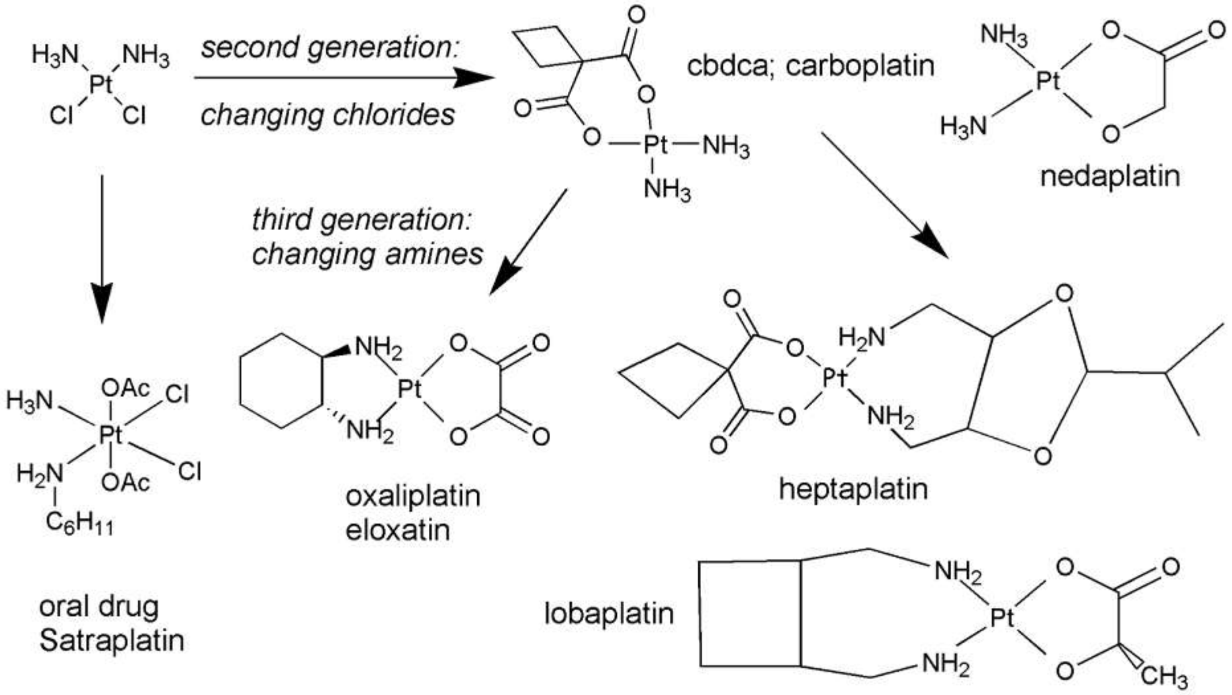
1.4 Application of platinum group metal chalcogen complexes

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 (*cis*-$[PtCl_2(NH_3)_2]$) and *cis*-diamminetetrachloroplatinum (*cis*-$[PtCl_4(NH_3)_2]$) (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 *cis*-platin paved the way for the second and third generation platinum(II) drugs, carboplatin and oxaliplatin while platinum(IV) (Scheme 7) complex sataraplatin 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 *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.



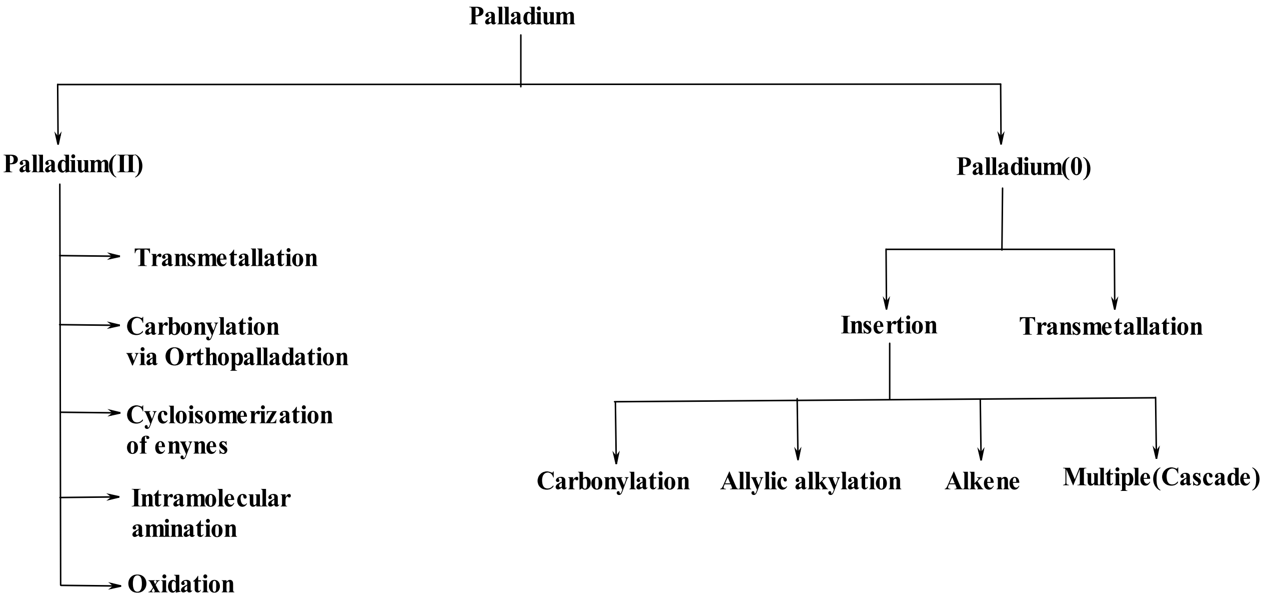
Scheme 7: Schematic presentation of various anticancer drugs of different generation

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.

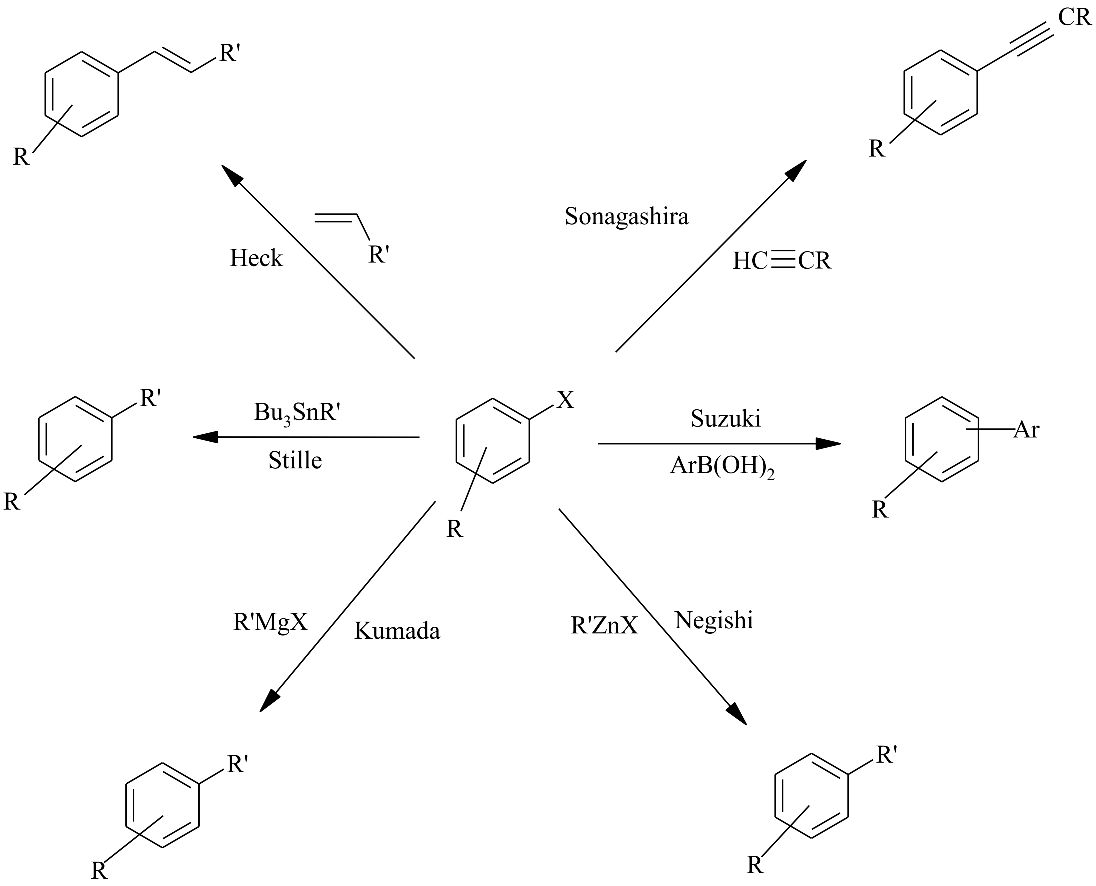
Cross coupling reactions

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 ororganic reactions

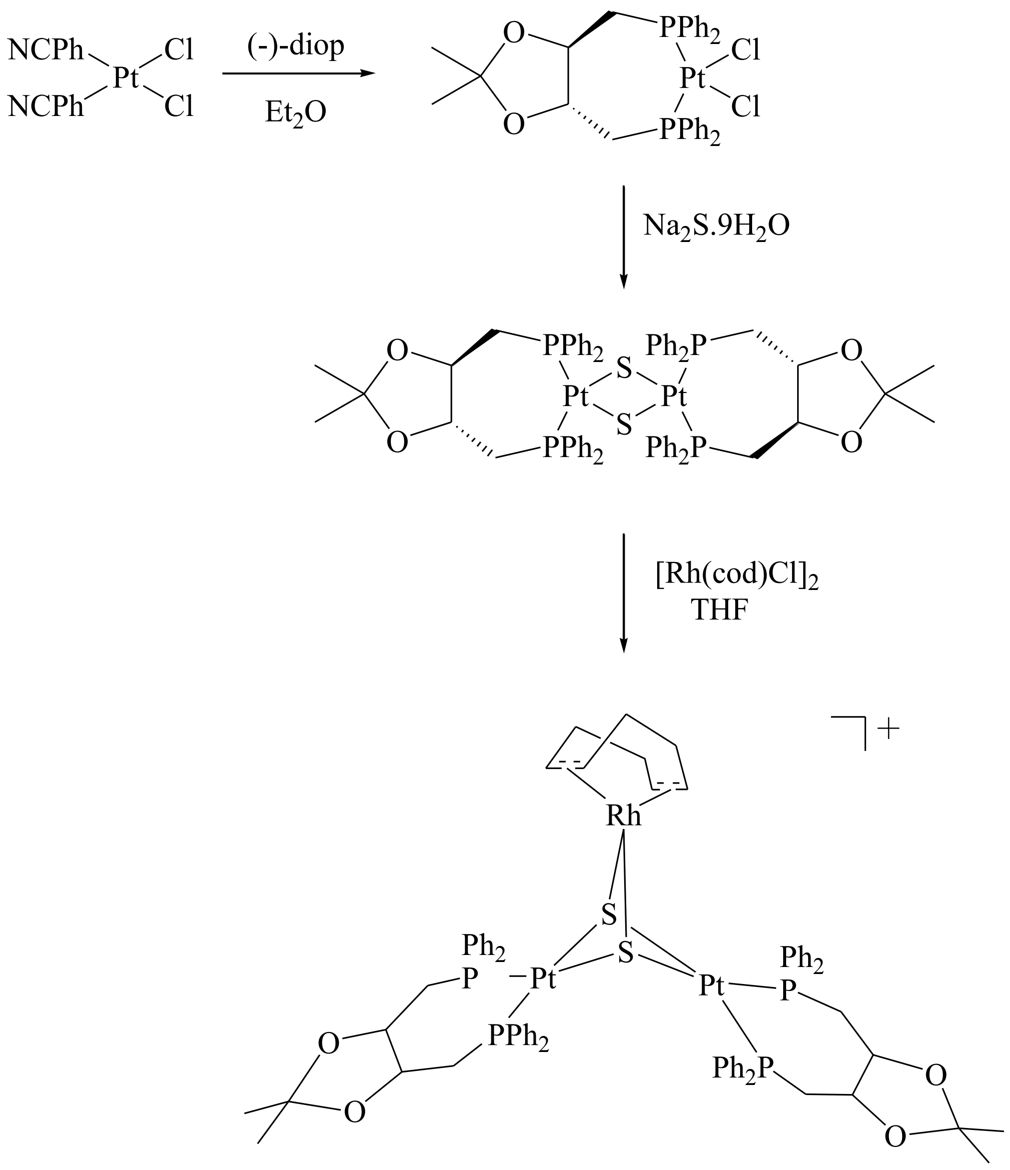
This chemistry has been greatly extended and elaborated over the years [137]. In general catalytic cycle for the cross-coupling reaction of organometallics, involves oxidative addition-transmetalation-reductive elimination sequences. Although each step involves further knotty processes including ligand 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

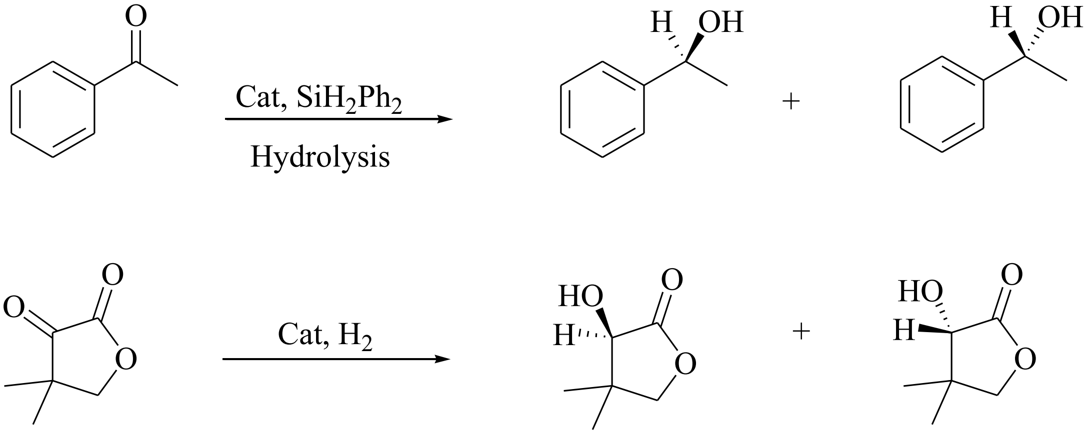
Oxidation of ketone

Brunner and co-workers synthesized the trinuclear complex $[Pt_2Rh(\mu\text{-}3\text{-}S)\{(-)\text{-}diop\}_2(COD)]Cl$ (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” $[Pt_2(\mu\text{-}S)_2\{(-)\text{-}diop\}_2]$ (Scheme 10) [139]. The tri-nuclear complex was used



Scheme 10

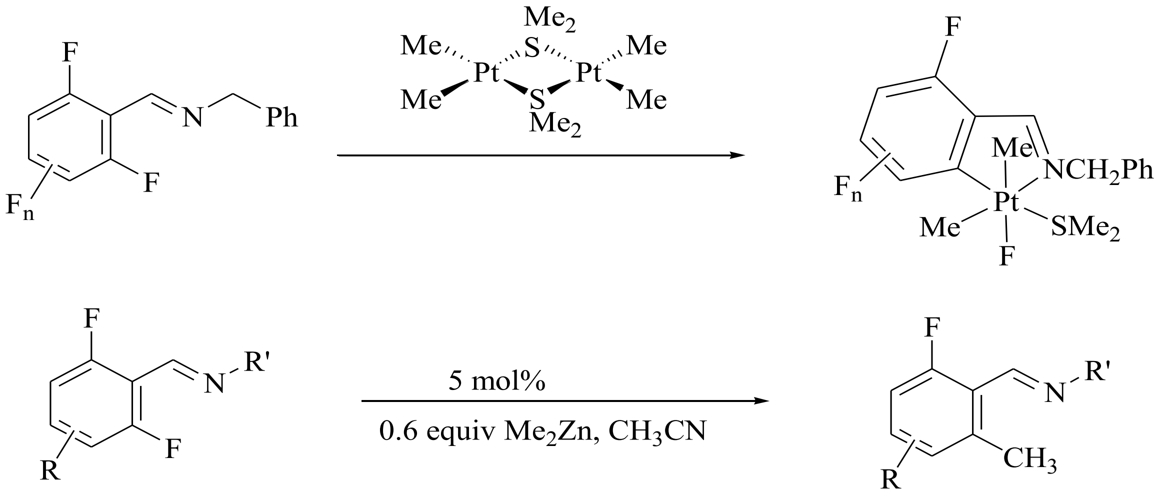
as a catalyst in the hydrosilyation of acetophenone with diphenylsilane and in the hydrogenation of ketopantolactone. Reaction wth diphenylsialne in the presence of rhodium(I) catalyst is a well-known method for the reduction of prochiral ketones to the corresponding alcohols [140]. Addition of a Si-H 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 [$Pt_2Rh(\mu_3\text{-}S)\{(-)\text{-diop}\}_2(COD)$]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 [$Pt_2Rh(\mu_3\text{-}S)\{(-)\text{-diop}\}_2(COD)$][Cl] gives a product yield of 14%-16% with a considerably higher enantioselectivity of 58-59% (Scheme 11).



Scheme 11

Selective Alkylation

Another platinum catalyst [$Pt_2(\mu\text{-}SMe_2)_2Me_4$] [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 Me_2Zn and obtain yield from 70% to 99%. The reaction is selective for *ortho* C-F activation with weaker aryl C-Br bonds (Scheme 12).

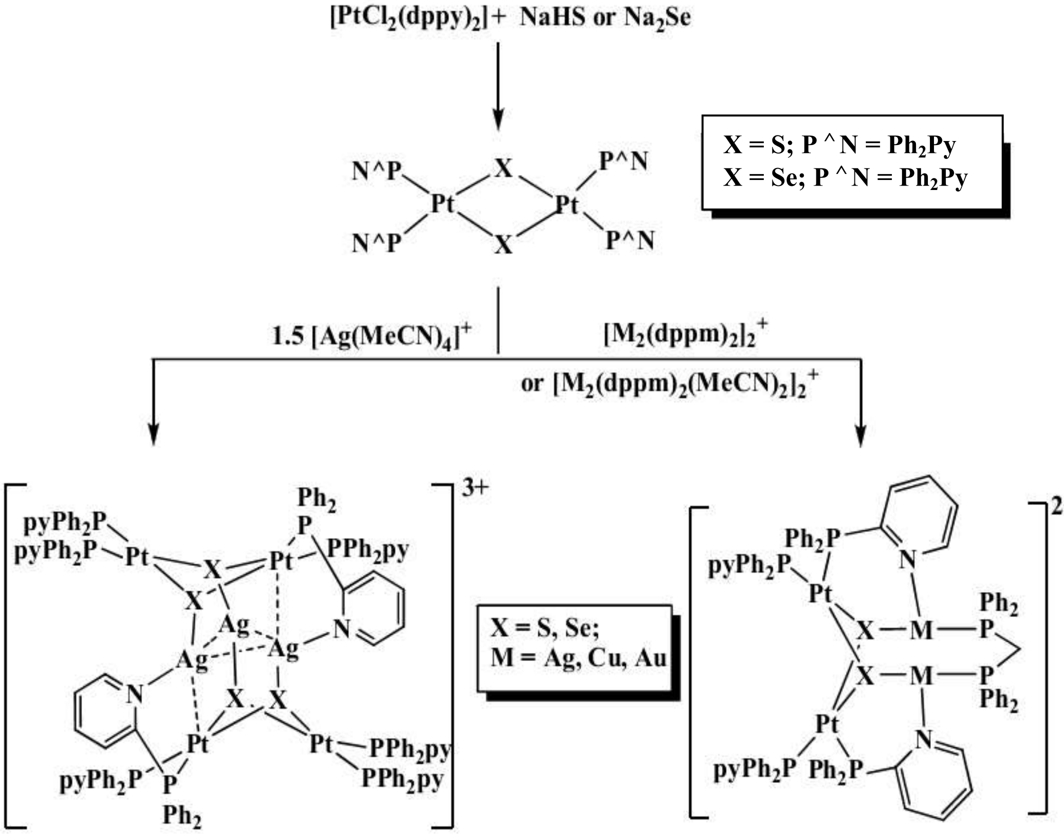


Scheme 12

1.4.3 Luminisecent properties

The diplatinum(II) complex $K_4[Pt_2(\mu\text{-}P_2O_5H_2)_4]$, which is often referred to as "platinum pop", is prepared from K_2PtC1_4 and phosphorous acid [22, 144]. The Pt_2 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, respective1y [l45, 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 Pt_2 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 Pt_2 complexes, the luminescence studies of platinum-chalcogen complexes have also attracted considerable interested. Yam and co-workers [148, 149] had synthesized platinum binuclear complex $[Pt_2(\mu\text{-}S)_2(dppy)_4]$ (dppy = Ph_2Ppy). 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 [$PtCl_2(dppy)_2$], [$Pt_2(\mu\text{-}S)_2(dppy)_4$] 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 [$Pt_2(\mu\text{-}S)_2(dppy)_4$] also show interesting luminescent properties. With additional supporting ligands from the nitrogen of dppy, [$Pt_2(\mu\text{-}S)_2(dppy)_4$] 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, [$Pt_2(\mu\text{-}Se)_2(dppy)_4$] [150], leading to similar results to [$Pt_2(\mu\text{-}S)_2(dppy)_4$] (Scheme 13)

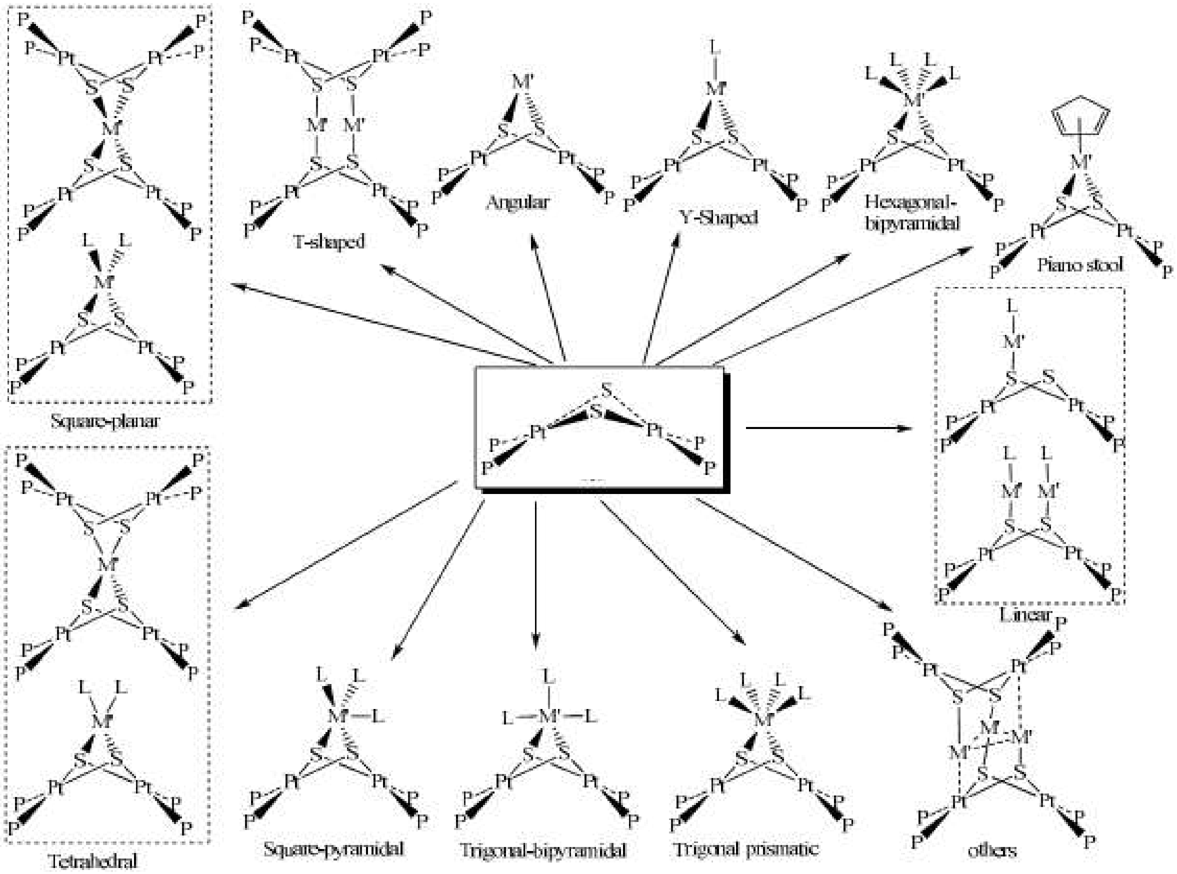


Scheme 13

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) [$X_2 \rightarrow$ 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, [$Pt_2(\mu\text{-}S)_2(P\text{-}P)_2$] [P-P = $2PPh_3$, 2dppy, dppp, dppf, $2PMe_2Ph$] 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, [$Pt_3(\mu_3\text{-}S)_2(PMe_2Ph)]Cl_2$, could be isolated from derivatization of the complex [$Pt_2(\mu\text{-}S)_2(PMe_2Ph)_2$] only after the synthesis of a series of heterometallic aggregates of general formula [$\{Pt_2(\mu\text{-}S)_2(PPh_3)_4\}_xML_y]^{n+}$ 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 [$Pt_2(\mu\text{-}S)_2(P\text{-}P)_2$] 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 $\{Pt_2S_2M'\}$ or $\{Pt_2S_2M'_2\}$ 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 $\{Pt_2(\mu\text{-}S)_2\}$ 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) amd 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.

2.1 Materials and methods

2.1.1 Galsswares

Glasswares fitted with inter-changeable standard ground joints were used. Special type of glass-wares like Schlenk, two necked flasks and three-way stopcocks with appropriate joints were used for synthesis and storage of moisture and air sensitive compounds. Precipitates formed during the reaction were filtered through G-3 and G-2 sintered discs. All the glasswares were immersed overnight in an alkali bath [5% NaOH in ethanol-water (1:1 v/v) mixture], washed thoroughly with water, rinsed with distilled water followed by acetone and dried at 120-130 °C overnight prior to experiment. Hot apparatus were kept in a desiccator containing fused $CaCl_2$ for cooling.

2.1.2 Experimental and analytical techniques

Analysis

Melting points were determined in glass capillary tubes sealed at one end and are uncorrected. Microanalysis of compounds (C, H, N and S) was carried out on a Thermo Fischer Flash EA-1112 CHNS instrument.

Spectroscopy

The IR spectra were recorded as Nujol mulls between CsI (200-4000 cm^{-1})/KBr (400-4000 cm^{-1}) plates on a Bomen MB-102 or Jasco (model FT-IR-6100) FT-IR spectrometer with a resolution of 4 cm^{-1}. The spectra were calibrated using a polystyrene film.

UV/Vis absorption spectra were recorded on a Bruins Instruments Omega 10 and JASCO V-630 PC spectrometer using quartz cuvettes with a diameter of 1 cm. The wavelength range covered in the spectrometer is 200-1100 nm with a resolution of ~1 nm. The molar extinction coefficient (ε) was calculated using the Lambert-Beer law which is expressed as

$$O.\ D. = \varepsilon.\ c.\ l$$

O. D. = absorbance, (an experimental quantity).

c = concentration of the absorbing molecule.

l = the thickness of the absorbing medium.

The ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$, $^{77}Se\{^{1}H\}$, $^{125}Te\{^{1}H\}$ and $^{195}Pt\{^{1}H\}$ NMR spectra (**Table 4**) were recorded on a Bruker Avance-II, 300MHz NMR spectrometer (in 5 mm thin-walled NMR tubes) operating at 300, 75.47, 121.49, 57.24, 94.86 and 64.52 MHz, respectively. Chemical shifts are relative to the internal chloroform peak at δ 7.26 ppm for ^{1}H and δ 77.0 ppm for ^{13}C and external 85% H_3PO_4 for ^{31}P; and Me_2Se for ^{77}Se (secondary reference Ph_2Se_2 δ 464 ppm); external [Te(dtc)$_2$] in $CDCl_3$ (δ 440 ppm relative to Me_2Te; dtc = N,N-diethyldithiocarbamate) for $^{125}Te\{^{1}H\}$ and Na_2PtCl_6 in D_2O for ^{195}Pt. A 90^0 pulse was used in every case.

Table 4: Properties [175] of some nuclear spin ½ nuclei

Nucleus	Natural abundance (%)	γ- values (10^{-7} rad $T^{-1}s^{-1}$)	Receptivity D^p	Magnetic moment (μ/μ_N)
Hydrogen (^{1}H)	99.98	26.75	1.000	4.837
Carbon (^{13}C)	1.11	6.73	$1.76x10^{-4}$	1.216
Phosphorus (^{31}P)	100	10.83	0.066	1.958
Selenium (^{77}Se)	7.58	5.10	5.26×10^{-4}	0.922
Tellurium (^{125}Te)	6.99	−8.453	2.21×10^{-3}	−1.528
Platinum (^{195}Pt)	33.8	5.75	3.36×10^{-3}	1.0398

Mass spectra were recorded on a time of flight mass spectrometer Waters QTOF micro (YA-105) at SIF of Indian Institute of Technology, Bombay. X-Ray photoelectron spectroscopy (XPS) was conducted in a UHV chamber (base pressure $< 2 \times 10^{-8}$ mbar) using a VG make, CLAM-2 model analyzer with a non-monochromatic twin Al/Mg X-ray source.

All the theoretical calculations were performed with the help of Prof. Ramiro Arratia-Perez. The Gaussian 03 [176] calculations were used for all calculations. The Complexes were fully optimized by using all electron Density Function Calculation [177, 178], employing Hirshfeld and Voronoi deformation density (VDD). Nuclear Independent Chemical Shift index (NICS) [179] and Electron Localization Function (ELF) [180] has also been employed for the determination of electronic behavior in ring. A negative value of the absolute shielding computed at a ring center or at some other point, usually at 1 Å above the ring center. Rings with large negative NICS values are considered aromatic, whereas rings with positive NICS values are regarded as antiaromatic.

Single Crystal X-Ray Crystallography

The single crystal X-ray structural analyses of several complexes were carried out on different X-ray diffractometers. The crystals were directly mounted on diffractometer after examining the quality of crystal under a polarizing microscope. Sometimes crystals were cut to the desired size before mounting. All the crystals were mounted at ambient temperature.

All the structures were solved by direct methods [181] and refinement [182] was on F^2 using data that had been corrected for absorption effects with an empirical procedure. Non-hydrogen atoms were modeled with anisotropic displacement parameters, hydrogen atoms in their calculated positions and using a weighting scheme of the form $w = 1/[\sigma^2(F^2) + (aP)^2 + bp]$

where P = (F^2 + $2Fc^2$)/3). Molecular structures were drawn using ORTEP [183]. Temperature, source of radiation, diffractometer and refinement details are given in Tables 5-10.

In compund $[Pd_3(\mu\text{-}Te)_2(dppp)_3]Cl_2 .3CHCl_3$ intensity data were collected at 150 K on a Oxford diffraction X caliber S using Mo-Kα radiation. The solvent and chloride molecules appear to be highly disordered thus it is difficult to make a reliable model of its position and distribution. Therefore, The SQUEEZE [184, 185] function was used to eliminate the contribution of electron density in the disordered solvent region from mesured intensity data (two 522 Å voids per unit cell containing 174 electron each). To minimize this effect the structure was submitted to further refinement cycles including complete set of geometrical restraints. Crstallographic data of the complex $[Pd_3(\mu\text{-}Te)_2(dppp)_3]Cl_2 .3CHCl_3$ are given in Table 8.

Intensity data of $[Pt\{\eta^2\text{-}SeC_5H_3(3\text{-}CONH_2)N\}\{SeC_5H_3(3\text{-}CONH_2)N\}(PPh_3)]$ and $[Pt(I)(Ph)(PPh_3)_2]$ were collected at 100 K with a Bruker APEX II CCD for using MoK_α radiation while for $[Pd\{\eta^2\text{-}SeC_5H_3(3\text{-}CONHPh)N\}\{SeC_5H_3(3\text{-}CONHPh)N\}(PPh_3)]$ and $[Pt(Cl_{0.5}I_{0.5})\{C_5H_3(3\text{-}CONHPh)N\}_2(PPh_3)_2].HCl$ data were collected with a Bruker APEX I CCD using Cu K_α radiation. All the crystals were mounted on Cryoloops with Paratone-N oil and their data were corrected for absorption using SADABS and structures were solved by direct methods.

For structure $[Pt\{\eta^2\text{-}SeC_5H_3(3\text{-}CONH_2)N\}\{SeC_5H_3(3\text{-}CONH_2)N\}(PPh_3)]$, all non-hydrogen atoms were refined anisotropically by full matrix least squares on F^2. Hydrogen atoms on nitrogen atoms N2 and N4 were found from a Fourier difference map and were refined isotropically with N-H distances of 0.87(0.02) Å. All other hydrogen atoms were placed in calculated positions with appropriate riding parameters.

Table 5: Crystallographic and structural determination data for [Pt(TeC_5H_4N)$_2$Te(PPh_3)] and [Pt{TeC_5H_3(3-Me)N}$_2$Te(PPh_3)].C_6H_6

Complex	[Pt(TeC_5H_4N)$_2$Te(PPh_3)]	[Pt{TeC_5H_3(3-Me)N}$_2$Te(PPh_3)].C_6H_6
chemical formula	$C_{28}H_{23}N_2PPtTe_3$	$C_{30}H_{27}N_2PPtTe_3.C_6H_6$
formula wt.	996.34	1102.53
Crystal size (mm^3)	0.40 x 0.40 x 0.10	0.30 x 0.30 x 0.05
Diffractometer	Rigaku AFC 7S	Rigaku AFC 7S
Temperature	298(2)	298(2)
Radiation (Å)	MoKα (0.7107)	MoKα (0.7107)
crystal system	monoclinic	Triclinic
space group	C2/*c*	P$\bar{1}$
unit cell dimensions		
a(Å)	39.040(7)	12.300(12)
b(Å)	13.261(4)	15.251(8)
c(Å)	11.9426(11)	10.029(7)
$\alpha(^0)$	90.00	107.38(3)
$\beta(^0)$	93.850(11)	99.51(6)
$\gamma(^0)$	90.00	83.25(4)
volume (Å^3)	6169(2)	1766(2)
ρ_{calcd}, g cm^{-3}	2.146	2.073
Z	8	2
μ (mm^{-1})/F(000)	7.400 / 3632	6.473/ 1024
θ for data collection (^{o})	2.72 to 27.49	2.52 to 27.50
Data/restraints/parameters	7078/0/317	8092/0/390
Final R_1, ωR_2 indices	0.0419/0.0980	0.0562/0.1249
R_1, ωR_2 (all data)	0.0874/0.1082	0.1775/0.1628
Goodness of fit on F^2	0.933	0.951

Table 6: Crystallographic and structural determination data for $[Pt\{PPh_2C(TeC_5H_4N)PPh_2\}_2].2CH_2Cl_2$ and $[Pt_2\{TeC_5H_3(3\text{-}Me)N\}_2(dppe)_2].[BPh_4]_2$

Complex	$[Pt\{PPh_2C(TeC_5H_4N)PPh_2\}_2].2CH_2Cl_2$	$[Pt_2\{TeC_5H_3(3\text{-}Me)N\}_2(dppe)_2].[BPh_4]_2$
Chemical formula	$C_{60}H_{48}N_2P_4PtTe_2.2CH_2Cl_2$	$C_{112}H_{100}B_2N_2P_4Pt_2Te_2$
Formula wt.	1541.03	2264.82
Crystal size (mm^3)	0.30 x 0.30 x 0.20	0.32 x 0.25 x 0.10
Diffractometer	Rigaku AFC 7S	Bruker Apex II CCD
Temperature(K)	298(2)	100(2)
Radiation (Å)	MoKα (0.7107)	MoKα (0.7107)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_{1/n}$	C2/c
Unit cell dimensions		
a (Å)	19.740(4)	30.256(4)
b(Å)	13.033(2)	16.828(2)
c(Å)	11.766(2)	22.048(5)
β(^{0})	90.618(15)	123.007(2)
Volume (Å^3)	3026.7 (10)	9414(3)
ρ_{calcd}, g cm^{-3}	1.691	1.598
Z	2	4
μ (mm^{-1})/F(000)	3.585 / 1496	3.695 / 4464
Limiting indices	$-25\leq h\leq 25$	$-36\leq h\leq 36$
	$0\leq k\leq 16$	$-20\leq k\leq -20$
	$-15\leq l\leq 8$	$-21\leq l\leq 26$
θ for data collection (^{o})	2.54 to 27.50	2.90 to 25.44
No of reflections collected	6934	8487
No of independent reflection	4975	6503
Data/restraints/parameters	6934/1/340	8487 / 0 / 560
Final R_1, ωR_2 indices	0.0514/0.1267	0.0287/ 0.0599
R_1, ωR_2 (all data)	0.0857/0.1478	0.0475/0.0666
Goodness of fit on F^2	1.040	1.017

Table 7: Crystallographic and structural determination data for $\{TeC_5H_3(3\text{-}Me)N\}_2$, $[Pd_2\{\mu\text{-}TeC_5H_3(3\text{-}Me)N\}_2(dppp)_2]Cl_2.3H_2O$, $[Pd_3(\mu\text{-}Te)_2(dppp)_3]Cl_2.3CHCl_3$ and $[PdCl\{Te(Cl)_2C_5H_3(3\text{-}Me)N\}(PPh_3)]$.

Complex	$\{TeC_5H_3(3\text{-}Me)N\}_2$	$[Pd_2\{\mu\text{-}TeC_5H_3(3\text{-}Me)N\}_2(dppp)_2]Cl_2.3H_2O$	$[Pd_3(\mu\text{-}Te)_2(dppp)_3]Cl_2.3CHCl_3$	$[PdCl\{Te(Cl)_2C_5H_3(3\text{-}Me)N\}(PPh_3)]$
Chemical formula	$C_{12}H_{12}N_2Te_2$	$C_{66}H_{64}Cl_2N_2P_4Pd_2Te_2.3H_2O$	$C_{81}H_{78}Cl_2P_6Pd_3Te_2.3CHCl_3$	$C_{24}H_{21}Cl_3NPPdTe$
Formula wt.	439.4	1602.2	2237.63	694.74
Crystal size (mm^3)	0.10 x 0.10 x 0.03	0.10 x 0.10 x 0.02	0.33 x 0.26 x 0.21	0.5 x 0.15 x 0.15
Diffractometer	Rigaku MM007 RA	Rigaku MM007 RA	Oxford diffraction X caliber S	Rigaku AFC 7S
Temperature	93(2)	93(2)	150(2)	298(2)
Radiation (Å)	MoKα (0.7107)	MoKα (0.7107)	MoKα (0.7107)	MoKα (0.7107)
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_{1/a}$
Unit cell dimensions				
a (Å)	6.804(2)	11.934(6)	14.2448(4)	17.000(14)
b(Å)	7.5995 (14)	13.083(7)	18.8456(6)	10.775(4)
c(Å)	7.7209(4)	13.460(7)	18.9875(5)	15.631(15)
α(^{0})	63.64(3)	114.084(2)	81.392(2)	-
β(^{0})	66.90(3)	99.385(4)	83.613(2)	115.51(6)
γ(^{0})	86.84(4)	111.686(5)	69.894(3)	-

Volume (Å^3)	325.58 (12)	1656.3(15)	4722.9(2)	2584(3)
Z	1	1	2	4
ρ_{calcd}, g cm^{-3}	2.241	1.606	1.573	1.786
μ (mm^{-1})/F(000)	4.455 / 202	1.629 / 794	1.623 / 2202	2.209 / 1344
No of reflections collected	1998	16863	57477	7091
No of independent reflection / No. of observed reflections with I>2σI	1126 / 1085	6038 / 4541	31378 / 10308	5940 / 1494
Data/restraints/parameters	1126 /12 /73	6038 / 0 / 365	31378 / 45 / 955	5940 / 132 / 162
Final R_1, ωR_2 indices	0.0339 / 0.0977	0.0657 / 0.1577	0.0748 / 0.1953	0.0793 / 0.1060
R_1, ωR_2 (all data)	0.0427 / 0.1449	0.0945 / 0.1727	0.2054 / 0.2172	0.3666 / 0.1549

Table 8: Crystallographic and structural determination data for $[Pt(SeC_4H_3N_2)_2(PPh_3)_2].2CH_2Cl_2$ and $[Pd(SeC_4H_3N_2)_2(PPh_3)].CH_2Cl_2$

Complex	$[Pt(SeC_4H_3N_2)_2(PPh_3)_2].2CH_2Cl_2$	$[Pd(SeC_4H_3N_2)_2(PPh_3)].CH_2Cl_2$
Chemical formula	$C_{44}H_{36}N_4P_2PtSe_2 .2CH_2Cl_2$	$C_{26}H_{21}N_4PPdSe_2.CH_2Cl_2$
Formula wt.	1205.57	769.68
Crystal size (mm^3)	0.11 x 0.04 x 0.03	0.15 x 0.10 x 0.10
Diffractometer	Rigaku MM007 RA	Rigaku MM007 RA
Temperature	93	93
Radiation (Å)	MoKα (0.7107)	MoKα (0.7107)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_{1/c}$	$P2_{1/n}$
Unit cell dimensions		
a (Å)	11.546(4)	14.726(4)
b(Å)	13.308(5)	10.539(3)
c(Å)	15.224(6)	19.055(6)
β(°)	107.359(8)	107.142(8)
Volume ($Å^3$)	2232.6(14)	2825.9(14)
ρ_{calcd}, g cm^{-3}	1.793	1.809
Z	2	4
μ (mm^{-1})/F(000)	5.123 / 1176	3.503 / 1504
Limiting indices	$-11\leq h\leq13$	$-17\leq h\leq17$
	$-11\leq k\leq16$	$-12\leq k\leq12$
	$-18\leq l\leq15$	$-17\leq l\leq 22$
θ for data collection (°)	2.40 to 25.34	1.55 to 25.36
No of reflections collected	4049	5090
No of independent reflection	3092	4336
Data/restraints/parameters	4049/0/268	5090/6/334
Final R_1, wR_2 indices	0.0504/0.0985	0.0372/0.0816
R_1, wR_2 (all data)	0.0736/0.1125	0.0476/0.0955
Goodness of fit on F^2	1.091	1.089

Table 9: Crystallographic and structural determination data for $[Pt\{SeC_5H_3(3\text{-}CONH_2)N\}_2(PPh_3)]$, $[Pd\{SeC_5H_3(3\text{-}CONHPh)N\}_2(PPh_3)]$, $[Pt(I)(Ph)(PPh_3)_2]$, $[Pt(Cl_{0.5}I_{0.5})\{C_5H_3(3\text{-}CONHPh)N\}(PPh_3)_2].HCl$

Complex	$[Pt\{SeC_5H_3(3\text{-}CONH_2)N\}_2(PPh_3)]$	$[Pd\{SeC_5H_3(3\text{-}CONHPh)N\}_2(PPh_3)]$	$[Pt(I)(Ph)(PPh_3)_2]$	$[Pt(Cl_{0.5}I_{0.5})\{C_5H_3(3\text{-}CONHPh)N\}(PPh_3)_2].HCl$
Chemical formula	$C_{30}H_{25}N_4O_2PPtSe_2$	$C_{42}H_{33}N_4O_2PPdSe_2$	$C_{42}H_{35}IP_2Pt$	$C_{50}H_{43}Cl_{1.50}I_{0.50}N_3OP_2Pt$
Formula wt.	857.52	921.01	923.63	1075.53
Crystal size (mm^3)	0.22 x 0.20 x 0.10	0.22 x 0.10 x 0.08	0.23 x 0.20 x 0.15	0.10 x 0.05 x 0.05
Diffractometer	Bruker Apex-II CCD	Bruker Apex-II CCD	Bruker Apex-II CCD	Bruker Apex-I CCD
Temperature	100(2)	100(2)	100(2)	100(2)
Radiation (Å)	Mo-K$_\alpha$ (0.7107)	Cu-K$_\alpha$ (1.5418)	Mo-K$_\alpha$ (0.7107)	Cu-K$_\alpha$ (1.5418)
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space group	$\mathrm{P}bca$	$\mathrm{P}2_1/n$	$\mathrm{C}2/c$	$\mathrm{P}\bar{1}$
Unit cell dimensions				
a (Å)	10.3684(15)	29.6439(16)	25.420(5)	11.8489(2)
b(Å)	20.019(3)	22.5901(13)	12.6658(18)	14.3967(3)
c(Å)	27.418(4)	33.5733(18)	11.476(4)	14.4913(3)
α(^{0})	90	-	-	88.5360(10)
β(^{0})	90	91.173(2)	113.546(14)	68.4110(10)
γ(^{0})	90	-	-	76.2830(10)

Volume (Å^3)	5690.9(14)	22478(2)	3387.3(13)	2227.81(8)
Z	8	24	4	2
ρ_{calcd}, g cm^{-3}	2.002	1.633	1.811	1.603
θ for data collection (°)	3.56-25.59	2.01-65.08	1.75-25.51	3.17-70.48
μ (mm^{-1})/F(000)	7.582 / 3280	6.959 / 10992	5.179 / 1792	10.433 / 1064
Index range	$-11\le h\le 12$ $-24\le k\le 21$ $-33\le l\le 31$	$-34\le h\le 34$ $-23\le k\le 25$ $-38\le l\le 39$	$-30\le h\le 27$ $-12\le k\le 15$ $-13\le l\le 13$	$-11\le h\le 14$ $-16\le k\le 17$ $-17\le l\le 16$
No of reflections collected	35034	118174	20338	19008
No of independent reflection / No. of observed reflections with I>2σI	5335 / 4393	36749 / 27026	3137 / 2672	7566 / 7293
Data/restraints/parameters	5335 / 4 / 361	36749 / 0 / 2815	3137 / 19 / 210	7566 / 50 / 554
Final R$_1$, ωR$_2$ indices	0.0216 / 0.0479	0.0837 / 0.2272	0.0337 / 0.0772	0.0282 / 0.0708
R$_1$, ωR$_2$ (all data)	0.0317 / 0.0513	0.1073 / 0.2512	0.0455 / 0.0821	0.0292 / 0.0716
Goodness of fit on F^2	1.036	1.093	1.061	1.089

Table 10: Crystallographic and structural determination data for $[Pd(SeMes)_2(dppe)].CHCl_3$, $[Pt(SeMes)_2(dppp)].1/2C_6H_6$, $[Pt(TeMes)_2(dppp)].3C_6H_6$, $[Pt(SeC_5H_4N)_2(dppm)]$, $[Pt\{SeC_5H(4,6\text{-}Me)N_2\}_2(dppm)].CH_2Cl_2$

Complex	$[Pd(SeMes)_2(dppe)]$ $.CHCl_3$	$[Pt(SeMes)_2(dppp)$ $].1/2C_6H_6$	$[Pt(TeMes)_2(dppp)]$ $.3C_6H_6$	$[Pt(SeC_5H_4N)_2(dppm)]$	$[Pt\{SeC_5H(4,6\text{-}Me)_2N_2\}_2(dppm)].$ CH_2Cl_2
Chemical formula	$C_{44}H_{46}P_2PdSe_2.CHCl_3$	$C_{45}H_{48}P_2PtSe_2.$ $1/2C_6H_6$	$C_{45}H_{48}P_2PtTe_2.$ $3C_6H_6$	$C_{35}H_{30}N_2P_2PtSe_2$	$C_{37}H_{36}N_4P_2Pt$ $Se_2.CH_2Cl_2$
Formula wt.	1020.44	1042.84	1334.38	893.56	1036.57
Crystal size (mm^3)	0.32 x 0.27 x 0.22	0.40 x 0.30 x 0.20	0.38 x 0.33 x 0.30	0.20 x 0.15 x 0.10	0.15 x 0.10 x 0.10
Diffractometer	Bruker Apex-II CCD	Rigaku AFS-7S	Bruker Apex-II CCD	Bruker Apex-II CCD	Bruker Apex-II CCD
Temperature	298	100	100	100	100
Radiation	Cu-K_α (1.5418)	Mo-K_α (.07107)	Mo-K_α(.07107)	Mo-K_α(.07107)	Mo-K_α(.07107)
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2_{1/c}$	$P2_{1/n}$	Pbcn	C2/c	Pna2(1)
Unit cell dimensions					
a (Å)	25.4053(10)	14.000(5)	20.927(3)	48.245(2)	15.8773(4)
b(Å)	15.4812(6)	22.376(7)	12.8611(16)	8.8359(4)	14.4948(4)
c(Å)	22.7010(9)	13.583(8)	20.875(3)	22.1322(10)	16.7069(5)
$\alpha(^0)$	-	90	90	-	90
$\beta(^0)$	101.6850(10)	98.25(4)	90	96.990(2)	90
$\gamma(^0)$	-	90	90	-	90

Volume (Å^3)	8743.4(6)	4211(3)	5618.3(12)	9364.6(7)	3844.90(18)
Z	8	4	4	12	4
ρ_{calcd}, g cm^{-3}	1.550	1.645	1.578	1.901	1.791
θ for data collection (°)	3.36-67.68	2.67-28.33	1.86-25.37	1.70-25.44	2.57-25.85
μ (mm^{-1})/F(000)	7.938 / 4096	5.170 / 2060	3.610 / 2620	6.958 / 5160	5.798/2016
Index range	$-29\leq h\leq 28$ $-15\leq k\leq 18$ $-27\leq l\leq 13$	$-10\leq h\leq 18$ $0\leq k\leq 29$ $-17\leq l\leq 17$	$-24\leq h\leq 25$ $-15\leq k\leq 15$ $-25\leq l\leq 25$	$-58\leq h\leq 57$ $-10\leq k\leq 10$ $-26\leq l\leq 26$	$-19\leq h\leq 19$ $-17\leq k\leq 13$ $-20\leq l\leq 20$
No of reflections collected	39051	11879	40961	61532	28372
No of independent reflection / No. of observed reflections with I>2σI	15171 / 14582	9922 / 4457	5156 / 4527	8678 / 7319	7412/6610
Data/restraints/parameters	15171 / 0 / 966	9922 / 0 / 484	5156 / 0 / 308	8678 / 0 / 569	7412/1/447
Final R$_1$, ωR$_2$ indices	0.0301 / 0.0774	0.0474 / 0.0905	0.0213 / 0.0478	0.0252/0.0477	.0250/.0513
R$_1$, ωR$_2$ (all data)	0.0289 / 0.0764	0.1702 / 0.1211	0.0274 / 0.0513	0.0362 / 0.0505	.0329/.0538
Goodness of fit F^2	1.001	.932	1.049	1.018	1.042

In the case of compound [Pd{η^2-SeC_5H_3(3-CONHPh)N}{SeC_5H_3(3-CONHPh)N}(PPh_3)],disorder associated with palladium and selenium atoms were treated by fixing occupancies of appropriate pairs: that is, for pair Pd1E, Pd2E (85,15 %); Pd1F, Pd2F (95,5%); Se1F, Se3F (88,12%); Se2E, Se3E (85,15%). Atom parts Pd2E, Pd2F, and Se3F were refined isotropically. Although numerous residual electron density peaks and a large weighting factor were noted in the final refinement, no attempt was made to address these factors.

In compound [Pt($Cl_{0.5}I_{0.5}$){C_5H_3(3-CONHPh)N}$_2$(PPh_3)$_2$].HCl, an iodine and chlorine atom were found to occupy similar positions and were refined with 50 % occupancy with Pt-I and Pt-Cl distances of Pt-I 2.66(0.01) and Pt-Cl 2.35(0.001) Å. Hydrogen atoms on nitrogen atoms N1 and N2 were found from a Fourier difference map and were refined isotropically with N-H distances of 0.87(0.02) Å. Disorder associated with the solvent acetonitrile was treated by using a two part model which resulted in 44.3/ 55.7 occupancies.

2.1.3 Materials

Solvents and Chemicals

All solvents used were of AR grade and dried by standard procedures, [186] followed by distillation under an inert atmosphere. Benzene (80° C) and toluene (110° C) were dried by refluxing them over sodium metal pieces and benzophenone, followed by distillation in an inert atmosphere. Diethyl ether (36 °C) and tetrahydrofuran (THF) (65-67° C) were dried by refluxing over P_2O_5 and finally dried over sodium metal and benzophenone and distilled under argon when blue color persisted. Dichloromethane (40 °C) was dried over calcium chloride followed by decantation and distillation. Methanol (65 °C) was refluxed over magnesium methoxide (prepared from magnesium turnings and methanol in the presence of catalytic amount of iodine) for 2 h and distilled under a nitrogen atmosphere.

Elemental selenium (99.99%), tellurium (99.99%), sodium borohydride and various tertiary phosphines (PPh_3, $\{PPh_2(C_5H_4N)\}$, dppm, dppe, dppp) were obtained from commercial sources (Aldrich/Strem) and used as such. The compounds, 2-bromopyrimidine, 2-chloro-4,6-dimethylpyrimidine [187], nicotinoyl based selenium ligands [188] and organoselenium and tellurium were prepared by literature methods and their synthesis is described below:

Dimesityldisulfide (Mes_2S_2)

The title compound was prepared by a reaction between MesMgBr (from MesBr (34.91 g, 17.5 mmol) and magnesium turnings (4.26 g, 17.5 mmol) and sulfur powder (5.61 g, 17.5 mmol) in diethylether at –78 °C. After completion of the reaction, contents were brought to room temperature and were treated with alkaline aqueous $K_3[Fe(CN)_6]$ (57.7 g, 17.5 mmol). The organic fraction was extracted with diethylether and dried over anhydrous $CaCl_2$. The solvent was removed under vacuum and the residue was recrystallised from ethylacetate as bright yellow crystals (8.9 g, 33%) m.p.: 105 ºC (Lit. 109 ºC [189]). Analysis Calcd. For $C_{18}H_{22}S_2$: C, 71.1; H, 7.2; S, 21.1 %. Found: C, 71.1; H, 7.2; S, 27.2 %.

Dimesityldiselenide (Mes_2Se_2)

This was prepared similar to Mes_2S_2 and recrystallised from ethylacetate as bright orange crystals (15.95 g, 32%), m.p.: 109 °C [190]. UVvis (CH_2Cl_2) λ_{max} in nm: 288 (13105); 370 (1240). ^1H NMR ($CDCl_3$) δ: 2.25 (s, 6H, 2,6-Me); 2.28 (s, 3H, 4-Me); 6.85 (s, 2H, 3,5-H).

$^{13}C\{^1H\}$ NMR (CDCl3) δ: 20.9 (s, 4-CMe); 24.1 (s, 2,6-CMe); 128.3 (s, 3,5-C); 128.9 (s, 1-C); 139.1 (s, 4-C); 143.7 (s, 2,6-C). $^{77}Se\{^1H\}$ NMR (CDCl3) δ: 371 ppm.

Bis(3-methyl-2-pyridyl)diselenide: $[SeC_5H_3(3\text{-}Me)N]_2$

To a THF suspension of Mg turnings (10.9 g, 448.6 mmol), containing a pinch of iodine was added 2 ml of iodomethane to initiate the reaction. A THF solution of isopropyl chloride (36.9 g, 469.8 mmole) was added drop by drop to the suspension over a period of 2 h at 0-5° C. After the complete addition of isopropyl chloride solution, the reaction mixture was stirred for 5 h and the Grignard reagent thus obtained was stored in a measuring cylinder under nitrogen (yield: 89%, 41.2 g).

2-Bromo-3-methyl pyridine (17.2 g, 100 mmol) was added drop wise to a vigorously stirred mixture of isopropylmagnesium chloride (10.3 g, 100.1 mmol) in THF. After stirring for 2h at room temperature the mixture was cooled in an ice bath for 10 min and elemental selenium (7.98 g, 101.1 mmol) was added. The mixture was stirred for 30 minutes at the same temperature (0^o C) and then followed by stirring at room temperature till all the selenium had dissolved. The reaction mixture was hydrolyzed with acidified water (prepared freshly by dissolving ammonium chloride in distilled water). The mixture was then extracted with diethyl ether (3 × 200 ml) and the organic layer was dried over anhydrous magnesium sulfate. The solvent was removed under vacuum to obtain yellow residue. The yellow aqueous layer was left for 2-3 days to obtain yellow crystalline product at the bottom of beaker which was filtered through filtration assembly and washed with distilled water and dried under vacuum for few hours. These residues obtained from organic and aqueous layer were purified by silica gel column chromatography with hexane/ethyl acetate (5:1) as eluent.

The crude diselenide was purified by silica gel column chromatography. The pure product was obtained by hexane/ethyl acetate (5:1) as eluent and was recrystallized from hexane-ethylacetate mixture as a yellow needle shaped crystalline solid (yield 9.00 g, 53%), m.p. 142-144° C [191]. Uv-vis λ_{max} (CH_2Cl_2): 240, 285 and 319 (sh) nm. ^{1}H NMR ($CDCl_3$) δ: 2.46 (s, Me), 7.01 (d, 4.5 Hz; H-5), 7.32 (d, 7.5 Hz; H-4), 8.28 (d, 4.5 Hz; H-6) (each s, ring protons). $^{13}C\{^1H\}$ NMR ($CDCl_3$) *δ*: 20.7 (s, Me); 121.9 (CH-4); 133.7 (s); 136.8 (s, CH-5); 147.9 (s, CH-6). $^{77}Se\{^1H\}$ NMR ($CDCl_3$) *δ*: 436 ppm.

Bis(2-pyridyl)diselenide: $(SeC_5H_4N)_2$

A similar procedure was used involving 2-bromo-pyridine (14.3 g, 90.5 mmol), isopropylmagnesium chloride (9.3 g, 90.4 mmol) and selenium (7.22 g, 91.4 mmol) to obtain a yellow oily liquid which was further oxidized with 3-4 drops of 30% hydrogen peroxide with vigorous stirring to give crude yellow product. The latter was purified by column chromatography using hexane/ethyl acetate (5:1) as eluent to afford crystalline solid (yield 7.2 g, 51%), m.p. 48° C [191]. Uv-vis λ_{max} (CH_2Cl_2): 243, 282 and 325 (sh) nm. ^{1}H NMR ($CDCl_3$) *δ*: 7.07 (t, J = 5.55 Hz, 1 H), 7.53 (t, J = 7.35 Hz, 1 H), 7.78 (d, J = 7.8 Hz, 1 H), 8.44 (d, J = 3.6 Hz, 1 H). $^{77}Se\{^1H\}$ NMR ($CDCl_3$) *δ*: 426 ppm.

Bis(4, 6-dimethyl-2-pyrimidyl)diselenide: $[SeC_4H(4,6\text{-}Me)_2N_2]_2$

To an aqueous solution of Na_2Se_2 (prepared from grey selenium powder (4.4 g, 55.72 mmol) and sodium borohydride (2.1 g, 55.44 mmol) in distilled water (100 cm^3) under an inert atmosphere at 0 °C), ethanolic solution (20 cm^3) of 2-chloro-4,6-dimethylpyrimidine (7.3 g, 51.18 mmol) was added drop-wise with stirring at the room temperature. After complete addition, the contents were heated at 70 °C for 7 h with stirring. The progress of the reaction was monitored by TLC till its completion. The contents were brought to room temperature followed by quenching by distilled water (100 ml). The organic layer was extracted in chloroform (3 × 50 ml) and dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated under vacuum to yield a brown solid which was purified on silica column. Initially 5:1 v/v hexane–ethyl acetate mixture was used followed by 4:1 v/v solvent mixture. The product eluted in 5:1 hexane–ethyl acetate mixture gave red crystals of diselenide, $\{SeC_4H(4,6\text{-}Me)_2N_2\}_2$ (yield 13.89 g, 67 %) (m.p. 143 ºC) Anal. Calcd. for $C_{12}H_{14}N_4Se_2$: C, 38.72; H, 3.79; N, 15.05% Found C, 38.69; H, 3.82; N, 15.20%. ^1H NMR ($CDCl_3$) δ: 2.37 (s, 12H, Me), 6.71 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 23.2 (Me), 117.2 (C-5), 165.7 (C-Se), 167.5 (C-4,6). $^{77}Se\{^1H\}$ NMR ($CDCl_3$) δ: 486 ppm. Mass (m/z) = 372 (M^+); 293 ($\{C_4H(4,6\text{-}Me)_2N_2\}_2Se$); 187 ($C_4H(4,6\text{-}Me)_2N_2SeH$) while the one eluted with 4:1 v/v solvent mixture gave yellow crystals of monoselenide, $[C_4H(4,6\text{-}Me)_2N_2]_2Se$ (yield 2.9 g, 18%, m.p. 118 ºC). Anal. Calcd. for $C_{12}H_{14}N_4Se$: C, 49.15; H, 4.81; N, 19.11% Found C, 49.39; H, 4.69; N, 18.87%.^1H NMR ($CDCl_3$) δ: 2.36 (s, 12H, Me), 6.81 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 23.7 (Me), 118.0 (C-5), 166.9 (C-Se), 167.5 (C-4,6). $^{77}Se\{^1H\}$ NMR ($CDCl_3$) δ: 588 ppm. Mass (m/z) = 293 (M^+); 187 ($C_4H(4,6\text{-}Me)_2N_2SeH$).

Bis(2-pyrimidyl)diselenide: $(SeC_4H_3N_2)_2$

To an aqueous solution of Na_2Se_2 (prepared from grey selenium powder (5.00 g, 63.32 mmol) and sodium borohydride (2.34 g, 61.77 mmol) in distilled water (100 cm^3) under an inert atmosphere at 0 °C) ethanolic solution (20 cm^3) of 2-bromopyrimidine (8.27 g, 52.04 mmol) was added drop-wise with stirring at room temperature. After complete addition, the contents were heated at 70 °C for 7 h with continuous stirring. The progress of the reaction was monitored by

TLC till its completion. The contents were brought to room temperature followed by quenching by distilled water (100 ml). The organic layer was extracted in chloroform (3 × 50 ml) and dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated under vacuum to yield a brown product which was purified on silica column. The product eluted in 5:1 hexane–ethyl acetate mixture gave red crystals of diselenide, $(SeC_4H_3N_2)_2$ (yield 12.8 g, 64 %, m.p. 112 ºC). Anal. for $C_8H_6N_4Se_2$; Calcd : C, 30.39; H, 1.91; N, 17.73% Found C, 30.37; H, 1.88; N, 17.82%. Mass m/z = 316 (M+); 237 ($\{C_4H_3N_2\}_2Se$). ^1H NMR ($CDCl_3$) δ: 7.02 (t, C*H*-5, 2H, 4.8 Hz); 8.51 (d, C*H*-4,6; 4H, 4.8 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 118.4 (C-5), 157.9 (C-4,6), 166.4 (C-Se). $^{77}Se\{^1H\}$ NMR ($CDCl_3$) δ: 490 ppm.

Bis(3-methyl-2-pyridyl)ditelluride: $[TeC_5H_3(3\text{-}Me)N]_2$

2-Bromo-3-methyl pyridine (10.3 g, 59.9 mmol) was added drop wise to a vigorously stirred mixture of isopropylmagnesium chloride (8.4 g, 81.7 mmol) in THF. After stirring for 2h at room temperature the mixture was cooled in an ice bath and tellurium powder (7.74 g, 60.6 mmol) was added. After all the tellurium had dissolved, the stirring was stopped and the reaction was diluted with acidified water. The mixture was then extracted with diethyl ether (3 X 150 ml) and the organic layer was dried over anhydrous sodium sulfate. The solvent was removed under vacuum and the residue was purified by silica gel column chromatography with hexane/ethyl acetate (5:1) as eluent (yield: 7g, 53%), m.p. 53° C [191]. ^1H NMR ($CDCl_3$) δ: 2.40 (s, Me), 7.15, 7.41, 8.30 (each s, ring protons). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 24.6 (s, Me); 122.5, 135.3, 138.3, 140.6, 148.3 $^{125}Te\{^1H\}$ NMR ($CDCl_3$) δ: 473 ppm.

Bis(2-pyridyl)ditelluride: $(TeC_5H_4N)_2$

Prepared similar to $\{TeC_5H_3(3\text{-}Me)N\}_2$ from 2-bromopyridine (14.3 g, 90.5 mmole), isopropylmagnesium chloride (11.1 mg, 107.9 mmol) and tellurium (11.6 g, 90.9 mmol) in THF (yield: 11.5 g, 62%,), m.p. 62° C [191]. ^{1}H NMR ($CDCl_3$) δ: 7.03 (t, 7.6 Hz), 7.39 (t, 7.6 Hz), 8.02 (d, 7.8 Hz), 8.43 (d). $^{13}C\{^1H\}$ NMR ($CDCl_3$) *δ*: 121.6, 131.2, 135.3, 137.0, 149.9 $^{125}Te\{^1H\}$ NMR ($CDCl_3$) *δ*: 439 ppm.

Bis(4, 6 dimethyl-2-pyrimidyl)ditelluride: $[TeC_4H(4,6\text{-}Me)_2N_2]_2$

Prepared similar to the synthesis of $[SeC_4H(4,6\text{-}Me)_2N_2]_2$ but the reaction was carried out in ethanol and the product was purified by column chromatography eluting with hexane–ethyl acetate mixture (5:1 v/v) and was obtained as blue crystals (yield 4.04 g, 61%, m.p. 159 ºC). Anal. Calcd. for $C_{12}H_{14}N_4Te_2$: C, 30.70; H, 3.01; N, 11.93% Found C, 30.85; H, 2.98; N, 12.10%. ^{1}H NMR ($CDCl_3$) δ: 2.37 (s, 12H, Me), 6.71 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 23.6 (Me), 117.8, 150.3 (C-Te), 166.9; $^{125}Te\{^1H\}$ NMR ($CDCl_3$) δ: 136 ppm. Mass (m/z) = 469 (M^+); 343 ($\{C_4H(4,6\text{-}Me)_2N\}_2Te$).

Bis(2-pyrimidyl)ditelluride: $[TeC_4H_3N_2]_2$

Prepared as mentioned above as dark red crystals, $[TeC_4H_3N_2]_2$ (yield 16.3 g, 72%, m.p. 131 ºC). Anal. Calcd. for $C_8H_6N_4Te_2$: C, 23.25; H, 1.46; N, 13.55% Found C, 23.12; H, 1.43; N, 13.49%. ^{1}H NMR ($CDCl_3$) δ: 6.96 (t, C*H*-5, 2H, 4.8 Hz); 8.45 (d, 4H, 4.8 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 118.7 (C-5), 149.4 (C-Te), 157.5 (C-4,6). $^{125}Te\{^1H\}$ NMR ($CDCl_3$) δ: 127 ppm. Mass (m/z) = 413 (M^+); 286 ($\{C_4H_3N_2\}_2Te$).

Diphenylditelluride (Ph_2Te_2)

The compound was prepared by a reaction between PhMgBr (30.84 g, 19.6 mmol) and magnesium turnings (4.77 g, 19.8 mmol) and tellurium powder (25 g, 19.6 mmol) in diethylether at –78 °C. The reaction mixture was processed similar to Mes_2S_2 to obtain reddish-orange solid (5 g, 30%) m.p. 63 ºC [192]. Anal. Calcd. For $C_{12}H_{10}Te_2$: C, 35.2; H, 2,4 %. Found: C, 35.2; H, 2.4%.

Dimesitylditelluride (Mes_2Te_2)

The synthesis of Mes_2Te_2 was carried out similar to Ph_2Te_2 and was recrystallized from diethyl ether as dark red crystals (6.8 g, 25%) m.p. 122 ºC. Anal. Calcd. For $C_{18}H_{22}Te_2$: C, 43.8; H, 4.5 %. Found: C, 43.8; H, 4.5 % [193].

[$Pb(SMes)_2$]

To a benzene-methanol solution of NaSMes [prepared by a reaction of $NaBH_4$ (0.388 g, 10.2 mmol) with dimesityldisulfide (1.502 g, 4.9 mmol) in methanol], a solution of $Pb(OAc)_2$ (1.882 g, 4.9 mmol) in methanol was added and stirred for 4 h at room temperature whereupon a yellow-brown precipitate formed which was filtered and washed with methanol, water, acetone and ether. The solid was dried in *vacuo* (0.516 g, 20%), m.p. 250 °C. Anal. Calcd for $C_{18}H_{22}S_2Pb$: C, 42.4; H, 4.3. Found: C, 42.3; H, 4.2.

[$Pb(SeC_5H_4N)_2$]

The synthesis of [$Pb(SeC_5H_4N)_2$] was carried out similar to [$Pb(SMes)_2$] and yellow green powder appeared (68 mg, 63%) m.p. 230-232 ºC. Analysis Calcd. For $C_{10}H_8N_2PbSe_2$: C, 23.0; H, 1.54; N 5.37 %. Found: C, 22.6; H, 1.54; N, 5.01 % [194].

Synthesis of metal precursors

$Na_2[PdCl_4]$ [195], $K_2[PtCl_4]$ [196], $[Pd(OAc)_2]_3$ [197] were prepared according to literature methods.

$[PtCl_2(PPh_3)_2]$[198]

To an ethanolic solution (10 cm^3) of PPh_3 (643 mg, 25 mmol), an aqueous solution (30 cm^3) of $K_2[PtCl_4]$ (500 mg, 12 mmol) was added with stirring continued for 2 h at 60 °C. A white precipitate appeared which was filtered and washed thoroughly with water and diethyl ether and air dried. Pertinent data are given in Table 11.

$[PdCl_2(PPh_3)_2]$[199]

To a dichloromethane solution (50 cm^3) of $[PdCl_2(PhCN)_2]$ (3.31 gm, 8.63 mmol) solid PPh_3 (4.53 gm, 17.3 mmol) was added and the reactants were stirred for 5h at room temperature. The yellow precipiate was filtered, washed with hexane and diethyl ether thoroughly to yield $[PdCl_2(PPh_3)_2]$ (6.23 gm, 95%). Similarly complexes $[PdCl_2(P^\frown P)]$ ($P^\frown P$ = dppm, dppe) were prepared in nearly 80% yield.

$[MCl_2(P^\frown P)]$

Complexes were prepared according to reported literature methods [200]. To a solution of $[PdCl_2(PhCN)_2]$ (0.89 g, 2.3 mmol) was added a solution of dppm (0.90 g, 2.3 mmol) in acetone and stirred for 2 h whereupon an off-white precipitate was formed. The precipitate was filtered, washed with water followed by diethyl ether and dried under reduced pressure. Similar procedure was employed for other phosphines, viz. dppe and dppp. Similarly, $[PtCl_2(dppm)]$ was prepared by adding a solution of dppm (0.31 g, 0.81 mmol) in acetone to an aqueous methanolic solution of K_2PtCl_4 (0.34 g, 0.82 mmol), and stirred for 2 h whereupon off-white precipitate was obtained. The precipitate was filtered, washed successively with water and ether and dried under vacuum. The procedure was repeated for other phosphines, viz. dppe and dppp (Table 11).

Table 11: Physical, analytical and NMR data of various platinum(II) and palladium(II) phosphine precursors

Complex	Recrystallization Solvent (% Yield)	Color	m.p. (^{o}C)	% Analysis Found (calcd.) C	% Analysis Found (calcd.) H	$^{31}P\{^{1}H\}$NMR in $CDCl_3$ δ [^{1}J(Pt-P) in Hz]
$[PtCl_2(PPh_3)_2]$	Chloroform (72)	White	310	54.69 (54.69)	3.80 (3.82)	14.4 [^{1}J(Pt-P) = 3087]
$[PtCl_2(dppm)]$	Chloroform (78)	White	330	45.88 (46.17)	3.32 (3.41)	–64.4 [^{1}J(Pt-P) = 3087]
$[PtCl_2(dppe)]$	Chloroform (82)	White	290	47.09 (47.00)	3.64 (3.64)	41.3 [^{1}J(Pt-P) = 3605]
$[PtCl_2(dppp)]$	Chloroform (60)	Pale flesh	230	48.00 (47.80)	3.78 (3.86)	–5.6 [^{1}J(Pt-P) = 3420]
$[PdCl_2(PPh_3)_2]$	Chloroform (69)	Yellow	270	61.60 (61.60)	4.54 (4.31)	23.1
$[PdCl_2(dppm)]$	Chloroform (63)	Cream	340	53.41 (53.46)	3.95 (3.95)	–54.2
$[PdCl_2(dppe)]$	Chloroform (90)	Pale buff	360	54.21 (54.24)	4.07 (4.20)	64.2
$[PdCl_2(dppp)]$	Chloroform (58)	White	>360	54.89 (54.99)	4.32 (4.44)	11.5

$[Pt(PPh_3)_4]$ [201]

To an aqueous ethanolic reaction mixture of $K_2[PtCl_4]$ (450 mg, 11 mmole) and PPh_3 (1.42 g, 54 mmole), an aqueous solution of $NaBH_4$ (123 mg, 32 mmole) was added with stirring which continued for 3h at room temperature whereupon a yellow precipitate formed. The latter was filtered, washed thoroughly with ethanol, cold water and warm ethanol to yield a yellow powder of $[Pt(PPh_3)_4]$. A similar method was used to prepare $[Pd(PPh_3)_4]$ [202].

$[Pt_2(dppm)_3]$ [203]

A mixture of $PtCl_2$(dppm) (276 mg, 42 mmole) and dppm (332 mg, 26 mmole) was suspended in 50 ml dry ethanol. The mixture was warmed until all suspended material dissolved. Eighteen drops of hydrazine hydrate were added to the orange solution, immediately producing a red color and an orange precipitate. The hot suspension was passed through a G -3 sintered disc and washed with dry ethanol. The solid product was purified by dissolving it in a minimum quantity of dichloromethane and immediately filtering the solution into cold ethanol. Finally reprecipitated solid was collected and dried under vacuum.

$[M(P^{\frown}P)_2]$ [204]

The compound $[PtCl_2(dppe)]$ (150mg, 23 mmole) was suspended in 15 ml of ethanol with dppe (90 mg, 23 mmole) and the mixture was refluxed until insoluble part had dissolved. An aqueous solution of $NaBH_4$ (19 mg, 50 mmole) was then added drop wise, which led to evolution of gas and the formation of a yellow precipitate. The resulting solution was stirred for about 2 h. The yellow precipitate was then filtered, washed with water, ethanol and re-crystallized from benzene-ethanol to yield $[Pt(dppe)_2]$. Similarly $[Pt(dppp)_2]$, $[Pd((P^{\frown}P)_2)]$ ($P^{\frown}P$ = dppe, dppp), were prepared (Table 12).

Table 12: Physical, analytical and NMR data of various platinum(0)/palladium(0) phosphine precursors

Complex	Crystallization Solvent (% Yield)	Color	%Analysis Found (calcd.)		$^{31}P\{^1H\}$NMR in $CDCl_3$ δ [^1J(Pt-P) in Hz]
			C	H	
$[Pt(PPh_3)_4]$	Benzene (81)	Ivory Yellow			
$[Pt_2(dppm)_3]$	Dichloromethane-ethanol (63)	Orange	58.48 (58.37)	4.32 (4.31)	40.6 [^1J(Pt-P) = 4507]
$[Pt(dppe)_2]$	Benzene-ethanol (75)	Yellow	67.19 (67.16)	5.01 (5.20)	30.2 [^1J(Pt-P) = 3728]
$[Pt(dppp)_2]$	Benzene-ethanol (66)	Yellow	67.83 (67.70)	5.48 (5.47)	–10.7 [^1J(Pt-P) = 3644]
$[Pd(PPh_3)_4]$	Toluene (83)	Yellow			–
$[Pd(dppe)_2]$	Benzene-ethanol (71)	Orange	74.29 (74.24)	5.47 (5.75)	55.3
$[Pd(dppp)_2]$	Benzene-ethanol (74)	Yellow	74.81 (74.60)	6.12 (6.03)	–

2.2 Synthesis of pyridyl and 3-methyl-2-pyridyltellurolate complexes of platinum(II)

2.2.1 Pyridyl and 3-methyl-2-pyridyltellurolate platinum(II) triphenyl phosphine complexes

$[Pt(TeC_5H_4N)_2(PPh_3)_2]$ and $[Pt(Te\text{-}C_5H_4N)_2Te(PPh_3)]$

(i) To a toluene solution (10 cm^3) of $(C_5H_4N)_2Te_2$ (67 mg, 0.16 mmol) a solution (30 cm^3) of $[Pt(PPh_3)_4]$ (201 mg, 0.16 mmol) in the same solvent was added, with stirring which continued for 4 h at room temperature. The solvent was evaporated in vacuo, and the residue was washed thoroughly with hexane followed by diethyl ether to remove liberated triphenylphosphine. The residue was recrystallized from benzene-acetone to afford two different products, *viz*., a yellow powder $[Pt(TeC_5H_4N)_2(PPh_3)_2]$ (yield 113 mg, 62%), and orange crystals of $[Pt(TeC_5H_4N)_2Te(PPh_3)]$ which were separated mechanically (yield 24 mg, 15%).

(ii) To a dichloromethane solution (15 cm^3) of $[PtCl_2(PPh_3)_2]$ (150 mg, 0.19 mmol) was added a methanolic solution (12 cm^3) of $Na(2\text{-}Te\text{-}C_5H_4N)$ [freshly prepared from $(C_5H_4N)_2Te_2$ (80 mg, 0.19 mmol) and $NaBH_4$ (16.4 mg, 0.22 mmol)]. The mixture was stirred for 5 h whereupon a clear orange solution was obtained. The solvents were evaporated under vacuum. The residue was washed thoroughly with hexane followed by diethyl ether. The product was extracted with benzene, filtered, and passed through a Florisil column. To the resulting solution acetone was added to produce orange crystals of $[Pt(TeC_5H_4N)_2Te(PPh_3)]$ (yield 57 mg, 30%) and a yellow powder $[Pt(TeC_5H_4N)_2(PPh_3)_2]$ (yield 112 mg, 52%).

[Pt{TeC$_5$H$_3$(3-Me)N}$_2$(PPh$_3$)$_2$] and [Pt{TeC$_5$H$_3$(3-Me)N}$_2$Te(PPh$_3$)]

(i) Prepared in a similar fashion as mentioned above adopting method (i), in 69% yield as an orange powder.

(ii) Prepared similar to above method (ii), and recrystallized from benzene-acetone which afforded [Pt{TeC$_5$H$_3$(3-Me)N}$_2$(PPh$_3$)$_2$] (yield 126 mg, 58%) and [Pt{TeC$_5$H$_3$(3-Me)N}$_2$Te(PPh$_3$)] (yield: 22 mg, 12%). The latter was separated mechanically as needle shaped orange crystals. When [Pt{TeC$_5$H$_3$(3-Me)N}$_2$(PPh$_3$)$_2$] was left in CDCl$_3$ solution for several hours, a new species [PtCl{TeC$_5$H$_3$(3-Me)N}(PPh$_3$)] together with a small amount of Ph$_3$PO (29.3 ppm) was identified.

[Pt(TeC$_5$H$_4$N)$_2${PPh$_2$(C$_5$H$_4$N)}$_2$] and [Pt(TeC$_5$H$_4$N)$_2$Te{PPh$_2$(C$_5$H$_4$N)}]

To a dichloromethane solution (20 cm^3) of [PtCl$_2$(PPh$_2$(C$_5$H$_4$N))$_2$] (110 mg, 0.14 mmol) was added a methanolic solution (8 cm^3) of Na(TeC$_5$H$_4$N) [freshly prepared from (C$_5$H$_4$N)$_2$Te$_2$ (57 mg, 0.14 mmol) and NaBH$_4$ (11 mg, 0.29 mmol)] and the mixture was stirred for 6 h. The solvents were evaporated under reduced pressure. The residue was washed thoroughly with hexane followed by diethyl ether. The residue was extracted with dichloromethane, filtered, and passed through a Florisil column. Addition of a few drops of hexane and slow evaporation gave a yellow powder of [Pt(TeC$_5$H$_4$N)$_2${PPh$_2$(C$_5$H$_4$N)}$_2$] (yield 103 mg, 65%) and red crystals of [Pt(TeC$_5$H$_4$N)$_2$Te{PPh$_2$(C$_5$H$_4$N)}] which were separated mechanically (yield 21 mg, 15%) (Table 13).

[Pt{TeC$_5$H$_3$(3-Me)N}$_2${PPh$_2$(C$_5$H$_4$N)}$_2$] and [Pt{TeC$_5$H$_3$(3-Me)N}$_2$Te{PPh$_2$(C$_5$H$_4$N)}]

(i) Prepared in a similar as above and recrystallized from benzene-acetone to obtain a yellow powder [Pt{TeC$_5$H$_3$(3-Me)N}$_2${PPh$_2$(C$_5$H$_4$N)}$_2$] (yield 98 mg, 61%) and orange crystals of

[Pt{TeC_5H_3(3-Me)N}$_2$Te{$PPh_2(C_5H_4N)$}] which were separated mechanically (yield 20 mg, 14%).

Table 13: Physical and analytical data for pyridyl and 3-methyl-2-pyridyltellurolate platinum(II) triphenyl phosphine complexes

Complex	Recrystallisation solvent (%yield)	m.p. (^oC)	% Analysis Found (Calcd.)		
			C	H	N
[Pt(TeC_5H_4N)$_2$(PPh_3)$_2$]	Benzene-acetone	145	47.2	3.4	2.2
	(62)		(48.8)	(3.4)	(2.5)
[Pt(TeC_5H_4N)$_2$Te(PPh_3)]	Benzene-acetone	138	34.9	2.2	1.7
	(15)		(33.8)	(2.3)	(2.8)
[Pt{TeC_5H_3(Me)N}$_2$(PPh_3)$_2$]	Benzene-acetone	171	50.3	3.7	1.9
	(69)		(49.7)	(3.7)	(2.4)
[Pt{TeC_5H_3(Me)N}$_2$Te(PPh_3)]	Benzene-acetone	158	38.7	2.9	2.6
	(12)		(39.2)	(3.0)	(2.5)
[Pt(TeC_5H_4N)$_2${$PPh_2(C_5H_4N)$}$_2$]	Dichloromethane	118-	42.1	3.1	4.1
	(65)	120	(42.4)	(3.1)	(4.2)
[Pt(TeC_5H_4N)$_2$Te{$PPh_2(C_5H_4N)$}]	Dichloromethane	131	32.8	2.2	4.34
	(15)		(32.5)	(2.5)	(4.21)
[Pt{TeC_5H_3(Me)N}$_2${$PPh_2(C_5H_4N)$}$_2$]	Benzene-acetone	158	48.8	3.8	4.3
	(61)		(47.6)	(3.5)	(4.8)

2.2.2. Pyridyl and 3-methyl-2-pyridyltellurolate platinum(II) complexes containing chelating phosphines

[Pt(TeC_5H_4N)$_2$(dppm)] and [Pt{$PPh_2C(TeC_5H_4N)PPh_2$}$_2$]

(i) To a toluene solution (10 cm^3) of $(C_5H_4N)_2Te_2$ (98 mg, 0.24 mmol), a solution (30 cm^3) of [Pt_2(dppm)$_3$] (175 mg, 0.11 mmol) in the same solvent was added with stirring which continued for 4 h at room temperature. The supernatant was decanted and the orange precipitate was washed thoroughly with hexane and diethyl ether, dried under vacuum to afford a yellow powder [Pt($TeC_5H_4N)_2$(dppm)] (yield 75 mg, 67%). The supernatant was passed through a Florisil column and the filtrate was dried under reduced pressure, to give an orange powder, [Pt{$PPh_2C(TeC_5H_4N)PPh_2\}_2$] (yield 32 mg, 21%).

(ii) To a dichloromethane solution (14 cm^3) of [$PtCl_2$(dppm)] (110 mg, 0.17 mmol) was added a methanol-benzene solution (10 cm^3) of Na(TeC_5H_4N) [freshly prepared from $(C_5H_4N)_2Te_2$ (72 mg, 0.17 mmol) in benzene and $NaBH_4$ (13.4 mg, 0.35 mmol) in methanol]. The mixture was stirred for 5 h whereupon a clear orange solution was obtained. The solvents were evaporated under vacuum. The residue was washed thoroughly with hexane followed by diethyl ether. The product was extracted with dichloromethane, filtered, and passed through a Florisil column. The resulting solution was concentrated (5 cm^3) under vacuum and hexane (0.5 cm^3) was added which on refrigeration at –5 °C afforded two different products, *viz*., orange crystals of [Pt{$PPh_2C(TeC_5H_4N)PPh_2\}_2$] (yield 104 mg, 45%) and a yellow powder, [Pt($TeC_5H_4N)_2$(dppm)] (yield 46 mg, 25%) which were separated manually.

[Pt{TeC_5H_3(3-Me)N}$_2$(dppm)] and [Pt{$PPh_2C(TeC_5H_3(3\text{-}Me)N)PPh_2\}_2$]

(i) Prepared similar to the above method (i), and recrystallized from benzene-hexane which afforded an orange powder, [Pt{$PPh_2C(TeC_5H_3(3\text{-}Me)N)PPh_2\}_2$] (yield 24 mg, 18%) and a yellow powder, [Pt{TeC_5H_3(3-Me)N}$_2$(dppm)] (yield 39 mg, 62%).

(ii) Prepared in a similar fashion adopting method (ii), and the crude product was extracted with benzene and recrystallized from benzene-hexane mixture to afford an orange powder, [Pt{$PPh_2C(TeC_5H_3(3\text{-}Me)N)PPh_2\}_2$] (yield 22%) and the benzene-insoluble part of the crude product which was extracted in dichloromethane and recrystallized from dichloromethane-diethyl ether mixture to give a yellow powder, [Pt{TeC_5H_3(3-Me)N}$_2$(dppm)] (Table 14).

[Pt(TeC_5H_4N)$_2$(dppe)]

(i) To a benzene solution (12 cm^3) of $(C_5H_4N)_2Te_2$ (54 mg, 0.13 mmol) a solution (30 cm^3) of [Pt(dppe)$_2$] (125 mg, 0.13 mmol) in the same solvent was added with stirring which continued for 3 h at room temperature. The solvent was evaporated in vacuum, and the residue was washed thoroughly with hexane followed by diethyl ether to remove liberated dppe. The residue was recrystallized from benzene-hexane mixture to afford a yellow powder (yield 86 mg, 68%).

(ii) To a benzene suspension (15 cm^3) of [$PtCl_2$(dppe)] (100 mg, 0.15 mmol) was added a methanolic solution (12 cm^3) of Na(TeC_5H_4N) [freshly prepared from $(C_5H_4N)_2Te_2$ (62 mg, 0.15 mmol) in benzene and $NaBH_4$ (13 mg, 0.34 mmol) in methanol]. The mixture was stirred for 3 h whereupon a clear orange solution was obtained. The solvents were evaporated under vacuum. The residue was washed thoroughly with hexane followed by diethyl ether. The product was extracted with acetone and passed through a Florisil column. To the resulting solution, hexane was added to precipitate the title complex as an orange powder (yield 98 mg, 65%).

[Pt{TeC_5H_3(3-Me)N}$_2$(dppe)]

To a benzene solution (10 cm^3) of {C_5H_3(3-Me)N}$_2Te_2$ (48 mg, 0.11 mmol) a solution (30 cm^3) of [Pt(dppe)$_2$] (110 mg, 0.11 mmol) in the same solvent was added with stirring which continued for 4 h at room temperature. The solvent was evaporated in vacuum, and the residue was washed thoroughly with hexane followed by diethyl ether to remove liberated dppe. The residue was recrystallized from benzene-hexane mixture to afford yellow powder (yield 81 mg, 71%).

[Pt{TeC_5H_3(3-Me)N}(dppe)Cl]

(i) To a benzene suspension (13 cm^3) of [$PtCl_2$(dppe)] (110 mg, 0.17 mmol) was added a methanolic solution (8 cm^3) of Na{TeC_5H_3(3-Me)N} [freshly prepared from {C_5H_3(3-Me)N}$_2Te_2$ (74 mg, 0.17 mmol) in benzene and $NaBH_4$ (13.7 mg, 0.36 mmol)]. The mixture was stirred for 3 h whereupon a clear orange solution was obtained. The solvents were evaporated under vacuum. The residue was washed thoroughly with hexane followed by diethyl ether. The product was extracted with acetone, filtered, and passed through a Florisil column. To the resulting solution hexane was added to yield an orange powder of Pt{TeC_5H_3(3-Me)N}(dppe)Cl (yield 104 mg, 74%). Conductivity measurements (μScm^2mol^{-1}): 3.0 ($CHCl_3$), 70.6 (CH_3CN), 83.3 (CH_3OH).

To prepare good quality crystals, larger anion, Ph_4B^- was used. Thus during the reaction, an acetone solution of $NaBPh_4$ (113 mg, 0.33 mmol) was added to the reaction mixture and stirred for 2 h. The whole solution was centrifuged for 10 minutes. The supernatant was decanted and dried under vacuum to afford an orange powder which was recrystallized from acetone-diethyl ether mixture to yield orange crystals of [Pt_2{TeC_5H_3(3-Me)N}$_2$(dppe)$_2$](BPh_4)$_2$ (yield 80 mg).

[Pt{TeC_5H_3(3-Me)N}$_2$(dppp)] and [Pt_3Te_2(dppp)$_3$]Cl_2

(i) To an acetone solution (15 cm^3) of [$PtCl_2$(dppp)] (97 mg, 0.14 mmol) was added a methanolic solution (12 cm^3) of Na{TeC_5H_3(3-Me)N} [freshly prepared from {C_5H_3(3-Me)N}$_2Te_2$ (69 mg, 0.16 mmol) in benzene and $NaBH_4$ (11.8 mg, 0.31 mmol)]. The mixture was stirred for 4 h whereupon a clear orange solution was obtained. The solvents were evaporated under vacuum. The residue was washed thoroughly with hexane followed by diethyl ether and dried under reduced pressure. The crude product was purified by column chromatography (neutral and active aluminum oxide); eluting with benzene/diethyl ether mixture from which a yellow powder, $[Pt\{TeC_5H_3(3\text{-}Me)N\}_2(dppp)]$ [(yield 58 mg, 39%) was isolated. After separation of $[Pt\{TeC_5H_3(3\text{-}Me)N\}_2(dppp)]$, the column was run using benzene/chloroform mixture (4:1 v/v) giving an orange powder of $[Pt_3Te_2(dppp)_3]Cl_2$ [(yield 107 mg, 35%). To this, a solution $AgSO_3CF_3$ (73 mg, 28 mmol) was added with stirring which continued for 1 h at room temperature. The contents were centrifuged for 5 minutes. The supernatant was decanted, filtered and dried under vacuum to afford a brown powder which was recrystallized from chloroform-diethyl ether mixture to yield yellowish-brown crystals of $[Pt_3Te_2(dppp)_3](SO_3CF_3)_2$.

(ii) To a benzene solution (10 cm^3) of $\{C_5H_3(3\text{-}Me)N\}_2Te_2$ (48 mg, 0.11 mmol) a solution (30 cm^3) of $[Pt(dppp)_2]$ (102 mg, 0.10 mmol) in the same solvent was added with stirring which continued for 4 h at room temperature. The solvent was evaporated in *vacuo* and the residue was washed thoroughly with hexane followed by diethyl ether to remove liberated dppp. The residue was extracted with benzene, filtered and passed through a Florisil column to give a yellow powder, $[Pt\{TeC_5H_3(3\text{-}Me)N\}_2(dppp)]$ (yield 44 mg, 42%) and a benzene insoluble part which was extracted with chloroform to afford orange powder of $[Pt_3Te_2(dppp)_3]Cl_2$ (yield 81 mg, 38%) (Table 14).

Table 14: Synthesis of pyridyl and 3-methylpyridyltellurolate platinum(II) complexes containing chelating phosphines

Complex	Recrystallisation solvent (%yield)	m.p. (^{o}C)	% Analysis: Found (Calcd.)		
			C	H	N
[Pt($TeC_5H_4N)_2$(dppm)]	Dichloromethane-hexane	163	42.58	3.08	3.42
	(25)		(42.42)	(3.05)	(2.82)
[Pt{$PPh_2C(TeC_5H_4N)PPh_2$}$_2$]	Dichloromethane -hexane	48	49.78	3.52	1.56
	(45)		(50.31)	(3.46)	(1.92)
[Pt{TeC_5H_3(3-Me)N}$_2$(dppm)]	Dichloromethane -hexane	170	43.89	3.34	2.64
	(62)		(43.61)	(3.36)	(2.75)
[Pt{$PPh_2C(TeC_5H_3$(3-Me)N)PPh_2}$_2$]	Benzene-hexane	110	53.10	3.78	1.97
	(18)		(53.21)	(3.74)	(2.00)
[Pt($TeC_5H_4N)_2$(dppe)]	Benzene-hexane	178	43.51	3.07	2.96
	(68)		(43.03)	(3.21)	(2.79)
[Pt{TeC_5H_3(3-Me)N}$_2$(dppe)]	Benzene-hexane	185	45.0	3.2	2.8
	(71)		(44.2)	(3.5)	(2.7)
[Pt_2{TeC_5H_3(3-Me)N}$_2$(dppe)$_2$]Cl_2	Acetone-hexane	193	45.68	3.62	1.91
	(74)		(45.28)	(3.56)	(1.65)
[Pt{TeC_5H_3(3-Me)N}$_2$(dppp)]	Benzene-diethyl ether	147	44.36	3.96	2.54
	(39)		(44.74)	(3.66)	(2.67)
[Pt_3Te_2(dppp)$_3$]Cl_2	Benzene-chloroform	169	45.26	3.96	—
	(35)		(45.28)	(3.66)	
[Pt_3Te_2(dppp)$_3$](SO_3CF_3)$_2$	Benzene-chloroform	152	42.34	3.21	—
	(21)		(41.96)	(3.30)	

2.3 Synthesis of pyridyl- and 3-methyl-2-pyridylthiolate, selenolate and tellurolate palladium(II) phosphine complexes

2.3.1 Reactions involving 1, 2-bis(diphenylphosphino)ethane palladium precursors

[Pd(SC_5H_4N)$_2$(dppe)]

This was prepared by a method different from earlier report [205]. To a benzene suspension of [PdCl_2(dppe)] (180 mg, 0.31 mmole) was added a dichloromethane solution of [Pb(SC_5H_4N)$_2$] (140 mg, 0.32 mmole) with stirring which continued for 3 h at room temperature whereupon an orange turbid solution was formed. The latter was centrifuged and passed through Celite and the filtrate was concentrated under reduced pressure. The residue was extracted with dichloromethane, filtered and passed through a Florisil column. Hexane was added to the resulting solution to give an orange powder (yield 147 mg, 65%) (Table 15).

[Pd(SeC_5H_4N)$_2$(dppe)]

(i) To a benzene solution (10 cm^3) of (SeC_5H_4N)$_2$ (62 mg, 0.20 mmol), a solution (30 cm^3) of [Pd(dppe)$_2$] (175 mg, 0.19 mmol) in the same solvent was added with stirring which continued for 4 h at room temperature. The orange solution was concentrated to 5 cm^3 under reduced pressure and on addition of diethyl ether (20 cm^3) a yellow precipitate was formed which was washed thoroughly with diethyl ether. The residue was recrystallized from acetone to afford yellow crystals of the title compound (yield 110 mg, 69%).

(ii) To a benzene suspension of [PdCl_2(dppe)] (130 mg, 0.23 mmol) was added a solution of Pb(SeC_5H_4N)$_2$ (122 mg, 0.23 mmol) with stirring which continued for 6 h at room temperature affording an orange turbid solution. The latter was centrifuged and passed through Celite and the filtrate was concentrated under reduced pressure. The residue was extracted with benzene, filtered, and passed through a Florisil column. Hexane was added to the resulting solution to give a yellow powder (yield 102 mg, 55%).

[Pd{SeC$_5$H$_3$(3-Me)N}$_2$(dppe)]

(i) Prepared in a similar fashion as [Pd(SeC$_5$H$_4$N)$_2$(dppe)] adopting method (i) in 68% yield as a yellow powder.

(ii) Prepared similar to [Pd(SeC$_5$H$_4$N)$_2$(dppe)] using method (ii), and recrystallized from dichloromethnae-hexane (yield 139 mg, 63%). Anal. calcd. for $C_{38}H_{36}N_2P_2PdSe_2$: C, 53.89; H, 4.28; N, 3.31%. Found: C, 53.97; H, 4.53; N, 3.76 %.

[Pd(TeC$_5$H$_4$N)$_2$(dppe)]

Prepared similar to above complex method (ii) using [PdCl$_2$(dppe)] (126 mg, 0.22 mmol) and Pb(TeC$_5$H$_4$N)$_2$ (135 mg, 0.22 mmol) benzene-methanol mixture in 67% (134 mg) yield.

[Pd{TeC$_5$H$_3$(3-Me)N}$_2$(dppe)]

Prepared similar to above (method ii) using [PdCl$_2$(dppe)] (116 mg, 0.20 mmol) and Pb{TeC$_5$H$_3$(3-Me)N}$_2$ (130 mg, 0.20 mmol) in benzene-methanol mixture in 70% (134 mg) yield.

[Pd$_3$(μ-Te)$_2$(dppe)$_3$]Cl$_2$

(i) To a toluene solution (10 cm^3) of (TeC$_5$H$_4$N)$_2$ (80 mg, 0.19 mmol), a solution (30 cm^3) of [Pd(dppe)$_2$] (175 mg, 0.19 mmol) in the same solvent was added with stirring which continued for 4 h at room temperature whereupon an orange precipitate formed. The supernatant was decanted and the precipitate was washed with hexane followed by diethyl ether. The residue was extracted from dichloromethane (which appears to give Cl^-)and after drying under vacuum and recrystallization from acetone-dichloromethane mixture gave red crystals of $[Pd_3(\mu\text{-}Te)_2(dppe)_3]Cl_2$ (yield 91 mg, 77%).

(ii) Similarly the reaction of $\{TeC_5H_3(3\text{-}Me)N\}_2$ (79 mg, 0.18 mmol) with $[Pd(dppe)_2]$ (168 mg, 0.19 mmol) gave $[Pd_3(\mu\text{-}Te)_2(dppe)_3]Cl_2$ which was recrystallized from acetone dichloromethane to afford red crystals (yield 78 mg, 69%).

(iii) To a benzene suspension (15 cm^3) of $[PdCl_2(dppe)]$ (250 mg, 0.43 mmol) was added a methanol-benzene solution (10 cm^3) of $NaTeC_5H_4N$ [prepared from $(TeC_5H_4N)_2$ (180 mg, 0.43 mmol) in benzene and $NaBH_4$ (33 mg, 0.87 mmol) in methanol]. The mixture was stirred for 3 h, whereupon a clear red solution was obtained. The solvents were evaporated under reduced pressure. The residue was washed with hexane followed by diethyl ether. The product was extracted with acetone-dichloromethane and passed through a Florisil column which on slow evaporation gave red crystals of $[Pd_3(\mu\text{-}Te)_2(dppe)_3]Cl_2$ (yield 210 mg, 79%). Similarly the reaction between $[PdCl_2(dppe)]$ (250 mg, 0.43 mmol) and $Na\{TeC_5H_3(3\text{-}Me)N\}$[from $\{TeC_5H_3(3\text{-}Me)N\}_2$ (195 mg, 0.44 mmol) in benzene and $NaBH_4$ (35 mg, 0.92 mmol) in methanol], after processing and recrystallization, afforded red crystals of $[Pd_3(\mu\text{-}Te)_2(dppe)_3]Cl_2$ (yield 194 mg, 73%).

2.3.2 Reactions involving 1, 3-bis(diphenylphosphino)propane palladium precursors

$[Pd(SC_5H_4N)_2(dppp)]$

Prepared in a manner similar to $[Pd(SC_5H_4N)_2(dppe)]$ using $[PdCl_2(dppp)]$ (100 mg, 0.17 mmol) and $Pb(SC_5H_4N)_2$ (75 mg, 0.18 mmol) in 58% (72 mg) yield as orange crystalline solid, m.p. 137 ºC (dec.).

$[Pd(SeC_5H_4N)_2(dppp)]$

(i) Prepared similar to $[Pd(SeC_5H_4N)_2(dppe)]$ (method i) using $(SeC_5H_4N)_2$ (30 mg, 0.096 mmol) and $[Pd(dppp)_2]$ (80 mg, 0.086 mmol) in benzene as a brown powder, (yield 48 mg, 67%) (Table 15).

(ii) To a benzene suspension of $[PdCl_2(dppp)]$ (90 mg, 0.15 mmol) was added a solution of $Pb(SeC_5H_4N)_2$ (83 mg, 0.16 mmol) with stirring which continued for 6 h at room temperature whereupon a turbid orange solution formed. The latter was centrifuged and passed through Celite and the solvent was evaporated under reduced pressure. The residue was washed with diethyl ether. The product was extracted with benzene, filtered and passed through a Florisil column and the resulting solution on addition of hexane produced an orange powder, $[Pd(SeC_5H_4N)_2(dppp)]$ (yield 41 mg, 32%). The benzene insoluble part was extracted with dichloromethane and precipitated by addition of hexane as a brown powder, $[Pd_2(\mu\text{-}SeC_5H_4N)_2(dppp)_2]Cl_2$ (yield 54 mg, 50%,). Even on prolonged stirring (16 h) of the reactants, both ($[Pd(SeC_5H_4N)_2(dppp)]$ and $[Pd_2(\mu\text{-}SeC_5H_4N)_2(dppp)_2]Cl_2$) products were formed.

$[Pd_2(\mu\text{-}SeC_5H_3(3\text{-}Me)N)_2(dppp)_2]Cl_2$

(i) To a benzene solution (10 cm^3) of $\{SeC_5H_3(3\text{-}Me)N\}_2$ (58 mg, 0.17 mmol) a solution (15 cm^3) of $[Pd(dppp)_2]$ (150 mg, 0.16 mmol) in the same solvent was added with stirring which continued for 5 h at room temperature. The contents were concentrated under reduced pressure and diethyl ether (15 ml) was added to precipitate a yellow powder. The residue was extracted with dichloromethane which on drying under vacuum afforded an orange powder, (yield 61 mg, 52%).

(ii) To a benzene suspension of [$PdCl_2$(dppp)] (60 mg, 0.10 mmol) was added a solution of Pb{SeC_5H_3(3-Me)N}$_2$ (57 mg, 0.10 mmol) with stirring which continued for 6 h at room temperature. The orange turbid solution was centrifuged and passed through Celite and the solvent was evaporated under reduced pressure. The orange residue was washed with diethyl ether. The product was extracted with dichloromethane, filtered, and passed through a Florisil column. To the resulting solution hexane was added to afford a brown powder (yield 50 mg, 68%).

[Pd(TeC_5H_4N)$_2$(dppp)]

To a benzene suspension of [$PdCl_2$(dppp)] (60 mg, 0.10 mmol) was added Pb(TeC_5H_4N)$_2$ (64 mg, 0.10 mmol) with stirring which continued for 6 h at room temperature whereupon a turbid red solution was obtained. The contents were centrifuged and passed through Celite and the solvent was reduced under vacuum. The residue was washed with hexane and diethyl ether. The product was extracted with benzene, filtered and passed through a Florisil column. To the resulting solution, hexane was added to obtain red crystals (yield 52 mg, 55%).

[Pd_2{μ-TeC_5H_3(3-Me)N}$_2$(dppp)$_2$]Cl_2

To a benzene suspension of [$PdCl_2$(dppp)] (80 mg, 0.14 mmol) was added a solution of Pb{TeC_5H_3(3-Me)N}$_2$ (91 mg, 0.14 mmol) with stirring which continued for 5 h at room temperature to give a turbid red solution. The contents were centrifuged for 10 minutes and the supernatant was passed through Celite. The solvent was removed under reduced pressure. The residue was washed with hexane and diethyl ether. The product was extracted with benzene, filtered and passed through a Florisil column. To the resulting solution, hexane was added to afford red crystals (yield 61 mg, 58%). The benzene insoluble part (yield 14 mg, 20%) was extracted with dichloromethane which on concentration gave an organge powder identified as $[Pd_3(\mu\text{-}Te)_2(dppp)_3]Cl_2$.

$[Pd_3(\mu\text{-}Te)_2(dppp)_3]Cl_2$

(i) To a toluene solution (10 cm^3) of $(TeC_5H_4N)_2$ (42 mg, 0.10 mmol), a solution (30 cm^3) of $[Pd(dppp)_2]$ (90 mg, 0.096 mmol) in the same solvent was added with stirring which continued for 4 h at room temperature. An orange precipitate formed during the reaction was filtered and washed thoroughly with diethyl ether. The precipitate was extracted with dichloromethane which on slow evaporation gave orange crystals of $[Pd_3(\mu\text{-}Te)_2(dppp)_3]Cl_2$ (yield 45 mg, 73%). Similarly the reaction between $\{TeC_5H_3(3\text{-}Me)N\}_2$ (43 mg, 0.10 mmol) and $[Pd(dppp)_2]$ (85 mg, 0.09 mmol) in toluene gave $[Pd_3(\mu\text{-}Te)_2(dppp)_3]Cl_2$ in 72% yield).

(ii) To a benzene suspension (15 cm^3) of $[PdCl_2(dppp)]$ (125 mg, 0.21 mmole) was added a methanol-benzene solution (10 cm^3) of $NaTeC_5H_4N$ [prepared from $(TeC_5H_4N)_2$ (90 mg, 0.22 mmole) in benzene and $NaBH_4$ (16.9 mg, 0.45 mmole) in methanol]. The mixture was stirred for 3 h, whereupon a clear red solution was obtained. The solvents were evaporated under reduced pressure. The residue was washed with hexane followed by diethyl ether. The product was extracted with dichloromethane and passed through a Florisil column. The resulting solution on slow evaporation gave orange-red crystals of $[Pd_3(\mu\text{-}Te)_2(dppp)_3]Cl_2$ (yield 86 mg, 65%). Similarly, reaction of $[PdCl_2(dppp)]$ (115 mg, 0.19 mmole) with $NaTeC_5H_3(3\text{-}Me)N$ [prepared from $\{TeC_5H_3(3\text{-}Me)N\}_2$ (90 mg, 0.21 mmole) in benzene and $NaBH_4$ (16.9 mg, 0.45 mmole) in methanol] gave orange-red crystals in 83% (101 mg) yield.

Table 15: Physcial and analytical data for pyridyl- and 3-methyl-2-pyridylthio, seleno and tellurolate palladium(II) phosphine complexes

Complex	Recrystallisation solvent (%yield)	m.p. (°C)	% Analysis : Found (Calcd.)		
			C	H	N
[Pd($SC_5H_4N)_2$(dppe)]	Dichloromethane (65)	181	59.91 (59.62)	4.38 (4.45)	3.51 (3.86)
[Pd($SeC_5H_4N)_2$(dppe)]	Acetone (69)	175	52.70 (52.80)	3.94 (3.93)	3.24 (3.42)
[Pd{SeC_5H_3(3-Me)N}$_2$(dppe)]	Acetone (68)	167	53.48 (53.89)	4.08 (4.28)	3.22 (3.31)
[Pd($TeC_5H_4N)_2$(dppe)]	Benzene-methanol (67)	189	47.69 (47.23)	3.38 (3.52)	3.48 (3.06)
[Pd{TeC_5H_3(3-Me)N}$_2$(dppe)]	Benzene-methanol (70)	181	48.88 (48.33)	3.72 (3.84)	2.48 (2.96)
[Pd_3(μ-Te)$_2$(dppe)$_3$]Cl_2	Acetone-dichloromethane (77)	193	50.70 (50.89)	3.46 (3.94)	
[Pd($SC_5H_4N)_2$(dppp)]	Dichloromethane (58)	58	59.91 (60.12)	4.38 (4.63)	3.51 (3.78)
[Pd($SeC_5H_4N)_2$(dppp)]	Benzene (67)	146	52.85 (53.35)	3.98 (4.11)	3.75 (3.36)

[Pd$_2$(μ-Se-C$_5$H$_4$N)$_2$(dppp)$_2$]Cl$_2$	Dichloromethane- hexane	159	54.09	4.23	1.84
	(50)		(54.03)	(4.25)	(1.96)
[Pd$_2$(μ-SeC$_5$H$_3$(3-Me)N)$_2$(dppp)$_2$]Cl$_2$	Dichloromethane	153	54.79	4.33	2.14
	(52)		(54.63)	(4.45)	(1.93)
[Pd(TeC$_5$H$_4$N)$_2$(dppp)]	Benzene- hexane	173	47.98	3.72	3.48
	(55)		(47.77)	(3.68)	(3.01)
[Pd$_2${μ-TeC$_5$H$_3$(3-Me)N}$_2$(dppp)$_2$]Cl$_2$	Benzene- hexane	179	51.88	4.38	2.10
	(58)		(51.20)	(4.17)	(1.81)
[Pd$_3$(μ-Te)$_2$(dppp)$_3$]Cl$_2$	Dichloromethane	212	51.43	4.23	
	(72)		(51.67)	(4.17)	
[Pd(TeC$_5$H$_4$N)$_2$(PPh$_3$)$_2$]	Acetone	137	52.84	3.69	2.56
	(67)		(53.00)	(3.67)	(2.69)
[Pd{TeC$_5$H$_3$(3-Me)N}$_2$(PPh$_3$)$_2$]	Acetone	164	53.99	4.08	2.65
	(62)		(53.85)	(3.95)	(2.62)
[PdCl{TeC$_5$H$_3$(3-Me)N}(PPh$_3$)]	Acetone	150	45.92	3.38	2.76
	(71)		(46.20)	(3.39)	(2.25)
[PdCl{Te(Cl)$_2$C$_5$H$_3$(3-Me)N}(PPh$_3$)]	Chloroform	110	41.83	3.45	1.87
	(16)		(41.49)	(3.04)	(2.01)

2.3.3 Reaction involving triphenylphosphine palladium complexes

[Pd(TeC$_5$H$_4$N)$_2$(PPh$_3$)$_2$]

To a benzene solution (10 cm^3) of (TeC$_5$H$_4$N)$_2$ (52 mg, 0.13 mmol), a solution (30 cm^3) of [Pd(PPh$_3$)$_4$] (140 mg, 0.12 mmol) in the same solvent was added with stirring which continued for 4 h at room temperature. The solvent was evaporated under vacuum and the residue was washed thoroughly with diethyl ether to remove liberated triphenylphosphine. The residue was recrystallized from acetone to afford a brown powder (yield 84 mg, 67%).

[Pd{TeC$_5$H$_3$(3-Me)N}$_2$(PPh$_3$)$_2$]

[Pd{TeC$_5$H$_3$(3-Me)N}$_2$(PPh$_3$)$_2$] was prepared by the reaction between {TeC$_5$H$_3$(3-Me)N}$_2$ (77 mg, 0.18 mmol) and [Pd(PPh$_3$)$_4$] (193 mg, 0.17 mmol) in benzene similar to [Pd{TeC$_5$H$_3$(3-Me)N}$_2$(PPh$_3$)$_2$] (yield 111 mg, 62%) (Table 15).

[PdCl{Te(Cl)$_2$C$_5$H$_3$(3-Me)N}(PPh$_3$)]

When a CDCl$_3$ solution of [Pd{TeC$_5$H$_3$(3-Me)N}$_2$(PPh$_3$)$_2$] was left for a few hrs, it turned greenish and after processing, green crystals of the title complex were manually separated. Similarly when the complex [PdCl{TeC$_5$H$_3$(3-Me)N}(PPh$_3$)], prepared according to reported method [206] and left in CDCl$_3$ solution for a few days turned dark green, depositing green crystals of [PdCl{Te(Cl)$_2$C$_5$H$_3$(3-Me)N}(PPh$_3$)] in the NMR tube.

2.4 Synthesis of pyrimidylselenolate and tellurolate complexes of platinum(II) and palladium(II)

[Pt($SeC_4H_3N_2$)$_2$(PPh_3)$_2$]

To a benzene solution (15 cm^3) of ($SeC_4H_3N_2$)$_2$ (38 mg, 0.12 mmol) a solution (30 cm^3) of [Pt(PPh_3)$_4$] (140 mg, 0.11 mmol) in the same solvent was added with stirring and the contents were stirred for 5 h at room temperature. The solvent was evaporated in *vaccuo* and the residue was washed thoroughly with hexane followed by diethyl ether to remove liberated phosphine. The residue was extracted with dichloromethane, filtered and passed through a Florisil column The ensuing solution on refrigeration at –5 °C afforded yellow crystals of the title complex (yield 82 mg, 70%) on prolonged standing in solution gave [Pt{η^2-$SeC_4H_3N_2$}{$SeC_4H_3N_2$}(PPh_3)] (Table 16).

[Pt{$SeC_4H(4,6\text{-}Me)_2N_2$}$_2$($PPh_3$)$_2$]

Prepared in a similar fashion adopting above method and recrystallized from dichloromethane-hexane mixture as yellow crystals (yield 103 mg, 74%) on prolonged standing in solution gave [Pt{η^2-$SeC_4H(4,6\text{-}Me)_2N_2$}({$SeC_4H(4,6\text{-}Me)_2N_2$}($PPh_3$)].

[Pd{η^2-$SeC_4H_3N_2$}{$SeC_4H_3N_2$}PPh_3)]

To a benzene solution (10 cm^3) of ($SeC_4H_3N_2$)$_2$ (48 mg, 0.15 mmol), a solution (30 cm^3) of [Pd(PPh_3)$_4$] (168 mg, 0.15 mmol) in the same solvent was added with continuous stirring for 4 h at room temperature. The solvent was evaporated under vacuum and the residue was washed thoroughly with diethyl ether to remove liberated triphenylphosphine and was recrystallized from dichloromethane to afford red crystals of the title complex (yield 75 mg, 75%).

[Pd{η^2-$SeC_4H(4,6\text{-}Me)_2N_2$}{$SeC_4H(4,6\text{-}Me)_2N_2$}($PPh_3$)]

Prepared similar to above method and recrystallized from dichloromethane gave red crystals (yield 65 mg, 68%).

[Pt{$SeC_4H_3N_2$}$_2$(dppp)]

Prepared similar to above method and recrystallized from dichloromethane as a yellow powder (yield 87 mg, 70%).

[Pt{$SeC_4H(4,6\text{-}Me)_2N_2$}$_2$(dppe)]

Prepared similar to above method using [$PtCl_2$(dppe)] (96 mg, 0.14 mmol) and $NaSeC_4H(4,6\text{-}Me)_2N_2$ [freshly prepared from {$SeC_4H(4,6\text{-}Me)_2N_2$}$_2$ (53 mg, 0.14 mmol) in benzene and $NaBH_4$ (12 mg, 0.32 mmol) in methanol] in yield 67% (93 mg).

[Pt{$TeC_4H(4,6\text{-}Me)_2N_2$}$_2$(dppe)]

Prepared and recrystallized similar to above method as a yellow powder (yield 106 mg, 68%).

[Pt{$SeC_4H(4,6\text{-}Me)_2N_2$}$_2$(dppp)]

Prepared in a similar fashion as above and recrystallized from dichloromethane as yellow powder (yield 85 mg, 64%,).

[Pt{$TeC_4H(4,6\text{-}Me)_2N_2$}$_2$(dppp)]

Prepared and recrystallized in a similar fashion as above, brown powder (yield 101 mg, 65%). When a $CDCl_3$ solution of the complex was left for more than 24 h, red crystals of [Pt_3(μ-

$Te)_2(dppe)_3]Cl_2$ (^{31}P NMR = -13.5 ppm) were formed, analysis and NMR data were consitent with other preparations.

$[Pt\{SeC_4H_3N_2\}_2(dppe)]$

To a benzene suspension (10 cm^3) of $[PtCl_2(dppe)]$ (90 mg, 0.13 mmol) was added a methanol-benzene solution (10 cm^3) of $NaSeC_4H_3N_2$ [freshly prepared from $(SeC_4H_3N_2)_2$ (50 mg, 0.16 mmol) in benzene and $NaBH_4$ (12 mg, 0.32 mmol) in methanol]. The reactants were stirred for 5 h at room temperature to give a yellow solution. The solvents were removed under vacuum and the residue was washed with diethyl ether and dried under reduced pressure. The product was extracted with dichloromethane, filtered and passed through a Florisil column. The resulting solution was concentrated (5 cm^3) under vacuum which on slow evaporation at room temperature gave a yellow powder (yield 79 mg, 64%). The latter in $CDCl_3$ solution on prolonged period afforded yellow crystals of a trinuclear complex of the compostion, $[Pt_3Se_2(dppe)_3]Cl_2$.

$[Pt\{TeC_4H(4,6\text{-}Me)_2N_2\}_2(dppm)]$

To a benzene suspension (10 cm^3) of $[PtCl_2(dppm)]$ (120 mg, 0.18 mmol) was added a methanol-benzene solution (10 cm^3) of $NaTeC_4H(4,6\text{-}Me)_2N_2$ [freshly prepared from $\{TeC_4H(4,6\text{-}Me)_2N_2\}_2$ (90 mg, 0.19 mmol) in benzene and $NaBH_4$ (15 mg, 0.40 mmol) in methanol]. The mixture was stirred for 6 h whereupon a turbid orange solution was formed. The solvents were decanted and the precipitate was washed thoroughly with diethyl ether and extracted with dichloromethane, filtered, and passed through a Florisil column. The resulting solution was concentrated (5 cm^3) under vacuum and hexane (0.5 cm^3) was added which on refrigeration at –5 ^{o}C afforded orange crystals (yield 139 mg, 72%).

[Pt_3(μ-Te)$_2$(dppe)$_3$]Cl_2

To a benzene suspension (14 cm^3) of [$PtCl_2$(dppe)] (120 mg, 0.18 mmol) was added a methanol-benzene solution (10 cm^3) of $NaTeC_4H_3N_2$ [freshly prepared from $(TeC_4H_3N_2)_2$ (75 mg, 0.18 mmol) in benzene and $NaBH_4$ (14 mg, 0.37 mmol) in methanol]. The mixture was stirred for 5 h whereupon an orange solution was obtained. The solvents were removed under reduced pressure. The residue was washed thoroughly with diethyl ether and dried under vacuum. The product was extracted with dichloromethane, filtered and passed through a Florisil column. The resulting solution was concentrated (5 cm^3) under vacuum and hexane (0.5 cm^3) was added which on refrigeration at –5 ^{o}C afforded an orange powder (yield 75 mg, 59%).

[Pt_3(μ-Te)$_2$(dppp)$_3$]Cl_2

Prepared similar to above method and recrystallized from dichloromethane-diethyl ether mixture as red crystals (yield 64 mg, 62%).

[Pd_3(μ-Se)$_2$(dppe)$_3$]Cl_2

Prepared similar to above method using [$PdCl_2$(dppe)] (96 mg, 0.17 mmole) and either $NaSeC_4H(4,6\text{-}Me)_2N_2$ [prepared from $\{SeC_4H(4,6\text{-}Me)_2N_2\}_2$ (62 mg, 0.17 mmole) in benzene and $NaBH_4$ (14 mg, 0.37 mmole) in methanol] or $NaSeC_4H_3N_2$ [prepared from $(SeC_4H_3N_2)_2$ (54 mg, 0.17 mmole) in benzene and $NaBH_4$ (13.3 mg, 0.35 mmole) in methanol] and extracted with dichloromethane which on slow evaporation gave an orange crystalline solid in 52-56% yield.

$[Pd_3(\mu\text{-}Se)_2(dppp)_3]Cl_2$

Prepared, extracted with dichloromethane and recrystallized in a similar fashion using $[PdCl_2(dppp)]$ and $NaSeC_4H_3N_2$ or $NaSeC_4H(4,6\text{-}Me)_2N_2$ as yellow crystalline solid in 70% yield.

$[Pd_3(\mu\text{-}Te)_2(dppe)_3]Cl_2$

Prepared in a similar fashion adopting method (i) in 61% yield as a red crystal, m.p. 193ºC (dec.). Anal. calcd. for $C_{78}H_{72}Cl_2P_6Pd_3Te_2$: C, 50.89; H, 3.94%. Found: C, 50.63; H, 3.79%. Similarly, prepared in a manner to above method (ii) using reaction of $[PdCl_2(dppe)]$ (101 mg, 0.18 mmole) with $NaTeC_5H_3N_2$ [prepared from $(TeC_5H_3N_2)_2$ (75 mg, 0.18 mmole) in benzene and $NaBH_4$ (14 mg, 0.37mmole) in methanol] gave red crystals in 63% (68 mg) yield.

$[Pd_3(\mu\text{-}Te)_2(dppp)_3]Cl_2$

Prepared in a similar fashion as above adopting method (i) in 72% yield as red crystals. Similarly, prepared in a manner as above method (ii) using reaction of $[PdCl_2(dppp)]$ (108 mg, 0.18 mmole) with $NaTeC_5H_3N_2$ [prepared from $(TeC_5H_3N_2)_2$ (77 mg, 0.19 mmole) in benzene and $NaBH_4$ (15 mg, 0.39 mmole) in methanol] gave red crystals in 69% (79 mg) yield (Table 16).

Table 16: Physical and analytical data for pyrimidylselenolate and tellurolate complexes of platinum(II) and palladium(II)

Complex	Recrystallisation solvent (%yield)	m.p.(^{0}C)	% Analysis: Found (Calcd.)		
			C	H	N
[Pt($SeC_4H_3N_2$)$_2$(PPh_3)$_2$]	Dichloromethane (70)	192	50.85 (51.02)	3.36 (3.50)	5.52 (5.41)
[Pt{SeC_4H(4,6-Me)$_2N_2$}$_2$(PPh_3)$_2$]	Dichloromethane (74)	208	52.31 (52.80)	4.21 (4.06)	5.28 (5.13)
[Pd{$SeC_4H_3N_2$}{η^2-$SeC_4H_3N_2$}(PPh_3)]	Dichloromethane (75)	169	45.73 (45.60)	3.30 (3.09)	7.89 (8.18)
[Pd{SeC_4H(4,6-Me)$_2N_2$}{η^2-SeC_4H(4,6-Me)$_2N_2$}(PPh_3)]	Dichloromethane (68)	182	48.28 (48.63)	3.78 (3.94)	7.63 (7.56)
[Pt{$SeC_4H_3N_2$}$_2$(dppe)]	Dichloromethane (64)	129	45.34 (44.89)	3.23 (3.32)	5.89 (6.16)
[Pt_3Se_2(dppe)$_3$]Cl_2	Chloroform (24)	268	47.12 (46.62)	3.79 (3.61)	
[Pt{$SeC_4H_3N_2$}$_2$(dppp)]	Dichloromethane (70)	183	45.67 (45.51)	3.55 (3.49)	5.98 (6.06)
[Pt{TeC_4H(4,6-Me)$_2N_2$}$_2$(dppm)]	Dichloromethane-hexane (72)	129	42.28 (42.36)	3.43 (3.46)	5.21 (5.34)
[Pt{SeC_4H(4,6-Me)$_2N_2$}$_2$(dppe)]	Dichloromethane (67)	176	46.91 (47.26)	3.78 (3.97)	5.72 (5.80)

$[Pt\{TeC_4H(4,6\text{-}Me)_2N_2\}_2(dppe)]$	Dichloromethane	163	43.12	3.48	5.51
	(68)		(42.94)	(3.60)	(5.27)
$[Pt\{SeC_4H(4,6\text{-}Me)_2N_2\}_2(dppp)]$	Dichloromethane	121	47.69	4.28	5.95
	(64)		(47.81)	(4.12)	(5.72)
$[Pt\{TeC_4H(4,6\text{-}Me)_2N_2\}_2(dppp)]$	Dichloromethane	174	43.92	3.89	4.89
	(65)		(43.49)	(3.74)	(5.20)
$[Pt_3(\mu\text{-}Te)_2(dppe)_3]Cl_2$	Dichloromethane-hexane	167	44.10	3.63	
	(59)		(44.47)	(3.44)	
$[Pt_3(\mu\text{-}Te)_2(dppp)_3]Cl_2$	Dichloromethane-diethyl ether	182	45.44	3.42	
	(62)		(45.28)	(3.66)	
$[Pd_3(\mu\text{-}Se)_2(dppe)_3]Cl_2$	Dichloromethane-hexane	293	54.01	4.39	
	(56)		(53.74)	(4.16)	
$[Pd_3(\mu\text{-}Se)_2(dppp)_3]Cl_2$	Dichloromethane-hexane	275	54.71	4.73	
	(70)		(54.49)	(4.40)	
$[Pd_3(\mu\text{-}Te)_2(dppe)_3]Cl_2$	Dichloromethane	193	51.13	3.67	
	(63)		(50.89)	(3.94)	
$[Pd_3(\mu\text{-}Te)_2(dppp)_3]Cl_2$	Dichloromethane	212	51.54	4.04	
	(69)		(51.67)	(4.18)	

2.5 Syntheis of nicotinamide based organoselenolate complexes of paltinum and palladium

[Pt{η^2-SeC$_5$H$_3$(3-CONH$_2$)N}{SeC$_5$H$_3$(3-CONH$_2$)N}(PPh$_3$)]

To a benzene suspension (10 cm^3) of [2-NC$_5$H$_3$(3-CONH$_2$)Se]$_2$ (49 mg, 0.12 mmol), a solution (30 cm^3) of [Pt(PPh$_3$)$_4$] (150 mg, 0.12 mmol) in the same solvent was added with stirring which continued for 4 h at room temperature. The solvent was evaporated under vacuum and the residue was washed thoroughly with diethyl ether to remove liberated triphenylphosphine. The residue was recrystallized from dichloromethane to afford yellow crystals (yield 66 mg (64%) (Table 17).

[Pd{η^2-SeC$_5$H$_3$(3-CONH$_2$)N}{SeC$_5$H$_3$(3-CONH$_2$)N}(PPh$_3$)]

Prepared similar to [Pt{η^2-SeC$_5$H$_3$(3-CONH$_2$)N}{SeC$_5$H$_3$(3-CONH$_2$)N}(PPh$_3$)] and recrystallized from dichloromethane-hexane mixture as orange crystals (yield 49 mg (72%)).

[Pt{η^2-SeC$_5$H$_3$(3-CONHPh)N}{SeC$_5$H$_3$(3-CONHPh)N}(PPh$_3$)]

Prepared similar to [Pt{η^2-SeC$_5$H$_3$(3-CONH$_2$)N}{SeC$_5$H$_3$(3-CONH$_2$)N}(PPh$_3$)] as a yellow powder (yield 70 mg (69%), m.p. 179 ^{o}C).

[Pd{η^2-SeC$_5$H$_3$(3-CONHPh)N}{SeC$_5$H$_3$(3-CONHPh)N}(PPh$_3$)]

Prepared similar to [Pt{η^2-SeC$_5$H$_3$(3-CONH$_2$)N}{SeC$_5$H$_3$(3-CONH$_2$)N}(PPh$_3$)] and recrystallized from benzene on refrigeration as dark red crystals (yield 67 mg, 73%).

[Pt{η^2-SeC$_5$H$_3$(3-CONHpym)N}{SeC$_5$H$_3$(3-CONHpym)N}(PPh$_3$)]

Prepared similar to [Pt{η^2-SeC$_5$H$_3$(3-CONH$_2$)N}{SeC$_5$H$_3$(3-CONH$_2$)N}(PPh$_3$)] as a red powder (yield 44 mg, 61%).

[Pt(Cl){SeC$_5$H$_3$(3-COOH)N}(PPh$_3$)$_2$]

To a benzene–methanol solution (20 cm^3) of [2-NC$_5$H$_3$(3-COOH)Se]$_2$ (59 mg, 0.15 mmol), added a solution (25 cm^3) of [Pt(PPh$_3$)$_4$] (175 mg, 0.14 mmol) in the same solvent with continuous stirring for 5 h at room temperature. The contents were concentrated under reduced pressure and diethyl ether (15 ml) was added to give a yellow precipitate which was filtered and recrystallized from dichloromethane-ethanol mixture as yellow crystals, (yield 104 mg (77%). Conductivity measurements (μScm^{2}mol^{-1}): 4.1 (CHCl$_3$), 8.4 (CH$_3$CN), 230.8 (CH$_3$OH).

[Pd(Cl){SeC$_5$H$_3$(3-COOH)N}(PPh$_3$)$_2$]

Prepared similar to [Pt(Cl){SeC$_5$H$_3$(3-COOH)N}(PPh$_3$)$_2$] as an orange powder, (yield 48 mg (38%). Conductivity measurements (μScm^{2}mol^{-1}): 1.2 (CHCl$_3$), 4.1 (CH$_3$CN), 198.2 (CH$_3$OH). However, further recrystallization of [Pd(Cl){SeC$_5$H$_3$(3-COOH)N}(PPh$_3$)$_2$] in dichloromethane-ethanol mixture gave a brown powder, [Pd(Cl){SeC$_5$H$_3$(3-COOH)N}(PPh$_3$)] (yield 46 mg (41%).

***trans*-[Pt(I){SeC$_5$H$_3$(3-CONHPh)N}(PPh$_3$)$_2$]**

To a benzene solution (10 cm^3) of [2-NC$_5$H$_3$(3-CONHPh)SeI] (64 mg, 0.16 mmol), a solution (15 cm^3) of [Pt(PPh$_3$)$_4$] (198 mg, 0.16 mmol) in the same solvent was added with stirring which continued for 5 h at room temperature. The contents were concentrated under reduced pressure and diethyl ether (15 ml) was added to yield a yellow precipitate which was filtered out and dried under vacuum to give a yellow powder (yield 132 mg (74%)).

When a $CDCl_3$ solution of *trans*-$[Pt(I)\{SeC_5H_3(3\text{-}CONHPh)N\}(PPh_3)_2]$ was allowed to stand at room temperature for 3-4 hrs, a new complex $[Pt(I)\{\eta^2\text{-}SeC_5H_3(3\text{-}CONHPh)N\}(PPh_3)]$ with the liberation of free phosphine converted in to phosphine oxide, was formed. When *trans*-$[Pt(I)\{SeC_5H_3(3\text{-}CONHPh)N\}(PPh_3)_2]$ was left in CH_2Cl_2 for recrystallization for more than two days, yellow crystals of $[Pt(I)(Ph)(PPh_3)_2]$ (yield 34 mg) were formed which were manually separated. The yellow-orange insoluble part, sticking to the flask, was separated and the filtrate (A) was collected. The insoluble part was dissolved in acetonitrile and filtered, from which an orange insoluble part was filtered out and identified as $[PtI_2(PPh_3)_2]$ (yield 17 mg). The acetonitrile filtrate on recrystallization gave cream crystals of $[Pt(Cl_{0.5}I_{0.5})\{C_5H_3(3\text{-}CONHPh)N\}(PPh_3)_2].HCl$ (16 mg). The filtrate-A on drying under vacuum yielded a brown powder which was thoroughly washed with diethyl ether and characterized as $[2\text{-}NC_5H_3(3\text{-}CO)SeNH]$ (10 mg).

$[Pd(I)\{\eta^2\text{-}SeC_5H_3(3\text{-}CONHPh)N\}(PPh_3)]$

To a benzene solution (10 cm^3) of $[2\text{-}NC_5H_3(3\text{-}CONHPh)SeI]$ (57 mg, 0.14 mmol), a solution (15 cm^3) of $[Pd(PPh_3)_4]$ (160 mg, 0.14 mmol) in the same solvent was added with stirring which continued for 6 h at room temperature, whereupon a brown powder formed. The powder was filtered out and dried under vacuum to give the title complex, $[Pd(I)\{\eta^2\text{-}SeC_5H_3(3\text{-}CONHPh)N\}(PPh_3)]$ (yield 28 mg (52%)). The supernatant solution was concentrated to 2 ml and on addition of diethyl ether (15 cm^3) a red powder, $[Pd(I)(Ph)(PPh_3)_2]$ (yield 16 mg, 28%,) was precipitated which was separated by filtering through a G-3 filtering unit and dried in *vacuo*. The filtrate was dried in vacuum to give a brown powder which was identified as $[2\text{-}NC_5H_3(3\text{-}CO)SeNH]$. (Table 17)

Table 17: Physcial and analytical data of nicotinamide based organoselenolate complexes of paltinum and palladium

Complex	Recrystallisation solvent (%yield)	m.p. (^{0}C)	% Analysis Found(calcd.)			IR (cm^{-1})	
			C	H	N	$\nu_{C=O}$	$\nu_{NH/OH}$
[Pt{SeC_5H_3(3-$CONH_2$)N}$_2$(PPh_3)]	Dichloromethane	193	41.84	2.89	6.56	1670	3340(asym)
	(64)		(42.02)	(2.94)	(6.53)		3285 (sym)
[Pd{SeC_5H_3(3-$CONH_2$)N}$_2$(PPh_3)]	Dichloromethane -hexane	189	45.98	2.99	6.85	1654	3337(asym)
	(72)		(46.86)	(3.27)	(7.28)		3150 (sym)
[Pt{SeC_5H_3(3-CONHPh)N}$_2$(PPh_3)]	Dichloromethane -hexane	179	49.89	3.41	5.58	1656	3295
	(69)		(49.96)	(3.29)	(5.55)		
[Pd{SeC_5H_3(3-CONHPh)N}$_2$(PPh_3)]	Benzene	174	53.94	3.54	6.35	1632	3294
	(73)		(54.77)	(3.61)	(6.08)		
[Pt{SeC_5H_3(3-CONHpym)N}$_2$(PPh_3)]	Dichloromethane	185	50.04	3.35	12.03	1654	3345
	(61)		(49.34)	(3.16)	(12.11)		
[Pt(Cl){SeC_5H_3(3-COOH)N}(PPh_3)$_2$]	Dichloromethane-ethanol	238	52.89	3.69	1.58	1602	3346
	(77)		(52.76)	(3.58)	(1.46)		
[Pd(Cl){SeC_5H_3(3-COOH)N}(PPh_3)$_2$]	Dichloromethane-ethanol	213	57.19	4.69	2.50	1595	3347
	(38)		(58.15)	(3.95)	(1.61)		
[Pd(Cl){SeC_5H_3(3-COOH)N}(PPh_3)]	Dichloromethane-ethanol	201	47.69	3.49	3.95	1590	3056
	(41)		(47.63)	(3.16)	(2.31)		
[Pt(I){SeC_5H_3(3-CONHPh)N}(PPh_3)$_2$]	Benzene-diethylether	151	51.72	3.43	2.34	1669	3051
	(74)		(51.34)	(3.50)	(2.49)		

$[Pt(I)(Ph)(PPh_3)_2]$	Dichloromethane	182	55.32	3.33	—	—	—
	(12)		(54.61)	(3.82)			
$[Pt(Cl_{0.5}I_{0.5})\{C_5H_3(3\text{-}CONHPh)N\}(PPh_3)_2].HCl$	Acetonitrile	168	55.72	3.89	2.64	1681	3054
	(11)		(55.73)	(3.90)	(2.71)		
$[Pd(I)\{SeC_5H_3(3\text{-}CONHPh)N\}(PPh_3)]$	Dichloromethane	138	46.32	3.15	3.67	1654	3344
	(52)		(46.69)	(3.13)	(3.63)		
$[Pd(I)(Ph)(PPh_3)_2]$	Dichloromethane	201	59.97	4.39	—	—	—
	(28)		(60.41)	(4.22)			

2.6 Syntheis of arylchalcogenolate complexes of palladium(II) and platinum(II)

2.6.1 Synthesis of palladium(II) complexes

[Pd(SMes)$_2$(dppe)]

To a benzene suspension of [PdCl$_2$(dppe)] (120 mg, 0.21 mmole), a dichloromethane solution of [Pb(SMes)$_2$] (110 mg, 0.22 mmole) was added with stirring which continued for 8 h at room temperature. The orange turbid solution was thus formed, was centrifuged and passed through Celite. The filtrate was concentrated under reduced pressure. The residue was extracted with dichloromethane, filtered and passed through a Florisil column. On addition of hexane to this solution resulted in to an orange powder which was filtered and dried under vacuum (yield 109 mg, 65%). Similarly [Pd(SMes)$_2$(dppp)] was prepared (Table 18).

[Pd(SeMes)$_2$(dppe)]

To a benzene suspension (12 cm^3) of [PdCl$_2$(dppe)] (100 mg, 0.17 mmol) was added a methanol-benzene solution (10 cm^3) of NaSeMes [prepared from (SeMes)$_2$ (72 mg, 0.18 mmol) in benzene and NaBH$_4$ (15 mg, 0.40 mmol) in methanol]. The mixture was stirred for 4 h, whereupon a clear red solution was obtained. The solvents were evaporated under reduced pressure. The residue was washed with hexane followed by diethyl ether. The product was extracted with chloroform and passed through a Florisil column which on slow evaporation gave red crystals of [Pd(SeMes)$_2$(dppe)] (yield 122 mg, 78%). Similarly [Pd(SeMes)$_2$(dppp)] was synthesized.

[Pd(TeMes)$_2$(dppe)]

To a benzene suspension (10 cm^3) of [PdCl$_2$(dppe)] (95 mg, 0.17 mmol) was added a methanol-benzene solution (10 cm^3) of NaTeMes [freshly prepared from (TeMes)$_2$ (85 mg, 0.17

mmol) in benzene and $NaBH_4$ (13 mg, 0.34 mmol) in methanol]. The reactants were stirred for 5 h at room temperature to give wine red solution. The solvents were removed under vacuum and the residue was washed with diethyl ether and dried under reduced pressure. The product was extracted with benzene, filtered and passed through a Florisil column. The resulting solution was concentrated (5 cm^3) under vacuum which on slow evaporation at room temperature gave red powder (yield 79 mg, 48 %,). When a $CDCl_3$ solution of this complex was left for several hours, red crystals of a trinuclear tellurido complex, $[Pd_3(\mu\text{-}Te)_2(dppp)_3]Cl_2$ were isolated.

Table 18: Physical and analytical data mesityl chalcogenolate complexes of palladium(II)

Complex	Recrystallization solvent (% yield)	m.p. (^oC)	% Analysis: Found (Calcd.)	
			C	H
$[Pd(SMes)_2(dppe)]$	Dichloromethane-hexane (65)	163	65.88 (65.46)	5.62 (5.74)
$[Pd(SeMes)_2(dppe)]$	Dichloromethane-hexane (78)	153	58.44 (58.69)	5.23 (5.15)
$[Pd(TeMes)_2(dppe)]$	Acetone (48)	145	52.97 (52.93)	4.59 (4.64)
$[Pd_3(\mu\text{-}Te)_2(dppe)_3]Cl_2$	Dichloromethane (42)	193	49.99 (50.89)	3.67 (3.94)
$[Pd(SMes)_2(dppp)]$	Dichloromethane-hexane (63)	161	65.73 (65.80)	5.73 (5.89)
$[Pd(SeMes)_2(dppp)]$	Dichloromethane-hexane (61)	148	58.89 (59.06)	5.16 (5.29)
$[Pd_3(\mu\text{-}Te)_2(dppp)_3]Cl_2$	Chloroform (50)	212	51.21 (51.67)	4.23 (4.18)

$[Pd_3(\mu\text{-}Te)_2(dppp)_3]Cl_2$

To a benzene suspension (15 cm^3) of $[PdCl_2(dppp)]$ (120 mg, 0.20 mmole) was added a methanol-benzene solution (10 cm^3) of NaTeMes [prepared from $(TeMes)_2$ (104 mg, 0.21 mmole) in benzene and $NaBH_4$ (15.9 mg, 0.42 mmole) in methanol]. The mixture was stirred for 3 h, whereupon a clear red solution was obtained. The solvents were evaporated under vaccum. The residue was washed with hexane followed by diethyl ether. The product was extracted with dichloromethane and passed through a Florisil column. The resulting solution on slow evaporation gave orange-red crystals of the title complex (yield 64 mg, 52%).

2.6.2 Synthesis of platinum complexes

$[Pt(SMes)_2(dppm)]$

To a benzene suspension of $[PtCl_2(dppm)]$ (100 mg, 0.15 mmole) was added a dichloromethane solution of $[Pb(SMes)_2]$ (82 mg, 0.16 mmole) with stirring which continued for 6 h at room temperature whereupon an yellow turbid solution was formed. The latter was centrifuged and passed through Celite and the filtrate was concentrated under reduced pressure. The residue was extracted with dichloromethane, filtered and passed through a Florisil column. Hexane was added to the resulting solution to give an yellow powder (yield 81 mg, 60%). Similarly $[Pt(SMes)_2(dppe)]$ and $[Pt(SMes)_2(dppp)]$ were prepared (Table 19).

$[Pt(SeMes)_2(dppm)]$

To a benzene suspension (15 cm^3) of $[PtCl_2(dppm)]$ (120 mg, 0.18 mmol) was added a methanol-benzene solution (10 cm^3) of NaSeMes [prepared from $(SeMes)_2$ (80 mg, 0.20 mmol) in benzene and $NaBH_4$ (16 mg, 0.42 mmol) in methanol]. The mixture was stirred for 4 h, whereupon a clear yellow solution was obtained. The solvents were evaporated under reduced pressure. The residue was washed with hexane followed by diethyl ether. The product was extracted with dichloromethane and passed through a Florisil column which on slow evaporation gave yellow crystals of [Pt(SeMes)$_2$(dppm)]. Similarly all other selonolate complexes were prepared.

[Pt(TeMes)$_2$(dppm)]

To a benzene suspension (10 cm^3) of [PtCl$_2$(dppm)] (125 mg, 0.19 mmol) was added a methanol-benzene solution (10 cm^3) of NaTeMes [freshly prepared from (TeMes)$_2$ (94 mg, 0.19 mmol) in benzene and NaBH$_4$ (15 mg, 0.40 mmol) in methanol]. The reactants were stirred for 5 h at room temperature to give a red solution. The solvents were removed under vacuum and the residue was washed with diethyl ether and dried under reduced pressure. The product was extracted with benzene, filtered and passed through a Florisil column. The resulting solution was concentrated (5 cm^3) under vacuum which on slow evaporation at room temperature gave red crystals (yield 86 mg, 42%). Similarly all other tellurolate complexes were prepared.

Table 19: Physical and analytical data for $[Pt(EAr)_2(P^{\cap}P)]$ (E = S, Se, Te)

Complex	Recrystallization solvent (% yield)	m.p. (°C)	% Analysis: Found (Calcd.)		
			C	H	S or N
$[Pt(TePh)_2(dppm)]$	Acetone-hexane (56)	167	45.23 (44.93)	3.49 (3.26)	
$[Pt(Tetol)_2(dppm)]$	Acetone-hexane (48)	159	45.83 (46.06)	4.01 (3.57)	
$[Pt(SMes)_2(dppm)]$	Dichloromethane-hexane (60)	172	58.12 (58.55)	5.23 (5.03)	7.71 (7.27)
$[Pt(SeMes)_2(dppm)]$	Dichloromethane-hexane (58)	197	53.01 (52.93)	4.83 (4.55)	–
$[Pt(TeMes)_2(dppm)]$	Benzene-diethyl ether (42)	181	48.62 (48.13)	4.44 (4.13)	–
$[Pt(SeC_4H_3N_2)_2(dppm)]$	Dichloromethane-hexane (67)	144	44.38 (44.25)	3.15 (3.15)	6.11 (6.25)
$[Pt\{SeC_4H(4,6\text{-}Me_2)N_2\}_2(dppm)]$	Dichloromethane-hexane (74)	127	46.84 (46.69)	3.88 (3.81)	5.91 (5.89)
$[Pt(Tetol)_2(dppe)]$	Acetone (56)	-	46.74 (46.60)	3.69 (3.71)	
$[Pt(SMes)_2(dppe)]$	Dichloromethane-hexane (64)	179	58.34 (58.98)	5.03 (5.17)	7.01 (7.15)

[Pt(SeMes)$_2$(dppe)]	Dichloromethane-diethyl ether	124	52.66	4.52	–
	(62)		(53.39)	(4.68)	
[Pt(TeMes)$_2$(dppe)]	Acetone-diethyl ether	178	48.38	4.31	–
	(51)		(48.61)	(4.27)	
[Pt{SeC$_5$H$_3$(3-Me)N}$_2$(dppe)	Dichloromethane-hexane	193	48.89	3.76	2.98
	(73)		(48.78)	(3.88)	(3.00)
[Pt(TePh)$_2$(dppp)]	Acetone-hexane	169	46.12	3.45	
	(52)		(46.06)	(3.57)	
[Pt(Tetol)$_2$(dppp)]	Acetone-hexane	187	47.01	3.77	
	(48)		(47.12)	(3.86)	
[Pt(SMes)$_2$(dppp)]	Acetone-hexane	161	59.21	5.43	6.89
	(54)		(59.39)	(5.31)	(7.04)
[Pt(SeMes)$_2$(dppp)]	Dichloromethane-hexane	168	54.09	4.66	–
	(69)		(53.84)	(4.82)	
[Pt(TeMes)$_2$(dppp)]	Benzene-diethyl ether	132	49.21	4.37	–
	(58)		(49.08)	(4.39)	
[Pt(SeC$_5$H$_4$N)$_2$(dppp)]	Dichloromethane-hexane	168	48.45	3.68	2.98
	(73)		(48.21)	(3.72)	(3.04)
[Pt{SeC$_5$H$_3$(3-Me)N}$_2$(dppp)]	Dichloromethane-hexane	134	49.54	4.11	2.91
	(71)		(49.32)	(4.03)	(2.95)

3.1 Chemistry of pyridyl and 3-methyl-2-pyridyltellurolate complexes of platinum

Oxidative addition reactions of diorganodichalcogenides (REER) to palladium(0) and platinum(0) complexes have been of considerable interest for quite some time [105]. This reaction finds applications in regio- and stereo-selective E-E addition to C≡C bonds in organic synthesis [113, 207-213] and also provides a convenient route to metal chalcogenolate complexes which have relevance in materials science [214].

3.1.1 Chemistry of non-chelated phosphine compounds of platinum with bis(2-pyridyl)ditellurides

The reactions of diorganoditellurides with Pd(0) and Pt(0) complexes were shown to be much more complex, affording several products [117]. For instance, the reaction of $[Pd(PPh_3)_4]$ with Th_2Te_2 in dichloromethane yields a hexanuclear complex, $[Pd_6Cl_2(Te_4)(TeTh)_2(PPh_3)_6]$, together with several other unidentified products [117,120]. When carried out in toluene, this reaction affords yet another hexanuclear complex, $[Pd_6(Te_4)(TeTh)_4(PPh_3)_6]$, while Chia and McWhinnie [215] have reported the formation of the expected binuclear compound $[Pd_2(\mu\text{-}TeTh)_2(TeTh)_2(PPh_3)_2]$. A similar reaction with $[Pt(PPh_3)_4]$, however, yielded $[Pt_3Te_2(Th)(PPh_3)_5]Cl$ and $[PtCl(Th)(PPh_3)_2]$ [120, 216]. The complexes, $[Pd_6Cl_2(Te_4)(TeTh)_2(PPh_3)_6]$, $[Pd_6(Te_4)(TeTh)_4(PPh_3)_6]$ and $[Pt_3Te_2(Th)(PPh_3)_5]Cl$, have tellurido-bridges which are formed via cleavage of Te-C bond. The cleavage of Te-C bonds has also been reported in reactions of telluro-ethers with platinum(0) compounds [217, 218]. The distinct reactivity of tellurium ligands may be attributed to comparable bond energies of Te-Te and Te-C bonds and increased metallic character of Te from lighter chalcogens (S or Se).

With this view, the chemistry of palladium(II) and platinum(II) complexes with hemilabile 2-pyridyltellurolate ligands (Te-C_5H_4N) [206] has been examined. The complexes observed exhibited distinct structural and reactivity features, which were different from those containing simpler organotellurolate ligands.

Synthesis and spectroscopy

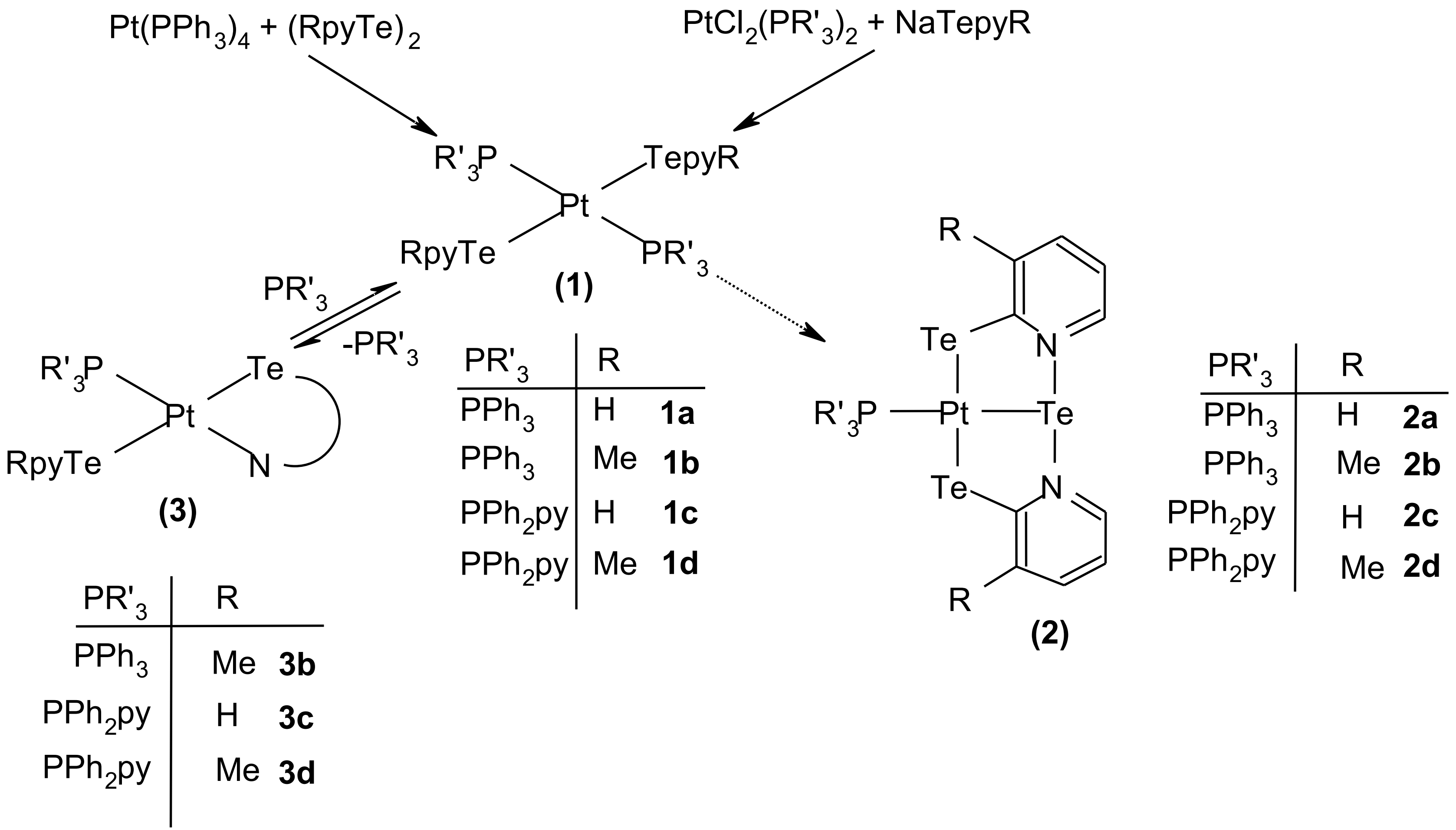
Reaction of [Pt(PPh_3)$_4$] with {C_5H_3(3-R) N}$_2$Te$_2$ (R = H or Me) at room temperature afforded yellow to orange products of oxidative addition, [Pt{TeC_5H_3(3-R)N}$_2$(PPh_3)$_2$] (**1**), together with small amounts of crystalline material, [Pt{TeC_5H_3(3-R)N}$_2$Te(PPh_3)] (**2**) (Scheme 15). Compounds **1** can also be obtained by treatment of [PtCl$_2$(PR_3)$_2$] with Na{TeC_5H_3(3-R)N}, readily prepared by the reductive cleavage of the Te-Te bond of corresponding bis(pyridyl)ditellurides with $NaBH_4$ in methanol (Scheme 15) as described earlier by us for [Pt{TeC_5H_3(3-Me)N}$_2$(PPh_3)$_2$] **(1b)** [206]. On attempted recrystallization of the products obtained from these reactions, compounds [Pt{TeC_5H_3(3-R)N}$_2$(PPh_3)$_2$] **(1)** were obtained as a yellow-orange powder, accompanied by crystalline [Pt{TeC_5H_3(3-R)N}$_2$Te(PPh_3)] (**2**).

The ^{31}P NMR spectra of [Pt{TeC_5H_3(3-R)N}$_2$(PPh_3)$_2$] **(1)** displayed single resonance with ^{195}Pt-^{31}P couplings. Compounds **1** undergo dissociation of the phosphine ligand in solution to give [Pt{η^2-TeC_5H_3(3-R)N}{TeC_5H_3(3-R)N}(PPh_3)] **(3)** and thus establish a dynamic equilibrium with **1**. The complexes **1a**, **1c** and **1d** exhibited a ^{31}P resonance at $\delta \sim 22$ ppm with $^1J \sim 3230$ Hz. The ^{195}Pt NMR spectrum of [Pt{TeC_5H_4N}$_2$(PPh_3)$_2$] **(1a)** displayed a triplet at $\delta = -4228$ ppm [^1J(Pt-P) = 3251 Hz], indicating coordination of two mutually trans triphenylphosphine ligand [87, 92]. The $^{31}P\{^1H\}$ NMR spectrum of [Pt{TeC_5H_3(3-Me)N}$_2$(PPh_3)$_2$] consists of a single resonance at 7.2 ppm with ^1J(Pt-P) = 3711 Hz. The former resonance has been assigned to [Pt(Te$\frown$NC_5H_3Me){TeC_5H_3(3-Me)N}(PPh_3)] (**3b**).

Coordination of one PPh_3 ligand in **3a** is further corroborated by ^{195}Pt NMR spectrum which showed a doublet centered at -4810 ppm, due to coupling with one ^{31}P nucleus. Several attempts to remove PPh_3 from the complex either by repeated recrystallization or by treatment with air to convert into $OPPh_3$ were unsuccessful. In solution complex $[Pt\{TeC_5H_3(3\text{-}Me)N\}_2(PPh_3)_2]$ (**1b**) exists as $[Pt(Te\frown NC_5H_3Me)\{TeC_5H_3(3\text{-}Me)N\}(PPh_3)]$ (**3b)** in which the PPh_3 ligand is trans to the nitrogen atom of the chelated $TeC_5H_3(3\text{-}Me)N$ ligand. The complexes **1c** and **1d**, when left in solution for a few hours, showed signals due to **3c** and **3d** in their ^{31}P NMR spectra with ^{1}J(Pt-P) of ~3830 Hz (Table 20).

The complexes $[Pt\{TeC_5H_3(3\text{-}R)N\}_2Te(PPh_3)]$ (**2**), isolated in low yields as orange crystalline solids during the synthesis of $[Pt\{TeC_5H_3(3\text{-}R)N\}_2(PPh_3)_2]$ (**1**), exhibit a single $^{31}P\{^{1}H\}$ NMR resonance at ~20 ppm with ^{195}Pt satellites. The magnitude of ^{1}J(Pt-P) (2945-3028 Hz) is indicative of a strong trans influence of the new, formally Te^0 ligand (see below). It is also within the range expected for platinum(II) telluride and tellurolate complexes [219]. In order to distinguish tellurolate and the coordinated tellurium atom, XPS measurements were carried out. The XPS chemical shifts for tellurium ($3d_{5/2}$ and $3d_{3/2}$) in different oxidation states appear in a narrow region. For instance, the shifts for Te metal [573.1 ($3d_{5/2}$) and 583.5 ($3d_{3/2}$) eV] [220], diphenylditelluride [573.9 ($3d_{5/2}$) and 584.3 ($3d_{3/2}$) eV] [220] and CdTe [576 ($3d_{5/2}$) and 586 ($3d_{3/2}$) eV] [221] differ only slightly and are only of limited diagnostic value [222] (cf. below). The XPS study of $[Pt\{TeC_5H_4N\}_2Te(PPh_3)]$ (**2a)** exhibited signals for tellurium at 575.0 ($3d_{5/2}$) and 585.4 ($3d_{3/2}$) eV.

All complexes are colored and show absorption in their uv-vis spectra in toluene solutions. The bands are red-shifted with respect to the ditelluride ligands. The highest occupied molecular orbital (HOMO) is considered to be centred on the tellurolate ligands, whereas the lowest unoccupied molecular orbital (LUMO) is probably delocalised with significant contributions from the phosphine co-ligand [93].



PR'3	R	
PPh$_3$	H	**1a**
PPh$_3$	Me	**1b**
PPh$_2$py	H	**1c**
PPh$_2$py	Me	**1d**

PR'3	R	
PPh$_3$	H	**2a**
PPh$_3$	Me	**2b**
PPh$_2$py	H	**2c**
PPh$_2$py	Me	**2d**

PR'3	R	
PPh$_3$	Me	**3b**
PPh$_2$py	H	**3c**
PPh$_2$py	Me	**3d**

Scheme 15: Reaction of [Pt(PPh$_3$)$_4$] and [PtCl$_2$(PR$_3$’)$_2$] with dipyridyl ditellurides and sodium 2-pyridyl tellurolates, respectively.

Table 20: ^{1}H, $^{31}P\{^{1}H\}$ and $^{195}Pt\{^{1}H\}$ NMR data for 2-pyridyltellurolate complexes of platinum(II) nonchelated phosphines

Complex		^{1}H δ in ppm	$^{31}P\{^{1}H\}$ δ in ppm	$^{195}Pt\{^{1}H\}$ δ in ppm
$[Pt(TeC_5H_4N)_2(PPh_3)_2]$	**1a**	7.08 (m, Ph + py), 7.49 (br), 7.88 (m); 7.99 (br, py)	23.5 [^{1}J (Pt-P) = 3241 Hz]	-4228 [t, ^{1}J(Pt-P) = 3251 Hz]
$[Pt(TeC_5H_4N)_2(PPh_2(C_5H_4N))_2]$	**1c**	5.32 (CH_2Cl_2), 6.20-8.12 (m, py + Ph)	23.3 [^{1}J (Pt-P) = 3222 Hz]	—
$[Pt\{TeC_5H_3(Me)N\}_2(PPh_2(C_5H_4N))_2]$	**1d**		22.2 [^{1}J (Pt-P) = 3231 Hz]	—
$[Pt(TeC_5H_4N)_2Te(PPh_3)]$	**2a**	6.15 (t, 6.6 Hz, C_5H_4N 2-H), 6.33 (td, 1.2 Hz (d), 6.6 Hz (t), C_5H_4N 2-H), 7.13 (m, C_6H_5), 7.48 (d, C_5H_4N), 8.11 (m, Ph), 8.59 (d, 6 Hz, 2-H, C_5H_4N)	21.1 [^{1}J(Pt-P) = 3028 Hz]	—
$[Pt\{TeC_5H_3(3\text{-}Me)N\}_2Te(PPh_3)]$	**2b**		21.3 [^{1}J (Pt-P) = 2982 Hz]	—
$[Pt(TeC_5H_4N)_2Te(PPh_2(C_5H_4N))]$	**2c**	5.31 (CH_2Cl_2); 6.90 (t, 6 Hz, Te-py), 7.14 (t, 6 Hz, Te-C_5H_4N) 7.43 (br, C_6H_5); 7.67 (d, 8 Hz, Te-C_5H_4N), 7.74 (br), 7.90 (br, C_6H_5); 8.39 (t), 8.72 (d, 6 Hz, Te-C_5H_4N), 8.81 (d, 6 Hz)	17.8 [^{1}J (Pt-P) = 2992 Hz]	—
$[Pt\{TeC_5H_3(Me)N\}_2Te\{PPh_2(C_5H_4N)\}]$	**2d**	2.26 (s, Me); 6.91 (t, 6 Hz, H-5, 2-Te-C_5H_3(Me)N), 7.11 (d, 7.2 Hz, H-4, 2-Te-C_5H_3(Me)N); 8.67 (d, 6 Hz, H-6, 2-Te-C_5H_3(Me)N); 7.43 (br), 7.95 (br) [Ph-P]; 7.77 (br m), 8.56 (t, 6 Hz) [py-P]	20.5 [^{1}J (Pt-P) = 2945 Hz]	—
$[Pt\{TeC_5H_3(3\text{-}Me)N\}_2(PPh_3)]$	**3b**	2.25 (s, Me); 6.973 (m, 6-H), 7.37 (m, C_6H_5), 7.81 (br), 8.65 (br, py)	7.2 [^{1}J (Pt-P) = 3768 Hz], -5.3 (PPh_3)	-4810 [d, ^{1}J (Pt-P) = 3713Hz]

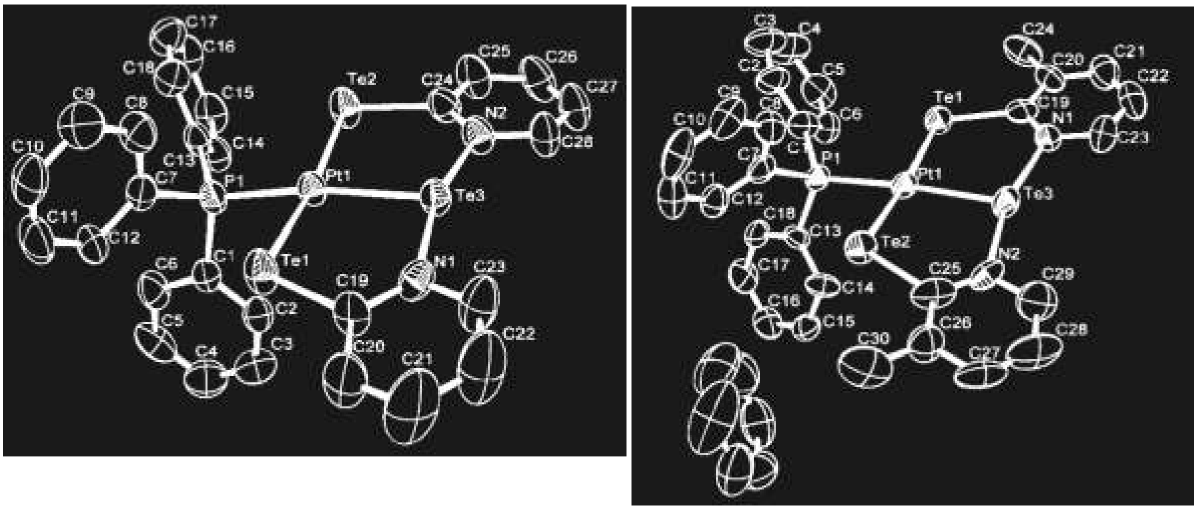
X-ray Crystallography

The molecular structures of [Pt{TeC_5H_4N}$_2$Te(PPh_3)] (**2a)** and [Pt{TeC_5H_3(3-R)N}$_2$Te(PPh_3)] (**2b.**C_6H_6) were established by single crystal X-ray diffraction analyses. ORTEP drawings with the atomic numbering scheme are shown in Figures 1 and 2, and selected interatomic parameters are summarized in Table 21.

The two structures are rather similar involving discrete molecules with distorted square planar environments around the platinum(II) center and a "Te_3P" coordination core. The two mutually trans 2-pyridinetellurolate ligands are bound by the central platinum(II) atom in a monodentate fashion through the tellurolate atoms. For both [Pt{TeC_5H_4N}$_2$Te(PPh_3)] (**2a**) and [Pt{TeC_5H_3(3-R)N}$_2$Te(PPh_3)] (**2b**) the nitrogen atoms of the pyridyl rings are conected to the "bare" tellurium atom (Te3) with a N1-Te3-N2 angle of about 166°. The deviation of the N-Te-N angle from linearity is rather small and may be assigned to repulsion from two non-bonding pairs of electrons. The tellurium(0) atoms (Te3) thus adopt a "bent T" configuration. Its geometry can be defined as distorted trigonal-bipyramidal with the platinum and two lone pairs at the equatorial positions and two pyridyl nitrogen atoms occupying the axial sites. Based on the isoelectronic relationship between Te^0 and I^{+I} the observed novel bis(pyridine)tellurium(0) structural motif in **1b** and **2b** can be compared with the well known, [223, 224] theoretically studied [225] and synthetically applied [226] bis(pyridine)iodonium cations.

$[C_5H_4N\text{-}I\text{-}C_5H_4N]^+$ $[C_5H_4N\text{-}Te\text{-}C_5H_4N]^0$

In both cases the empty 5p orbital interacts with the pyridine lone pairs, leading to the straightened N-E-N angle and, for [Pt{TeC_5H_4N}$_2$Te(PPh_3)] (**2a)**, to the observed XPS shift in the direction of Te^{-II}. The chelate-promoted coplanarity of the bis(pyridine)element entity in **1b** and **2b** was noted [224] and analyzed [225] similarly for $[C_5H_4N\text{-}I\text{-}C_5H_4N]^+$. The steric



(a) **(b)**

Figure 1: The molecular structures of (a) $[Pt(TeC_5H_4N)_2Te(PPh_3)]$ and (b) $[Pt\{TeC_5H_3(3\text{-}Me)N\}_2Te(PPh_3)].C_6H_6$

requirements by the pyridyl tellurolates groups are probably responsible for the slightly increased deviation of $(C_5H_4)N\text{-}E\text{-}N(C_5H_4)$ from 180^o [224] in the present situation. This deviation, however, receives additional stabilization through coordination of all three Te atoms to the metal in a tridentate fashion. Remarkably, all Pt-Te distances (2.5690(19)-2.612(3) Å) are similar and are slightly longer than those reported for $[PtCl(TeCH_2CH_2NMe_2)(PR_3)]$ (2.5261(5) Å) [93] but are comparable to those in complexes containing tellurolate ligands trans to phosphine (e.g., cis-$[Pt(TeTh)_2(dppe)]$ (2.607, 2.6594(9) Å) [227]. cis-$[Pt(1,2\text{-}Te_2C_6H_4)(PPh_3)_2]$ (2.586(1) Å) [228] or trans-$[Pt(TeCOC_6H_4Me\text{-}4)_2(PEt_3)_2]$ (2.592(1), 2.632(2) Å) [229]. The Pt-P distances are as expected [227, 228]. The slight lengthening of the Pt-Te distances may be attributed to the strong trans influence of tellurolate. The Te-N distances (2.297(7)-2.357(7) Å) are well within the range reported in organotellurium compounds, e.g., $R_2Te(N_3)_2$ (2.180-2.253 Å) [230], $[\{Ph_2TeN_3\}_2O]$ (2.397(8) Å) [231] or $[\{Ph_2Te(NCS)\}_2O]$ (2.40(1) Å) [232].

Table 21: Selected bond lengths (Å) and angles (°) of [Pt(TeC$_5$H$_4$N)$_2$Te(PPh$_3$)] **2a** and [Pt{TeC$_5$H$_3$(3-Me)N}$_2$Te(PPh$_3$)].C$_6$H$_6$ (**2b.**C$_6$H$_6$)

	[Pt(TeC$_5$H$_4$N)$_2$Te(PPh$_3$)] (**2a**)		[Pt{TeC$_5$H$_3$(3-Me)N}$_2$Te(PPh$_3$)].C$_6$H$_6$ (**2b.**C$_6$H$_6$)	
	Exp.	Calc.[a]	Exp.	Calc.[a]
Pt1-Te1	2.5940(7)	2.659	2.588(3)	2.662
Pt1-Te3	2.5752(6)	2.631	2.569(2)	2.643
Pt1-Te2	2.5720(7)	2.638	2.612(3)	2.686
Te3-N1	2.357(7)	2.386	2.35(1)	2.388
Te3-N2	2.297(7)	2.373	2.32(1)	2.410
Pt1-P1	2.282(2)	2.298	2.283(3)	2.297
Te2-C24	2.103(9)	2.119	2.11(2) (Te2-C25)	2.162
Te1-C19	2.088(8)	2.119	2.10(1)	2.162
N2-Te3-N1	166.1(2)	166.3	165.4(4)	166.8
N2-Te3-Pt1	96.6(2)	96.4	97.1(3)	96.1
N1-Te3-Pt1	96.6(2)	96.6	97.5(3)	96.9
C24-Te2-Pt1	104.6(2)	104.2	104.8(5)(C25-Te2-Pt1)	104.3
C19-Te1-Pt1	104.6(2)	104.4	106.4(4)	104.9
Te3-Pt1-Te1	92.83(2)	92.4	91.59(6)	91.9
Te2-Pt1-Te3	92.56(2)	92.5	91.40(7)	91.5
Te2-Pt1-Te1	172.74(2)	173.4	173.99(4)	171.6
P1-Pt1-Te2	89.29(6)	89.4	86.99(10)	86.8
P1-Pt1-Te3	171.40(6)	171.8	175.56(9)	173.6
P1-Pt1-Te1	86.10(6)	86.3	90.40(10)	90.4

[a] PBE/ZORA+SO calculations.

Density functional calculations

In order to gain more insights over the charge distributions for **2a** and **2b**, all-electron Density Functional calculations were done, employing the Hirshfeld and Voronoi deformation density (VDD) which are partitioning schemes for selected atoms and fragments [233]. The calculated data suggests that the three tellurium atoms (Te1, Te2 and Te3) exhibit similar charge density. We performed a detailed analyses focusing on the charge distribution for the Te3 and Pt1 atoms, and the fragments denoted by the 2-pyridiltellurolate ([Te-py]$^{1-}$ and [Te-pyMe]$^{1-}$ for **2a** and **2b**, respectively), and the triphenylphosphine (PPh_3) ligands (Table 3). Similar results are observed for Hirshfeld and VDD analyses, thus herein we focus on the former. The Hirshfeld analyses, shows that the platinum (Pt1) atom gains about 0.132 ē from the triphenylphosphine and about 0.966 ē from each pyridiltellurolate ligands, to give a total charge of -0.059 in the region defined by the Hirshfeld scheme. Similar conclusions are obtained for **2b**. Thus, the calculations are consistent with the suggestion that the tri-coordinated tellurium(0) atom (Te3) act as a zero valent ligand.

Table 22: Hirshfeld and VDD charge analyses for selected atoms and fragment for **2a** and **2b**

	2a		**2b**	
	Hirshfeld	VDD	Hirshfeld	VDD
Atoms				
Te3	-0.001	-0.081	-0.004	-0.072
Pt1	-0.059	-0.115	-0.078	-0.142
Te1	-0.001	-0.061	-0.003	-0.049
Te2	-0.005	-0.060	-0.007	-0.047
Fragments				
[2-Te-py]$^{1-}$ 1[b]	-0.034	-0.008	-0.041	-0.017
[2-Te-py]$^{1-}$ 2[c]	-0.038	-0.006	-0.045	-0.017
PPh_3	+0.132	+0.208	+0.150	+0.251

[a] Refers to the fragment formed by Te1-C19-C20-C21-C22-C23-N1 for **2a**, and Te1-C19-C20-C24-C21-C22-C23-N1 for **2b**.

[b] Refers to the fragment formed by Te2-C24-C25-C26-C27-C28-N2 for **2a**, and Te2-C25-C26-C30-C27-C28-C29-N2 for **2b.**

Additionally, the Nuclear Independent Chemical Shift index (NICS) [234] and Electron Localization Function (ELF) [235] including spin-orbit interaction has been evaluated to determine the electronic behavior on the five membered-ring constituted by Te-C-N-Te-Pt atoms. The value of the NICS index in the center of the ring are -7.46 ppm and -7.55 ppm, for **2a** and **2b** respectively, which denote a similar aromatic behavior as benzene (-7.89 ppm).

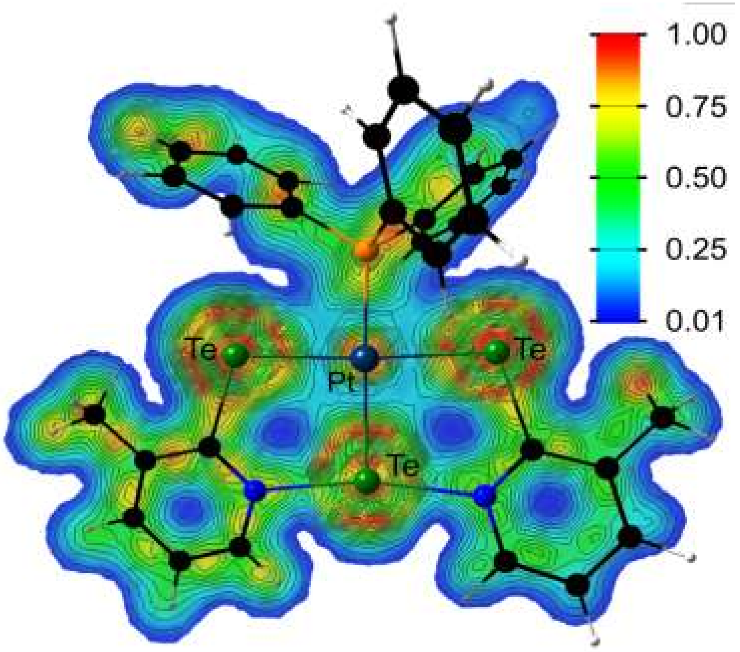


Figure 2: ELF values for the five membered-ring conformed by Te-C-N-Te-Pt.

Moreover, the values of the ELF (η) function are conveniently defined between 0 and 1 (0≤ELF≤1), where 0.5 is for a homogeneous electron gas at a density equal to the local density of the system. In this sense, ELF = 1 denote a perfect localization and 0.5 for a perfect delocalization [236]. Values between ~0.0 and 0.5 denote delocalization in low-density regions [236]. In Figure 3, the ELF values for **2b** are given for the Te-C-N-Te-Pt plane denoting typical values for delocalization in the main group rings: ELF = 0.71 between Te-C- and C-N-, and values less than ELF = 0.5 between N-Te- (ELF = 0.43), Te-Pt- (ELF =

0.25) and Pt-Te- (ELF = 0.25), respectively. These ELF values are in accord with the electronic delocalization in the five membered-rings suggested by the NICS index. Furthermore, **2a** exhibits a similar aromatic behavior.

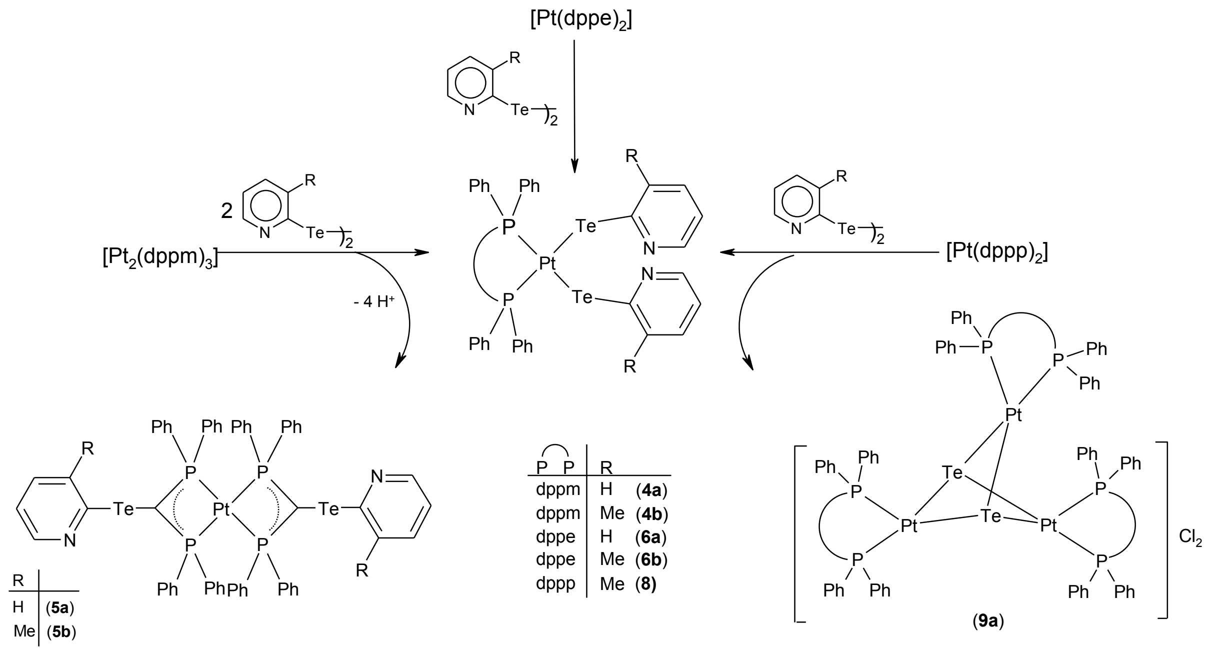
3.1.2 Chemistry of chelated phosphine compounds of platinum with bis(2-pyridyl)ditellurides

Recent theoretical calculations by Morokuma, *et. al.* on oxidative addition of E-E bond to Pd(0) and Pt(0) have revealed that the M-TeR bond energy is the lowest in $[Pt(ER)_2(PR'_3)_2]$) (E = S, Se or Te) complexes and Pt-ER bond is stronger than the Pd-ER linkage [31]. It has also been shown that the transition state involving activation of RE-ER by $M^o(PR_3)_2$ species requires deformation in the P-M-P angle [31].

Pyridyl tellurolates are hemilabile ligands and can bind metal atoms in different ways, *viz*. through tellurium atom, through nitrogen atom or in a bidentate mode (Te$^\frown$N; chelating or bridging). Unlike simple tellurolate ligands (e. g. $PhTe^-$), the presence of both hard (N) and soft (Te) atoms in pyridyl tellurolate ligand may contribute to reactivity and overall stability of the resulting complexes. In the above section 3.1.1 formation of a serendipitous product, $[Pt(Te)(TeAr)_2(PPh_3)]$ (Ar = C_5H_4N and $C_5H_3(Me)N$), containing bare Te^0 coordinated to platinum(II), together with the expected products, $[Pt(TeAr)_2(PPh_3)_2]$, in the reactions of $[Pt(PPh_3)_4]$ with dipyridyl ditellurides has been discussed. Thus platinum(0) complexes containing chelating diphosphines with varying degree of P-M-P angles have been chosen, and their oxidative addition reactions with dipyridyl ditellurides have been studied.

Synthesis and spectroscopy

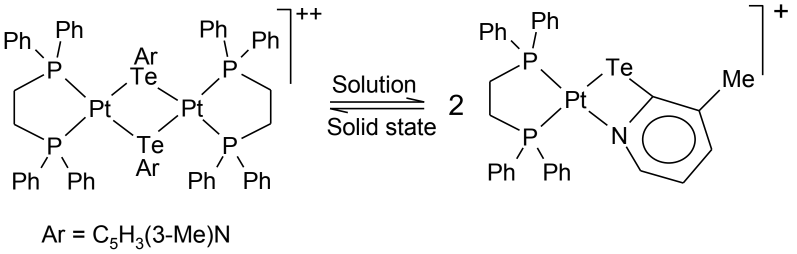
Treatment of $[Pt_2(dppm)_3]$ with $\{C_5H_3(3\text{-}R)N\}_2Te_2$ (R = H or Me) in toluene at room temperature gave an oxidative addition product, $[Pt\{TeC_5H_3(3\text{-}R)N\}_2(dppm)]$ (**4**) (R = H (**4a**) and Me (**4b**)) in ~65% yield as a yellow powder together with an orange crystalline product identified as [Pt{$PPh_2C(TeC_5H_3(3\text{-}R)N)PPh_2$}$_2$] (**5**) (R = H (**5a**) and Me (**5b**) in ~ 20% yield (Scheme 16). The substitution reaction between [$PtCl_2$(dppm)] and $NaTeC_5H_3(3\text{-}R)N$, prepared *in-situ* by reductive cleavage of Te–Te bond in the corresponding ditellurides by methanolic $NaBH_4$, also gave **4** and **5** (Scheme 17). The ^{31}P NMR spectra of **4** displayed a single resonance at δ ~ –52 ppm with $^{195}Pt–^{31}P$ coupling of ~ 2600 Hz indicative of tellurolate ligand trans to the phosphine ligand [97, 206, 237]. The ^{195}Pt NMR spectrum of [Pt{$TeC_5H_3(3\text{-}Me)N$}$_2$(dppm)] (**4b**) exhibited a triplet at δ –4712 ppm with ^1J(Pt–P) of 2650 Hz due to coupling with two equivalent phosphorus nuclei. The ^{31}P NMR spectra of **5** exhibited a signal at –29.3 (**5a**) and –25.1 (**5b**) ppm with $^{195}Pt–^{31}P$ coupling of ~1900 Hz. The resonance is considerably deshielded with respect to the signal for **4**. The magnitude of ^1J(Pt–P) suggests that the strong trans influencing phosphine ligands are mutually trans, which is further confirmed by X-ray structural analysis of **5a** (see later).



Scheme 16: Oxidative addition reactions of [Pt($P^\frown P$)$_2$] with dipyridyl ditellurides

The formation of **4** in these reactions is rather intriguing as the methylene carbon is attacked by $TeC_5H_3(3\text{-}R)N$ moeity and is also deprotonated. Deprotonation of methylene proton in dppm and related ligands R_2PCH_2L (L = SMe, NHR, PR_2, *etc.*) is well documented [18, 238]. For instance, reactions of $[MIr(CO)_3(dppm)_2]$ (M = Ir or Rh) with CH_2I_2 or $CH_2(I)CN$ did not yield the expected oxidative addition product, instead products formed by deprotonation of one of the dppm ligands, $[MIr(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(Ph_2PCHPPh_2)dppm)]$ are isolated [239]. The reactions of $[Pt_2(\mu\text{-}OH)_2(dppm)_2]^{2+}$ with $LiN(SiMe_3)_2$ in THF deprotonates dppm ligand rather than the bridging OH to give $[Pt_2(\mu\text{-}OH)_2(Ph_2PCHPPh_2)_2]$ [240]. Simialrly, in amido-bridged complexes, $[Pt_2(\mu\text{-}NHR)_2(dppm)_2]^{2+}$, deprotonation of dppm by $LiN(SiMe_3)_2$ proceeds via amido group [241]. Double deprotonation of dppm ligand has also been reported [242]. For example, reaction of $[Ru(CNR)_2(dppm)_2]^{2+}$ with $[AuCl(PPh_3)_2]$ in the presence of KOH affords $[Ru(CNR)_2\{PPh_2C(AuPPh_3)_2PPh_2\}_2]^{2+}$ [242b] In the present study, double deprotonation of dppm ligand appears to be brought out by strong nucleophilicity of the pyridyltellurolate ligand both in the oxidative addition and substitution reactions. During the oxidative addition reaction, the activated ditellurides by platinum center attacks the dppm ligand to give $Ph_2PCHTeArPPh_2$ and ArTeH (Ar = pyridyl group). The former on oxidative addition to platinum(0) may give "$Ph_2PCTeArPPh_2$" species. In case of substitution reaction, the tellurolate ion attacks the chelating dppm to give "$Ph_2PCHTeArPPh_2PtCl_2$" which in the presence of base generates "$Ph_2PCTeArPPh_2Pt$".

The reaction of $[Pt(dppe)_2]$ with $\{C_5H_3(3\text{-}R)N\}_2Te_2$ gave exclusively an oxidative addition product, $[Pt\{TeC_5H_3(3\text{-}R)N\}_2(dppe)]$ (**6**) (R = H (**6a**), Me (**6b**)) in ~70% yield. Alternatively, the **3** could be obtained by the reaction of $[PtCl_2(dppe)]$ with two equivalent of $NaTeC_5H_3(3\text{-}R)N$ as described earlier by Jain and co-workers [206]. This reaction in case of 3-methyltellurolate ligand gave a complex of composition, $Pt\{TeC_5H_3(3\text{-}Me)N\}(dppe)Cl$ (**7a**). The latter complex is a non-electrolyte in chloroform (3.0 μScm^2mol^{-1}) while it is a 1:1 elelctrolyte in methanol (83.3 μScm^2mol^{-1}) and acetonitrile (70.6 μScm^2mol^{-1}). This suggests that the complex exists as a monomeric neutral species with monodentate tellurolate ligand in chloroform while in methanol and acetonitrile it adopts an ionic structure with chelating tellurolate ligand and chloride as counter anion. During the preparation of **7a,** addition of $NaBPh_4$ to the reaction flask resulted in the formation BPh_4 salt, $[Pt_2\{TeC_5H_3(3\text{-}Me)N\}_2(dppe)_2](BPh_4)_2$ (**7b**). The ^{31}P NMR data of $[Pt\{TeC_5H_3(3\text{-}Me)N\}_2(dppe)]$ (**6b**) and **7b** are in agreement with those reported earlier [206]. The magnitude of $^1J(Pt–P)$ in $[Pt\{TeC_5H_3(3\text{-}R)N\}_2(dppe)]$ (**6**) is consistent with mononuclear *cis* tellurolate complexes [227, 243]. It is interesting to note that the **7b** is a centrosymmetric dimer stablized by Te-bridges (see later, X-ray crysatallography) and the ^{31}P NMR spectrum showed two signals with different $^1J(Pt–P)$ values. A similar ^{31}P NMR pattern has been reported for $[Pt_2(\mu\text{-}SeCH_2CH_2NMe_2)_2(dppe)_2]^{2+}$ [92] Initially, in the absence of X-ray structural analysis [92, 206], an asymmetric Pt–E (E = Se or Te) bridges have been suggested for these complexes. It is likely that in solution, a monomeric species containing chelating tellurolate ligand may form (eq-1). The strong *trans* influence of the phosphine ligand may weaken the Pt–Te–Pt bridge. Such a mononuclear species would show two ^{31}P NMR resonances with different $^1J(Pt–P)$ coupling constants, one due to Ph_2P group trans to nitrogen ($^1J(Pt–P)$ = 3267 Hz) and another for the trans to the tellurolate ligand ($^1J(Pt–P)$ = 2940 Hz).



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The reaction of $[Pt(dppp)_2]$ with $\{C_5H_3(3\text{-}R)N\}_2Te_2$ in benzene, in addition to oxidative addition product, $[Pt\{TeC_5H_3(3\text{-}Me)N\}_2(dppe)]$ (**8**) gave an ionic trinuclear complex, $[Pt_3Te_2(dppp)_3]Cl_2$ (**9a**). Similarly substitution reaction of $[PtCl_2(dppp)]$ with

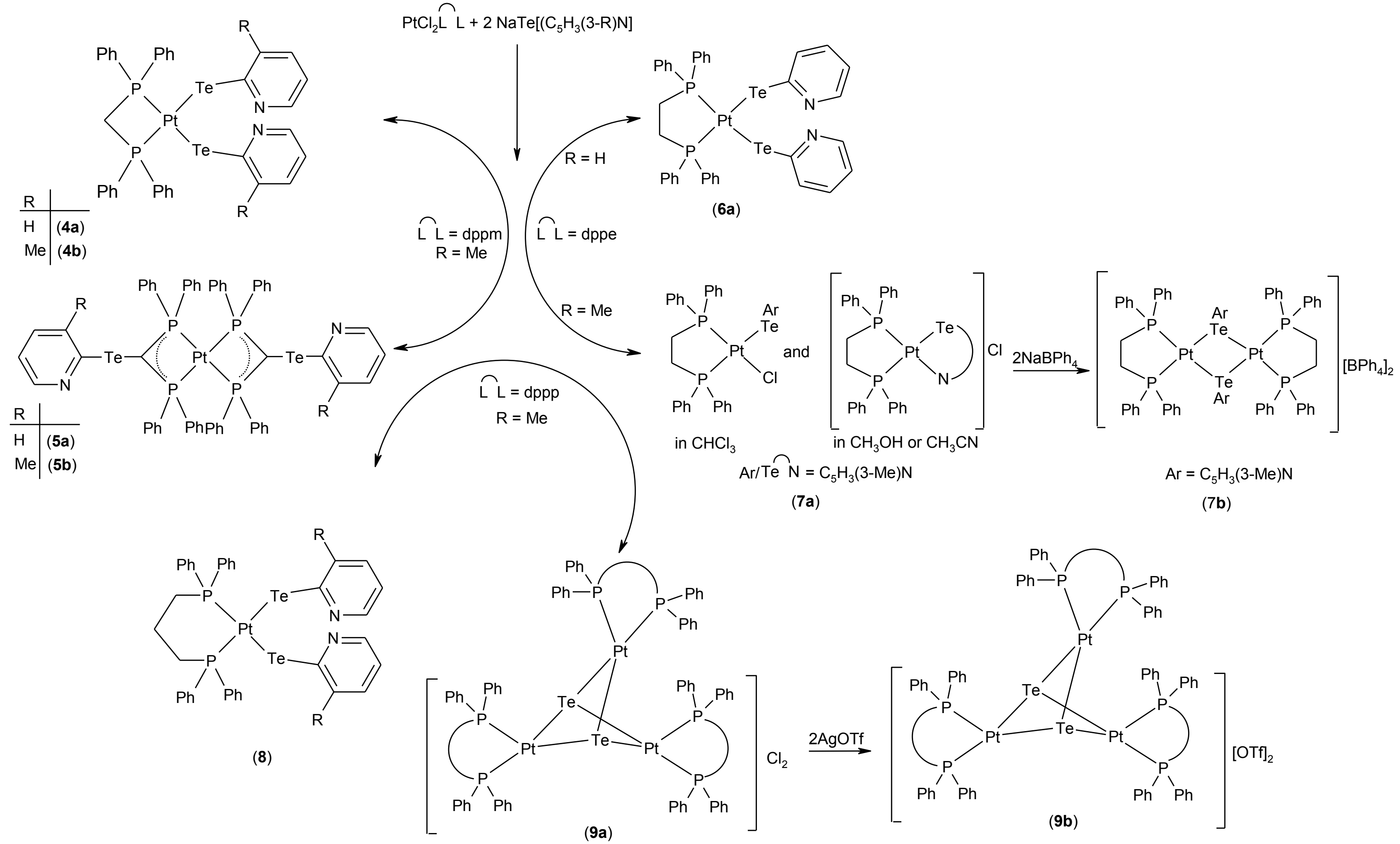
$NaTeC_5H_3$(3-Me)N gave a mixture of **8** and **9a** which were seperated by column chromatography. Treatment of **9a** with AgOTf gave the corresponding OTf complex, $[Pt_3Te_2(dppp)_3][OTf]_2$ (**9b**). Formation of similar tellurido-bridged trinuclear platinum complex, $[Pt_3(\mu\text{-}Te)_2(Th)(PPh_3)_5]Cl$ has been reported by oxidative addition reaction of Th_2Te_2 (Th = 2-thienyl, C_4H_3S) to $[Pt(PPh_3)_4]$ in dichloromethane [120].

The ^{31}P NMR spectrum of **8** exhibited a singlet at δ –10.3 ppm with ^1J(Pt–P) of 2744 Hz while the spectrum of **9b** showed a resonance at lower frequency **(**δ –13.6 ppm) with ^1J(Pt–P) of 2965 Hz. The NMR data are consistent with the reported values [244]. The chemical structure of **9b** was confirmed by X-ray structural analysis. There are two independent tellurido-bridged (Pt–Te = 2.62 Å (av); Pt–Te bond distance in $[Pt_3(\mu\text{-}Te)_2(PEt_3)_6]^{2+}$ [245] and $[Pt_3(\mu\text{-}Te)_2(Th)(PPh_3)_5]Cl$ (Th = 2-thienyl, C_4H_3S) [120] is 2.604 and 2.630 Å, respectively) cations in the crystal, one molecule has a two-fold symmetry while the other has a three-fold symmetry.

X-ray crystallography

The molecular structures of $[Pt\{Ph_2PC(TeC_5H_4N)PPh_3\}_2]$ (**5a**). $2CH_2Cl_2$ and $[Pt_2\{\mu\text{-}TeC_5H_3(3\text{-}Me)N\}_2(dppe)_2][BPh_4]_2$ (**7b**), established by X-ray diffraction analysis are shown in Figures 3 and 4. Selected interatomic parameters are summarized in Tables 24 and 25.

The platinum atom in **5a** adopts a distorted square planar configuration defined by a 'P_4' coordination core. The chelate P1–Pt1–P2 angle is acute (70.66°); as a consequence the adjacent angles are opened-up. The Pt–P distances are similar (2.31-2.33 Å) and are slightly longer than those reported for $[PtSe_4(dppe)]$ (2.24 Å), [246] $[Pt_3(\mu\text{-}Stol)_4(dppm)_2][CF_3SO_3]_2$ (2.25 Å),[237] and $[Pt\{o\text{-}C_6H_4(PPh_2)_2\}(PhC{\equiv}CPh)]$ (2.26 Å) [247]. The Te–C distances are as expected [206, 248]. Various angles involving C-1 carbon vary between 100.5-131.1° indicative of trigonal (allylic type) configuration.



Scheme 17: Reactions of $[PtCl_2(P^{\frown}P)]$ with sodium 2-pyridyl tellurolates

Table 23: ^{1}H, and ^{31}P{^{1}H} NMR data for 2-pyridyltellurolate complexes of platinum(II) chelated phosphines

Complex		^{1}H NMR δ in ppm	^{31}P{^{1}H} NMR δ in ppm
[Pt(TeC$_5$H$_4$N)$_2$(dppm)]	**4a**	4.40 (t, ^{2}J(P–H) = 10 Hz, ^{3}J(Pt–H) = 53 Hz); 6.57 (d); 6.76 (dt, 1.8 Hz d, 7.5 Hz (t) (C$_5$H$_4$N)); 7.09–7.79 (m, Ph); 8.04 (d, 7.8 Hz, C$_5$H$_4$N); 8.46 (dd, 1, 4 Hz, C$_5$H$_4$N)	–53.0 [^{1}J(Pt–P) = 2547 Hz)]
[Pt{TeC$_5$H$_3$(3-Me)N}$_2$(dppm)]	**4b**	2.44 (s, Me), 3.16 (d, dppm –PCH$_2$), 6.92 (dd, C$_5$H$_3$N 2H), 7.28 (br, Ph), 7.43 (d, C$_5$H$_3$N 2H), 7.71 (br, Ph), 7.93 (dd, C$_5$H$_3$N 2H), 8.245 (d, C$_5$H$_3$N 2H)	–51.9 [^{1}J (Pt–P) = 2632 Hz]
[Pt{PPh$_2$C(TeC$_5$H$_4$N)PPh$_2$}$_2$]	**5a**	7.02 (dd, C$_5$H$_4$N); 7.04-7.74 (m, Ph); 8.04 (d, 7 Hz, C$_5$H$_4$N); 8.45 (d, 1.8 Hz, C$_5$H$_4$N)	–29.3 [^{1}J(Pt–P) = 1909 Hz)]
[Pt{PPh$_2$C(TeC$_5$H$_3$(3-Me)N)PPh$_2$}$_2$]	**5b**	2.44 (s, Me), 7.06 (d, C$_5$H$_3$N 2H), 7.18(m, Ph), 7.30 (d, C$_5$H$_3$N 2H), 7.36 (q, Ph), 7.49(m, Ph), 7.65(dd, C$_5$H$_3$N 2H), 7.69(br, Ph), 8.31(d, C$_5$H$_3$N 2H)	–25.6 [^{1}J(Pt–P) = 1913 Hz)]
[Pt(TeC$_5$H$_4$N)$_2$(dppe)]	**6a**	2.10 (m, dppe 6H), 6.63 (d, C$_5$H$_4$N 2H), 6.72 (t, C$_5$H$_4$N), 7.30–7.35 (m, Ph), 7.84 (d, 3.6 Hz, C$_5$H$_4$N)	46.1 [^{1}J (Pt–P) = 2887 Hz]

$\mathrm{[Pt\{TeC_5H_3(3\text{-}Me)N\}_2(dppe)]}$	**6b**	2.08 (s, *Me*$\mathrm{C_5H_3N}$); 2.02 (m, $\mathrm{CH_2CH_2}$); 6.57 (d,d, 5, 7 Hz, H-5); 6.77 (d, 7.5 Hz, H-4); 7.27-7.37 (m, $\mathrm{C_6H_5}$); 7.56 (d, 5 Hz, H-6); 7.71-7.77 (m, $\mathrm{C_6H_5}$)	44.8 [^{1}J (Pt–P) = 2947 Hz]
$\mathrm{Pt\{TeC_5H_3(3\text{-}Me)N\}(dppe)Cl}$	**7a**	2.09 (s, Me), 2.86 (br, dppe –$\mathrm{CH_2}$), 6.70 (m, $\mathrm{C_5H_3(3\text{-}Me)N}$), 7.00 (m), 7.36 –7.87 (m, Ph), 8.24 (d, $\mathrm{C_5H_3(3\text{-}Me)N}$)	41.9 [^{1}J (Pt–P) = 2940 Hz], 36.7 [^{1}J (Pt-P) = 3267 Hz]
$\mathrm{[Pt_2\{TeC_5H_3(3\text{-}Me)N\}_2(dppe)_2](BPh_4)_2]}$	**7b**	–	42.1 [^{1}J (Pt–P) = 2944 Hz], 36.7 [^{1}J (Pt-P) = 3259 Hz]
$\mathrm{[Pt\{TeC_5H_3(3\text{-}Me)N\}_2(dppp)]}$	**8**	1.86 (s, Me); 2.52 (br); 3.04–3.15 (m) $\mathrm{CH_2}$; 6.45–7.79 (m, Ph + $\mathrm{C_5H_3N}$)	–10.3 (^{1}J (Pt–P) = 2740 Hz)]
$\mathrm{[Pt_3Te_2(dppp)_3](SO_3CF_3)_2}$	**9b**	2.94 (br, dppp –$\mathrm{CH_2}$), 7.11–7.63 (m, Ph)	–13.6 [^{1}J (Pt–P) = 2965 Hz]

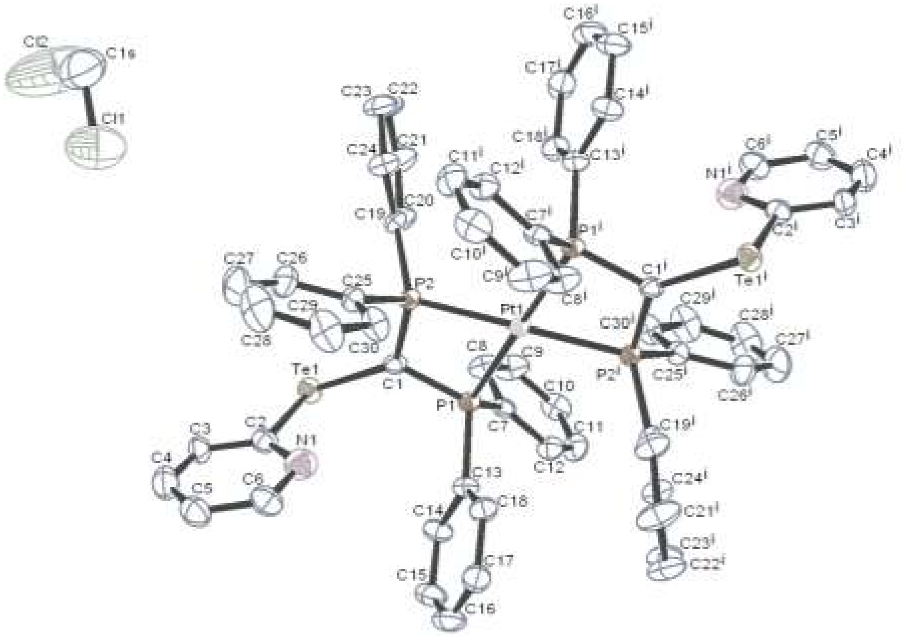


Figure 3: Molecular structure of [Pt{PPh$_2$C(TeC$_5$H$_4$N)PPh$_2$}$_2$].2CH$_2$Cl$_2$

Table 24: Selected bond lengths (Å) and angles (°) of [Pt{PPh$_2$C(TeC$_5$H$_4$N)PPh$_2$}$_2$].2CH$_2$Cl$_2$

Pt1-P1	2.3292(17)	Te1-C2	2.144(8)
Pt1-P2	2.3116(18)	P1-C1	1.742(8)
Te1-C1	2.059(7)	P2-C1	1.750(7)
P2-Pt1- P2'	180.00(9)	C19-P2-Pt1	115.8(2)
P2-Pt-1 P1'	109.34(6)	P1-C1-P2	100.5(4)
P2-Pt1-P1	70.66(6)	P1-C1-Te1	131.1(4)
C1-Te1-C2	99.3(3)	P2-C1-Te1	127.6(4)
C1-P2-Pt1	94.6(3)	N1-C2-Te1	121.9(7)
C25-P2-Pt1	117.8(3)		

Compound **7b** is a centrosymmetric dimer comprised of two distorted square planar platinum atoms which are held together by tellurolato bridges. Coordination around each platinum is defined by P$_2$Te$_2$ donor set from a chelating dppe ligand and two tellurolate ligands. The Pt–P and Pt–Te distances are as expected [203, 217, 249]. The four membered Pt_2Te_2 ring is planar with C_5H_3(3-Me)N groups adopting an *anti* configuration.

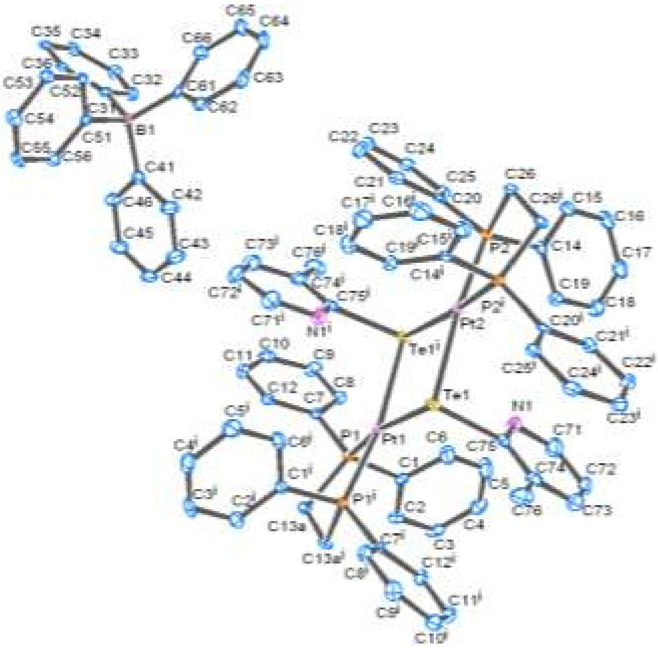


Figure 4: Crystal structure of $[Pt_2\{TeC_5H_3(3\text{-}Me)N\}_2(dppe)_2].(BPh_4)_2$

Table 25: Selected bond lengths (Å) and angles (°) of $[Pt_2\{TeC_5H_3(3\text{-}Me)N\}_2(dppe)_2].[BPh_4]_2$

Pt(1)-P(1)	2.2555(11)	Pt(2)-P(2)	2.2523(11)
Pt(1)-Te(1)	2.6382(4)	Pt(2)-Te(1)	2.6318(4)
Pt(1)-Te(1)#1	2.6383(4)	Te(1)-C(75)	2.168(5)
P(1)-Pt(1)-Te(1)	168.98(3)	P(2)-Pt(2)-Te(1)	173.36(3)
P(1)-Pt(1)-Te(1)#1	95.87(3)	Te(1)#1-Pt(2)-Te(1)	85.064(19)
Te(1)-Pt(1)-Te(1)#1	84.806(19)	C(75)-Te(1)-Pt(2)	94.09(12)
P(2)#1-Pt(2)-P(2)	85.72(6)	C(75)-Te(1)-Pt(1)	90.65(12)
P(2)#1-Pt(2)-Te(1)#1	173.36(3)	Pt(2)-Te(1)-Pt(1)	95.066(16)
P(2)-Pt(2)-Te(1)#1	94.99(3)	N(1)-C(75)-Te(1)	114.6(3)
P(2)#1-Pt(2)-Te(1)	95.00(3)		

Theoretical Calculations

The bonding, charge transfer and geometry of compounds **[**Pt{TeC_5H_3(3-R)N}$_2$(dppm)] (**4**), [Pt{PPh_2C(TeC_5H_3(3-R)N)PPh_2}$_2$] (**5**) and [Pt_3Te_2(dppp)$_3$]$^{2+}$ (**9**) have been analyzed through relativistic density functional calculations [233]. The formation of the product **4** and **5**, shows a clear preference for **4**. These systems differs by the substitution of the dppm ligand with a {C_5H_3(3-Me)N}Te moiety which leads to changes in the ligand to metal charge transfer. In order to characterize the latter point, we performed a detailed charge analysis employing the Hirshfeld partitioning schemes of the electron density, focusing on the charge distribution between the dppm and {PPh_2C(TeC_5H_3(3-R)N)$_2PPh_2$} ligands in systems **4** and **5**, respectively. The calculations characterize a more efficient charge donation towards the Pt centre for **4** (0.37 e), in comparison to **5** which shows an almost negligible donation (0.08 e). These results suggest that a stronger bond is formed between Pt and dppm ligand in compound **4**, accounting for the above described preference (see text).

The formation of system **9**, which exhibits a [Pt_3(dppp)$_3$]$^{6+}$ core stabilized by a [Te_2]$^{4-}$ fragment as ligand, participate in the making of the Pt-Te bond that results from the direct 5*d*-Pt-5*p*-Te interaction. The molecular orbital diagram in Figure 5, denotes the contribution from the [Te_2]$^{4-}$ towards the electronic structure of [Pt_3Te_2(dppp)$_3$]$^{2+}$ which arises mainly from the σ, π, π* and σ* 5*p*-Te combinations.

The HOMO (Figure 6) is formed mainly by a 5*d*-5*p* bonding interaction between the Pt_3 and the σ* combination of Te_2, while the LUMO shows an antibonding interaction involving a π*combination of Te_2. The charge donation from the Te_2 moiety towards the core, rise an overall charge transfer of about 1.73 e leading to a [Te_2]$^{2.27-}$ and [Pt_3(dppp)$_3$]$^{4.27+}$ fragments.

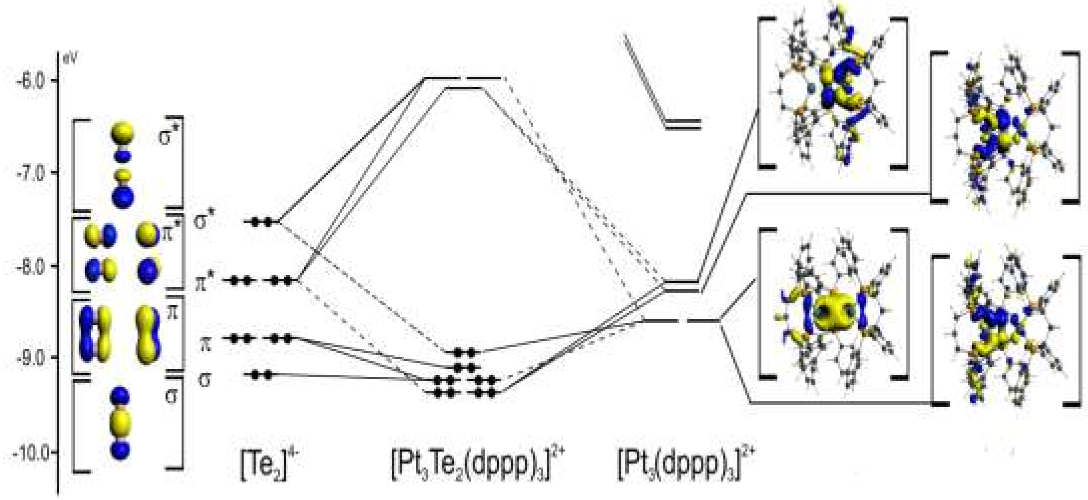


Figure 5: Molecular Orbital diagram describing the core fragment interaction and $[Te_2]^{4-}$ in compound **9**.

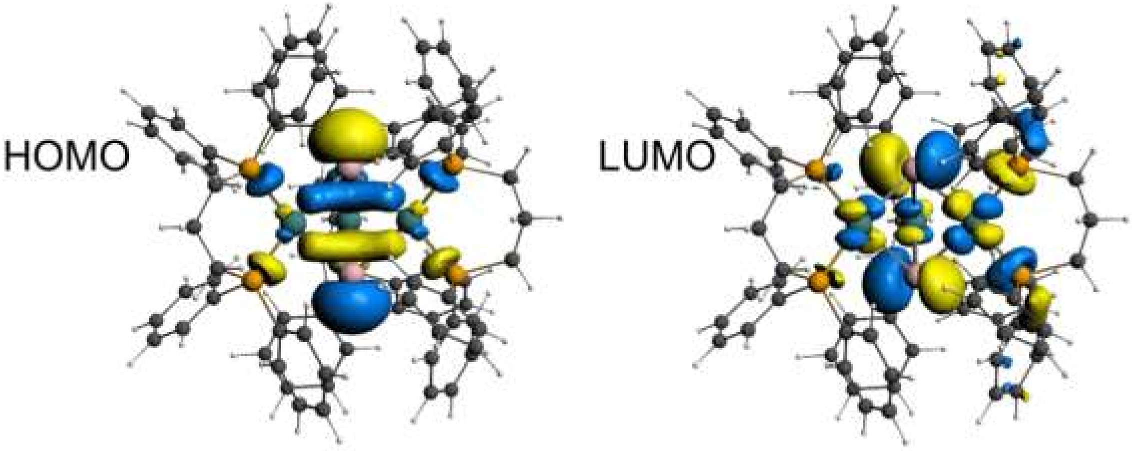


Figure 6: Isosurface of the HOMO and LUMO of compound **9**

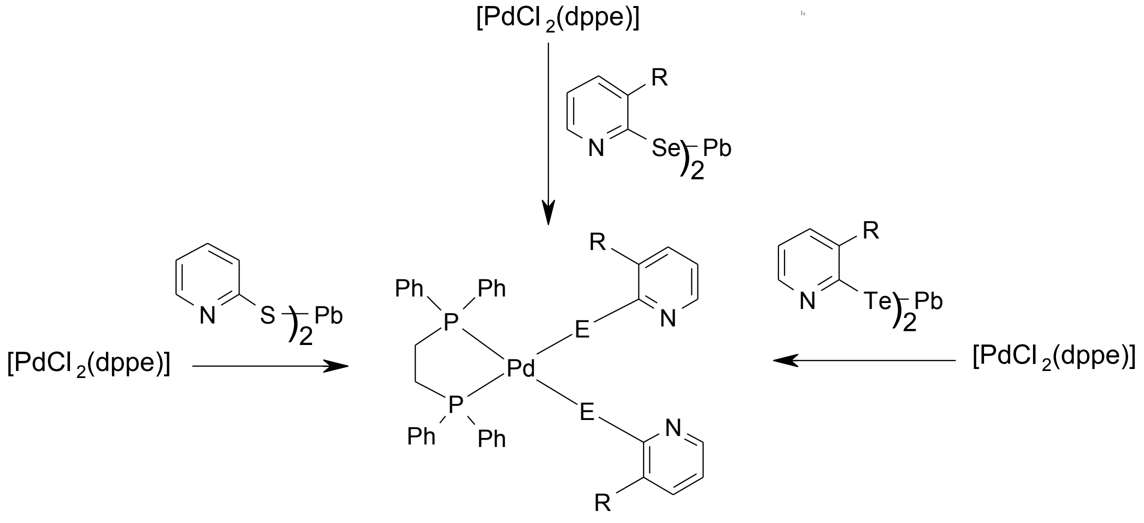
3.2 Chemistry of pyridyl- and 3-methyl-2-pyridylthiolate, selenolate and tellurolate complexes of palladium

Oxidative addition reactions of E-X (E = heteroatom, X = H [250], C [217] or heteroatom [210, 212] to zero-valent Group 10 metal complexes have attracted considerable attention for quite some time [251]. The remarkable reactivity of Ni^0 and Pd^0 has been used in synthetic chemistry as their reactions, in general, give high product yield with great selectivity under mild conditions [252]. These complexes are not only used as precursors but several of them are envisaged as active species in catalytic reactions. The corresponding platinum(0) complexes, on the other hand, due to their superior stability, provide an opportunity to understand the mechanistic details and learn about the nature of complexes involved in such reactions [253].

With the above perspective palladium(0) phosphine complexes with varying degree of P–Pd–P angles (chelating diphosphines and PPh_3) have been chosen and studied their reactions with dipyridyldichalcogenides. Substitution reactions of $[PdCl_2(P^\frown P)]$ with pyridylchalcogenolate ions have also been examined to find the nature of products formed in such reactions and also compare them with those obtained from oxidative addition reactions.

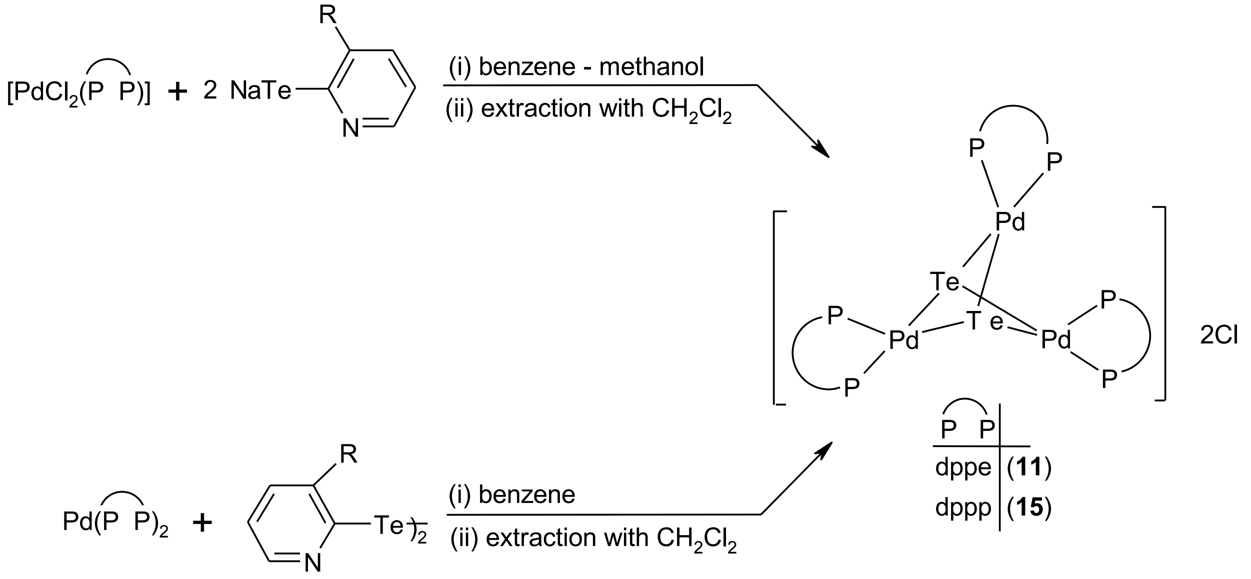
Synthesis and spectroscopy

Reactions of 2-chalcogenopyridine ligands with palladium(0) and palladium(II) precursors afforded a variety of complexes depending on the nature of chalcogen atom, palladium precursor and the reaction conditions (Schemes 18-22). The treatment of $[PdCl_2(dppe)]$ with lead salts of 2-pyridinechalcogenolates gave mononuclear palladium complexes, $[Pd\{EC_5H_3(3\text{-}R)N\}_2(dppe)]$ (E = S, Se, Te) (**10**) as yellow-to-orange powder (Scheme 18). Similar substitution reactions between $[PdCl_2(dppe)]$ and $NaTeC_5H_3(3\text{-}R)N$, prepared by reductive cleavage of Te–Te bond of dipyridylditellurides by $NaBH_4$ in methanol, gave an organge precipitate which on extraction with dichloromethane afforded a tellurido-bridged trinuclear palladium(II) complex, $[Pd_3(\mu\text{-}Te)_2(dppe)_3]Cl_2$ (**11**) (Scheme 19) as a red crystalline solid which was isolated in good yield. Similarly, **11** was formed when a palladium(0) precursor, $[Pd(dppe)_2]$, was treated with dipyridylditellurides in benzene followed by extraction with dichloromethane (Scheme 19). Morley and co-workers have reported the formation of the platinum analogue of **11** by an oxidative addition reaction of tellurium powder with $Pt(dppe)_2$ followed by extraction with dichloromethane at room temperature [246]. Interestingly, the corresponding reaction of dipyridyldiselenides with $[Pd(dppe)_2]$ afford oxidative addition products, $[Pd\{SeC_5H_3(3\text{-}R)N\}_2(dppe)]$ (R = H (**10b**); Me (**10c**)) (Scheme 20).

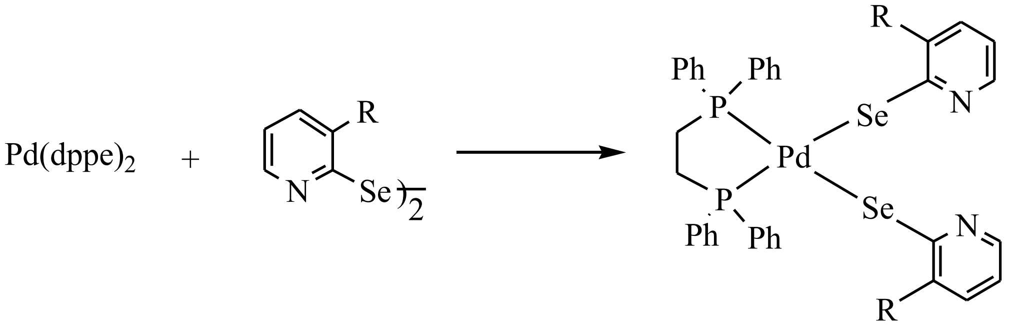


E	R	
S	H	(**10a**)
Se	H	(**10b**)
Se	Me	(**10c**)
Te	H	(**10d**)
Te	Me	(**10e**)

Scheme 18: Reactions of $[PdCl_2(dppe)]$ with lead 2-pyridine chalcogenolates



Scheme 19: Reactions of $[PdCl_2(P^\frown P)]$ and $Pd(P^\frown P)_2$ ($P^\frown P$ = dppe or dppp) with sodium 2-pyridyl tellurolates and dipyridyl ditellurides, respectively.



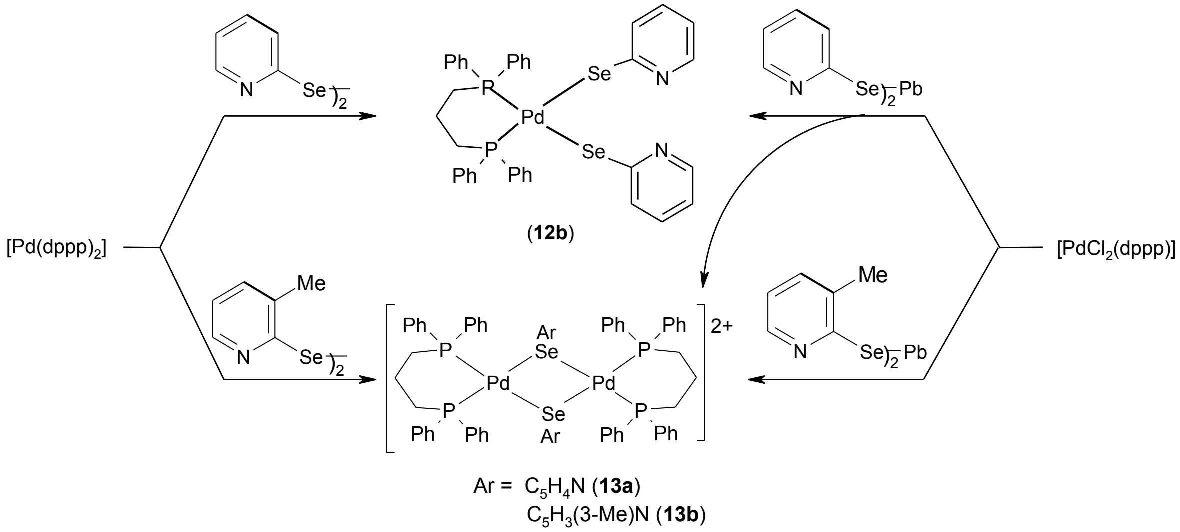
10 b (R = H)
10 c (R = Me)

Scheme 20: Oxidative addition reactions of $Pd(dppe)_2$ with dipyridyl diselenides

The reactions of 2-seleno/telluoro-pyridines with “Pd(dppp)” species were markedly different from those involving “Pd(dppe)” species as described above. The reaction of $Pb(SC_5H_4N)_2$ with $[PdCl_2(dppp)]$ gave expected mononuclear complex, $[Pd(SC_5H_4N)_2(dppp)]$ (**12a**) as described in the literature [205]. However the reaction of $[PdCl_2(dppp)]$ with $Pb(SeC_5H_4N)_2$ afforded a mixture of mononuclear, $[Pd(SeC_5H_4N)_2(dppp)]$ (**12b**) and binuclear, $[Pd_2(\mu\text{-}SeC_5H_4N)_2(dppp)_2]Cl_2$ (**13a**) complexes

(Scheme 21) even on prolonged stirring of the reactants at room temperature. In contrast, the similar reaction with Pb$\{SeC_5H_3(3\text{-}Me)N\}_2$ gave exclusively a dimeric complex, $[Pd_2(\mu\text{-}SeC_5H_3(3\text{-}Me)N)_2(dppp)_2]Cl_2$ (**13b**). Interestingly, treatment of $(SeC_5H_4N)_2$ with $[Pd(dppp)_2]$ yielded mononuclear complex, $[Pd(SeC_5H_4N)_2(dppp)]$ (**12b**) while $\{SeC_5H_3(3\text{-}Me)N\}_2$ gave the binuclear complex **13** (Scheme 21). The complexes **13a** and **13b** appear to be formed either by partial substitution of one chloride from $PdCl_2(dppp)$ with a selenolate ligand or by nucleophilic attack of CH_2Cl_2 on the bis substituted products. We attribute the former route for the formation of **13a** and **13b** as the ^{31}P NMR spectrum of a $CDCl_3$ solution of **12b** remained unchanged for several hours. The reaction of $[PdCl_2(dppp)]$ with $[Pb(TeC_5H_4N)_2]$ yielded $[Pd(TeC_5H_4N)_2(dppp)]$ (**12c**) which slowly converted to a dimeric species in halogenated solvents, $[Pd_2(\mu\text{-}TeC_5H_4N)_2(dppp)_2]Cl_2$ (**14a**). The reaction of $[PdCl_2(dppp)]$ with Pb$\{TeC_5H_3(3\text{-}Me)N\}_2$, on the other hand, gave a mixture of products from which the dimeric $[Pd_2\{\mu\text{-}TeC_5H_3(3\text{-}Me)N\}_2(dppp)_2]Cl_2$ (**14b**) and trimeric tellurido-bridged complexes, $[Pd_3(\mu\text{-}Te)_2(dppp)_3]Cl_2$ (**15**) could be isolated. Treatment of either $[PdCl_2(dppp)]$ with $NaTeC_5H_3(3\text{-}R)N$ (Scheme 19) or $[Pd(dppp)_2]$ with $\{TeC_5H_3(3\text{-}Me)N\}_2$ (Scheme 21) invariably lead to the formation of **15**. Since the isolation of $[Pt_3(\mu\text{-}S)_2(PMe_2Ph)_6]^{2+}$ cluster by Chatt and Mingos in 1970 [254], considerable work has been reported on chalcogenido-bridged trinuclear clusters [255] with predominance of the sulfido-bridged derivatives [256]. However, there are only a few reports describing tellurido-bridged derivatives which are often isolated in poor yields [79, 244]. During the present investigation, **15** has been isolated in fairly good yield.

The formation of Te-C bond cleaved products (**11** and **15**) and **14** is rather intriguing. It appears that initially bis tellurolate complexes, "$[Pd\{TeC_5H_3(3\text{-}R)N\}_2(P^\frown P)]$" are formed in both the reactions, viz. (i) oxidative addition of $\{TeC_5H_3(3\text{-}R)N\}_2$ to $[Pd(P^\frown P)_2]$ and (ii) substitution reaction between $[PdCl_2(P^\frown P)]$ and $NaTeC_5H_3(3\text{-}R)N$. When the bis products are dissolved/ extracted in halogenated solvents ($CDCl_3$ or CH_2Cl_2), nucleophilic attack at coordinated tellurolate ligand takes place giving products like **11** and **15**. Nucleophilic attack at coordinated selenolate and tellurolate ligand is documented in the literature [229].

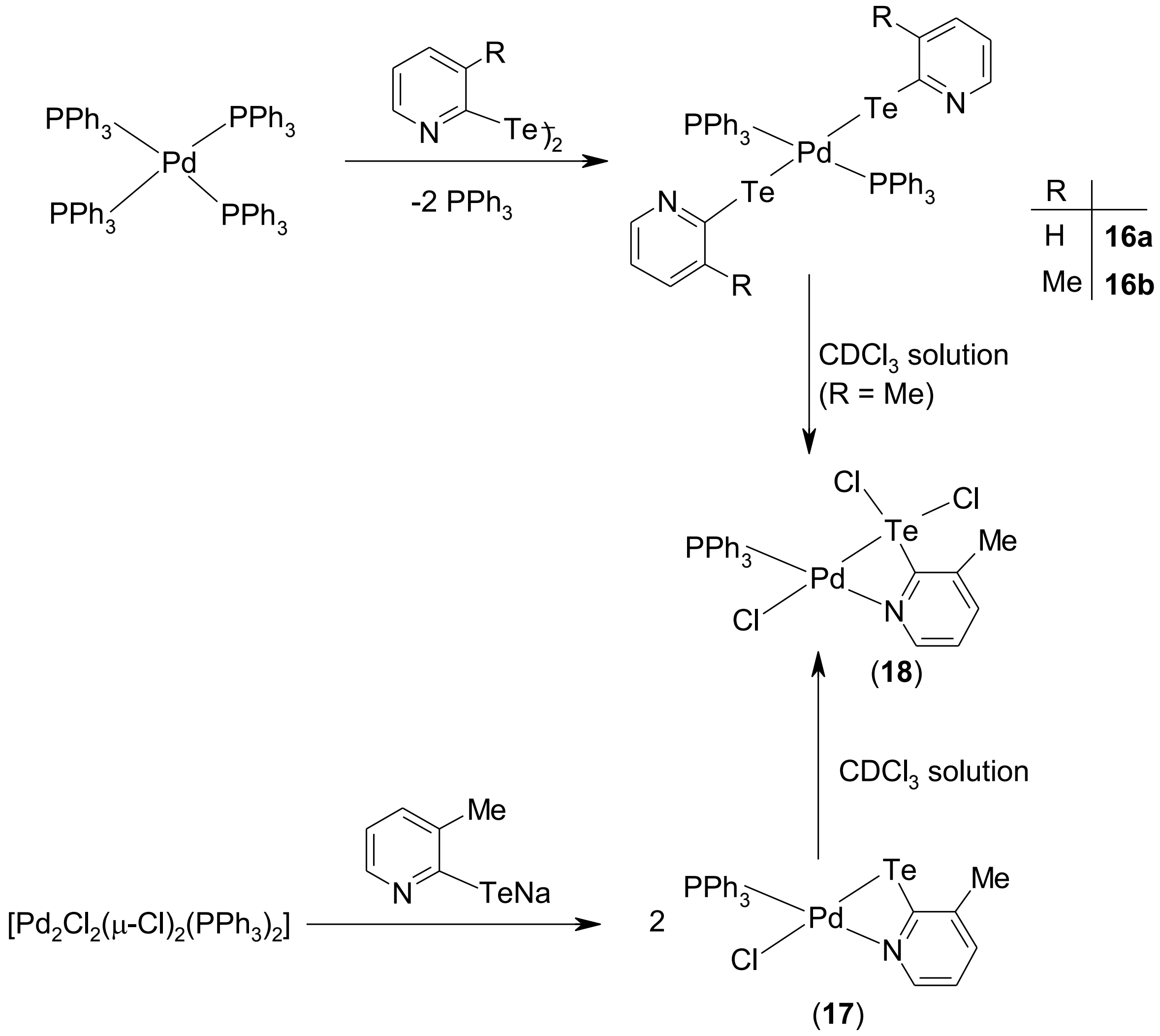


Scheme 21: Reactions of [Pd(dppp)$_2$] and [$PdCl_2$(dppp)] with dipyridyl diselenides and lead 2-pyridine selenolates, respectively

The ^{31}P NMR spectra of [Pd{EC_5H_3(3-R)N}$_2$($P^{\frown}P$)] ($P^{\frown}P$ = dppe, dppp) exhibited single resonances (Table 26). The chalcogen dependance on the ^{31}P NMR chemical shift is evident. With a given diphosphine ligand, the ^{31}P NMR resonance is progressively shielded, e.g. [Pd(EC_5H_4N)$_2$(dppe)] (δ ^{31}P NMR = 59.5 (E = S); 54.6 (E = Se) and 51.5 (E = Te) ppm). The nuclearity of the complex also influenced the ^{31}P NMR chemical shifts which are shielded with increasing nuclearity of the complex, e.g. [Pd(TeC_5H_4N)$_2$(dppp)] (δ ^{31}P = –4.6 ppm); [Pd_2{μ-TeC_5H_3(3-Me)N}$_2$(dppp)$_2$]$^{2+}$ (δ ^{31}P = –9.6 ppm) and [Pd_3(μ-Te)$_2$(dppp)$_3$]$^{2+}$ (δ ^{31}P = –11.0 ppm).

The complexes $[Pd_2\{\mu\text{-}SeC_5H_3(3\text{-}R)N\}_2(dppp)_2]^{2+}$ showed two ^{31}P NMR signals in solution whereas corresponding tellurolates displayed a single resonance at –9.6 ppm. For the latter a dimeric structure has been established by X-ray crystallography (see later). It is likely that the selenolate complexes are monomeric in solution containing chelating pyridyl selenolate. Similar behaviour has been observed for the analogous platinum derivatives [257]. For mononuclear complex two ^{31}P NMR resonances would be expected, one due to phosphorus *trans* to the chalcogen atom and another *trans* to the nitrogen atom.

Treatment of $[Pd(PPh_3)_4]$ with dipyridyl ditellurides readily gave oxidative addition products, *trans*-$[Pd\{TeC_5H_3(3\text{-}R)N\}_2(PPh_3)_2]$ (**16**) (R = H (**16a**) or Me (**16b**)) (Scheme 22). It is noteworthy that the similar reaction with $[Pt(PPh_3)_4]$ with dipyridyl ditellurides, in addition to the expected product *trans*-$[Pd\{TeC_5H_3(3\text{-}R)N\}_2(PPh_3)_2]$, also gave a serendipetous complex, $[Pt(Te)\{TeC_5H_3(3\text{-}R)N\}_2(PPh_3)]$ [249]. The complex **16b**, when left in $CDCl_3$ solution, afforded green crystals of a new derivative, $[PdCl\{Te(Cl)_2C_5H_3(3\text{-}Me)N\}(PPh_3)]$(**18**) which was structurally characterized. Recently syntheis of palladium complexes of the type $[PdCl(TeC_5H_4N)(PR_3)]$ has been described [206]. To assess whether such complexes also undergo similar reactions, the complex $[PdCl\{TeC_5H_3(3\text{-}Me)N\}(PPh_3)]$ ($^{31}P\{^1H\}$ NMR δ: 29.04 ppm) was left in $CDCl_3$ for several hours, green crystals of **18** ($^{31}P\{^1H\}$ NMR δ: 28.0 ppm) were seperated. The bridging sulfido ligands in palladium and platinum complexes, $[M_2(\mu\text{-}S)_2(PR_3)_4]$ are known to be susceptible to nucleophilic attack by various halogenated compounds like $CHCl_3$, CH_2Cl_2, R'X, HCl to yield $[M_2(\mu\text{-}S)(\mu\text{-}SR')(PR_3)_4]X$ [219]. In the present case the coordinated tellurolato ion is further oxidized in $CDCl_3$ solution. Recently a complex, $[CpFe(CO)_2(TePhI_2)]$, in which ‘$ArTeX_2$’ fragment is coordinated to a metal atom, has been isolated by a reaction between $[CpFe(CO)_2I]$ and PhTeI [258] .



Scheme 22: Reactions of triphenylphosphine palladium precursors with 2-telluropyridines.

X-ray crystallography

The molecular structures of $\{TeC_5H_3(3\text{-}Me)N\}_2$, $[Pd_2\{\mu\text{-}TeC_5H_3(3\text{-}Me)N\}_2(dppp)_2]Cl_2.3H_2O$, $[Pd_3(\mu\text{-}Te)_2(dppp)_3]Cl_2.3CHCl_3$ and $[PdCl\{2\text{-}Te(Cl)_2C_5H_3(3\text{-}Me)N\}(PPh_3)]$, established by X-ray diffraction analyses are shown in Figures 7-10. Selected interatomic parameters are summarized in Tables 27-29.

The molecular structure of $\{TeC_5H_3(3\text{-}Me)N\}_2$ is shown in Figure 7. The Te–Te bond length (2.7199(17) Å) is slightly longer than that in dipyridylditellurides, *viz.* bis(2-

Table 26: ^{1}H, ^{31}P{^{1}H} and ^{77}Se/^{125}Te{^{1}H} NMR data for 2-pyridylchalcogenolate complexes of palladium(II) complex

Complex		^{1}H δ in ppm	^{31}P{^{1}H} δ in ppm	^{77}Se/^{125}Te δ in ppm
[Pd(SC$_5$H$_4$N)$_2$(dppe)]	**10a**	2.87 (m, –PCH$_2$), 6.77 (t), 6.94 (d, 8.1 Hz, C$_5$H$_4$N), 7.10 (t, 7.8 Hz, Ph), 7.47 (m, C$_5$H$_4$N), 7.81 (m, Ph), 8.45 (br, C$_5$H$_4$N);	59.5	
[Pd(SeC$_5$H$_4$N)$_2$(dppe)]	**10b**	2.61-2.68 (m, CH$_2$, dppe), 7.10-7.56 (m, Ph), 7.81 (m), 8.45 (d, C$_5$H$_4$N), 8.55 (d, C$_5$H$_4$N);	54.6	
[Pd{SeC$_5$H$_3$(3-Me)N}$_2$(dppe)]	**10c**	2.16 (s, Me), 2.78 (m, dppe), 6.67 (m), 7.00-7.51 (m, Ph), 7.87 (m, C$_5$H$_3$(3-Me)N), 8.29 (d, 4.5 Hz, C$_5$H$_3$(3-Me)N)	54.5 (br)	
[Pd(TeC$_5$H$_4$N)$_2$(dppe)]	**10d**	2.46 (m, –PCH$_2$), 6.52 (br), 6.65 (t, C$_5$H$_4$N), 6.87(br), 7.17-7.90 (m, Ph), 8.03 (d, 7.8 Hz, C$_5$H$_4$N), 8.45 (br, C$_5$H$_4$N);	51.1	
[Pd{TeC$_5$H$_3$(3-Me)N}$_2$ (dppe)]	**10e**	2.28 (br, PCH$_2$), 2.42 (s, Me), 6.99 (m, C$_5$H$_3$(3-Me)N), 7.29-7.48 (m, Ph), 8.21 (d, 4.5 Hz, C$_5$H$_3$(3-Me)N)	52.8	
[Pd$_3$(μ-Te)$_2$(dppe)$_3$]Cl$_2$	**11**	2.30 (m, –PCH$_2$), 6.86 (t, 8.1 Hz), 7.14 (m), 7.43 (br), 7.68 (m)	46.1	195
[Pd(SC$_5$H$_4$N)$_2$(dppp)]	**12a**	2.48 (m, CH$_2$), 3.20-3.35 (br, PCH$_2$), 6.03 (t, 12.3 Hz, C$_5$H$_4$N), 6.38 (t, 12.9 Hz, C$_5$H$_4$N), 6.72-7.76 (m, Ph + C$_5$H$_4$N), 7.93 (br, C$_5$H$_4$N)	7.1	
[Pd(SeC$_5$H$_4$N)$_2$(dppp)]	**12b**	2.76 (m, PCH$_2$), 3.45 (m, CH$_2$), 6.38 (br, C$_5$H$_4$N), 7.00-7.73 (m, Ph + C$_5$H$_4$N), 8.37 (d, 4.2 Hz, C$_5$H$_4$N, H-6)	3.9	308

$[Pd(TeC_5H_4N)_2(dppp)]$	**12c**	2.28 (m, $–PCH_2$), 3.76 (br, dppp $–CH_2$), 6.68 (br, Ph), 6.86 (m, C_5H_4N), 7.04 (br, Ph + C_5H_4N), 7.39 (m, Ph), 7.23 (m, ph) 7.79 (br, Ph), 8.01 (d, 7.8 Hz C_5H_4N), 8.48 (dd, 4.5 Hz, 3.9Hz, C_5H_4N)	–4.6	
$[Pd_2(\mu\text{-}Se\text{-}C_5H_4N)_2(dppp)_2]Cl_2$	**13a**	2.46 (m, $–PCH_2$), 2.51 (br, $–CH_2$), 6.11 (t, C_5H_4N), 6.26 (br, C_5H_4N), 6.46 (t, 6 Hz, C_5H_4N), 6.80-7.90 (m, Ph), 8.44 (dd, 6 Hz, 1 Hz, C_5H_4N)	15.5, 0.9	160
$[Pd_2(\mu\text{-}SeC_5H_3(3\text{-}Me)N)_2(dppp)_2]Cl_2$	**13b**	2.01 (s, Me), 3.19 (br, PCH_2), 6.19 (br, $C_5H_3(3\text{-}Me)N$), 6.38 (t, 5.4 Hz, $C_5H_3(3\text{-}Me)N$), 7.40 (br, Ph), 7.72 (m, Ph), 8.29 (d, 4.5 Hz, $C_5H_3(3\text{-}Me)N$);	15.4, –1.2	132
$[Pd_2\{\mu\text{-}TeC_5H_3(3\text{-}Me)N\}_2(dppp)_2]Cl_2$	**14b**	2.34 (s, Me), 3.18 (br, dppp, $–CH_2$), 6.13 (t, $C_5H_3(3\text{-}Me)N$), 6.60 (br, $C_5H_3(3\text{-}Me)N$), 7.04-7.80 (m, Ph), 8.45 (d, C_5H_4N)	–9.6	
$[Pd_3(\mu\text{-}Te)_2(dppp)_3]Cl_2$	**15**	3.12 (br, dppp $–CH_2$), 7.18 (br), 7.47 -7.81 (m)	–11.0	–497
$[Pd(TeC_5H_4N)_2(PPh_3)_2]$	**16a**	7.46 (d, C_5H_4N), 7.56 (dd, Ph), 7.60-7.69 (m, Ph), 8.09 (d, C_5H_4N), 8.45 (br, C_5H_4N)	28.4	
$[Pd\{TeC_5H_3(3\text{-}Me)N\}_2(PPh_3)_2]$	**16b**	2.47 (s, Me), 7.05 (br, $C_5H_3(3\text{-}Me)N$), 7.35 (br, $C_5H_3(3\text{-}Me)N$), 7.46-7.71 (m, Ph), 8.30 (br, $C_5H_3(3\text{-}Me)N$);	29.4	
$[PdCl\{TeC_5H_3(3\text{-}Me)N\}(PPh_3)]$	**17**	2.07 (s, Me), 6.84 (t, $C_5H_3(3\text{-}Me)N$) 7.28 (d, $C_5H_3(3\text{-}Me)N$), 7.46-7.67 (m, Ph), 7.89 (d, $C_5H_3(3\text{-}Me)N$)	29.04	
$[PdCl\{Te(Cl)_2C_5H_3(3\text{-}Me)N\}(PPh_3)]$	**18**	2.51 (s, Me), 7.43 (m, Ph + $C_5H_3(3\text{-}Me)N$), 7.83 (m, Ph), 8.83(d, $C_5H_3(3\text{-}Me)N$)	27.8	

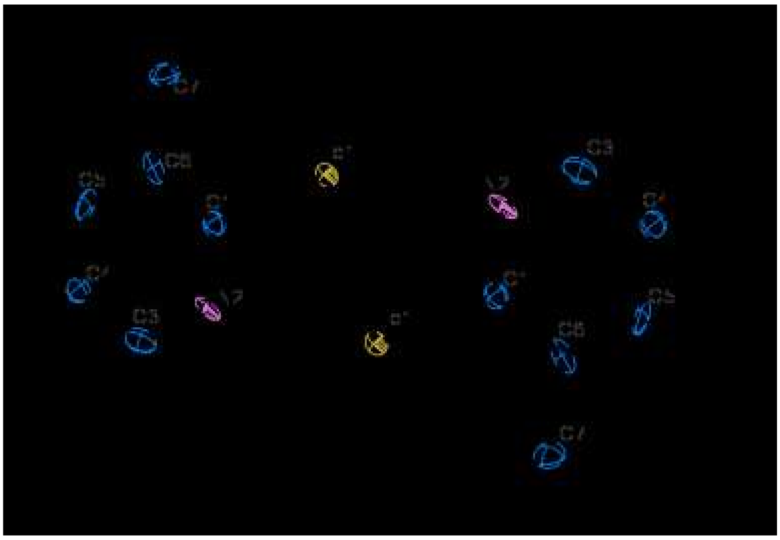


Figure 7: ORTEP diagram of $\{C_5H_3(3\text{-}Me)N\}_2Te_2$ [Interatomic parameters: bond lengths (Å) : Te1-C1, 2.136(11); Te1-Te1^i, 2.7199(17); bond/ torsion angles (^{o}), C1-Te1-Te1^i, 87.7(3), N2-C1-Te1, 115.7(8), C6-C1-Te1, 120.1(8), Te1^i-Te1-C1-N2, 0.0(8), Te1^i-Te1-C1-C6, 177.8(8), C1-Te1-Te1^i-C1^i, 180].

pyridyl)ditelluride (2.68(6) Å) [191], bis(2,5-dibromo-3-pyridyl)ditelluride (2.68(15) Å) [191] and bis(2,5-dibromo-6-methyl-3-pyridyl)ditelluride (2.69(11) Å) [191], but shorter than for bis(8-dimethylaminonaphthyl)ditelluride (2.765(1) Å) [259, 260]. There are intramolecular secondary Te….N interactions (3.015 Å) (cf. sums of covalent and van der waals radii of Te and N are 2.15 and 3.61 Å, respectively) which are absent in other dipyridylditellurides [191]. Because of these secondary Te….N interactions the two pyridyl rings and Te–Te linkage are coplanar with C–Te–Te–C torsion angle of 180^o (in case of bis(2-pyridyl)ditellurides the C–Te–Te–C torsion angle is 86.3(2)$^{o\ 2}$ [191]). The existence of Te…N interactions may also contribute to the lengthening of Te–Te bond [259]. The Te–C distances (2.136(11) Å) are similar to those reported in diorgano ditellurides.

The cationic complexes, $[Pd_2(\mu\text{-}TeC_5H_4N)_2(dppp)_2]^{2+}$ and $[Pd_2\{\mu\text{-}TeC_5H_3(3\text{-}Me)N\}_2(dppp)_2]^{2+}$ are isostrutural and both contain two tellurolato-bridges. The complexes are centrosymmetric dimers formed by two distoted square planar palladium atoms each coordinated to chelated dppp ligand and two bridging tellurolate groups. Due to a poor R factor for the former complex, structural data are not discussed here. The Pd–P distances are well in agreement with the reported values [227, 261]. The Pd–Te distances (~ 2.63 Å) are longer than those reported for palladium complexes containing non-bridging tellurolate ligands, e.g. $[PdCl(TeCH_2CH_2CH_2NMe_2)(PR_3)]$ ($PR_3 = PPr_3$ (Pd–Te = 2.5095(8) Å); $PMePh_2$ (Pd–Te = 2.5156(6) Å) [93], $[PdCl\{2\text{-}TeC_5H_3(3\text{-}Me)N\}(PPh_3)]$ (Pd–Te = 2.5606(8) Å) [206], but similar to those in other bridging systems, e.g. $[PdCl(\mu\text{-}TeCH_2CH_2CH_2NMe_2)]_2$ ($Pd\text{–}Te_{(av)}$ = 2.54 Å) [99], tellurolate ligands. The observed distances can however be compared with the $[Pd(TePh)_2(dppe)]$ (2.6361(9) Å) a complex containing tellurolate ligand *trans* to the strong *trans* influencing phosphine ligand [227]. The four-membered Pd_2Te_2 ring is planar with $C_5H_3(3\text{-}Me)N$ groups adopting an anti configuration. The geometry around the bridging tellurolate is pseudo-tetrahedral as indicated by the bond angles at tellurium.

The molecular structure of $[Pd_3(\mu\text{-}Te)_2(dppp)_3]Cl_2$ shows that the complex consists of three square planar "$[PdTe_2(dppp)]$" fragments sharing two μ_3–Te ligands. The central Pd_3Te_2 core adopts a trigonal bipyramidal configuration. The Te^{2-} ligands lie above and below the equilateral Pd_3 triangle (Pd_1–Pd_2, 3.506 Å, Pd_1–Pd_3, 3.537 Å and Pd_2–Pd_3, 3.352 Å). The Te….Te separation (3.326 Å) can be compared with $[Pd_2(\mu\text{-}Te)_2(dppe)_2]$ (Te….Te = 3.319(1) Å) [262] and $[Pt_3(\mu\text{-}Te)_2(dppe)_3][BPh_4]_2$ (Te….Te = 3.432(1) Å) [79]. The Pd–P and Pd–Te [80, 262] distances are as expected.

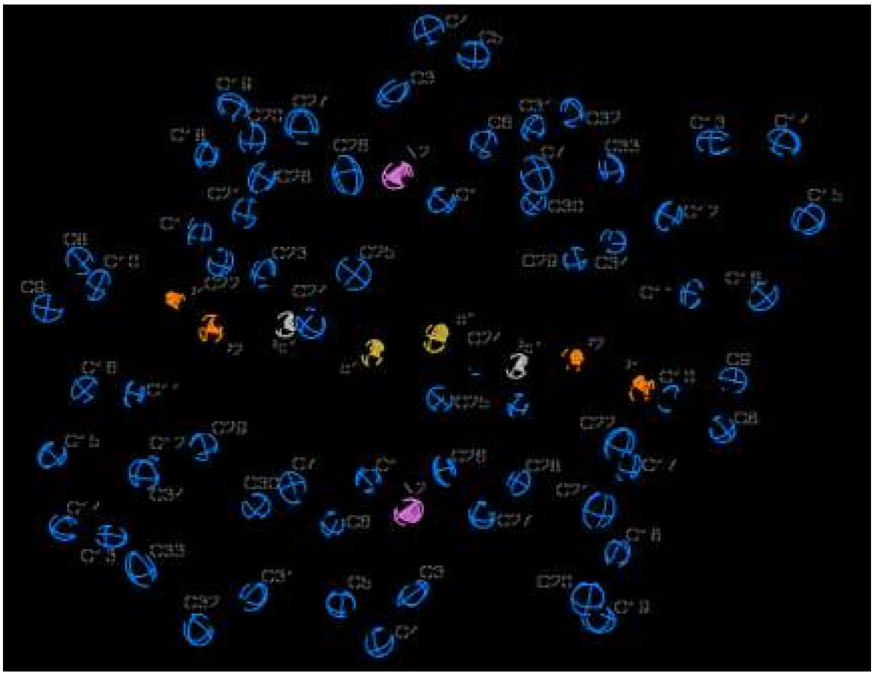


Figure 8: ORTEP diagram of $[Pd_2\{\mu\text{-}TeC_5H_3(3\text{-}Me)N\}_2(dppp)_2]Cl$

Table 27: Selected bond lengths (Å) and angles (^{o}) of $[Pd_2\{TeC_5H_3(3\text{-}Me)N\}_2(dppp)_2]Cl_2.3H_2O$

Pd1-Te1	2.6299(15)	P1-C11	1.800(8)
Pd1-Te1'	2.6391(17) 2	P1-C17	1.820(6)
Pd1-P1	2.282(2)	P2-C10	1.824(7)
Pd1-P2	2.294(2)	P2-C23	1.817(8)
Te1-C1	2.148(8)	P2-C29	1.830(8)
P1-C8	1.811(8)	Pd1-Pd1'	3.888
P1-Pd1-Te1	91.20(5)	Pd1-Te1-Pd1'	96.11(2) 2
P2-Pd1-Te1	167.01(6)	C8-P1-Pd1	116.0(2)
P1'-Pd1-Te1	172.79(5) 2	C11-P1-Pd1	114.1(2)
P2'-Pd1-Te1	90.54(5) 2	C17-P1-Pd1	109.3(2)
P1-Pd1-P2	95.32(7)	C10-P2-Pd1	117.8(2)
Te1-Pd1-Te1'	83.89(2) 2	C23-P2-Pd1	116.5(2)
C1-Te1-Pd1	95.5(2)	C29-P2-Pd1	106.7(3)
C1-Te1-Pd1'	85.7(2) 2		

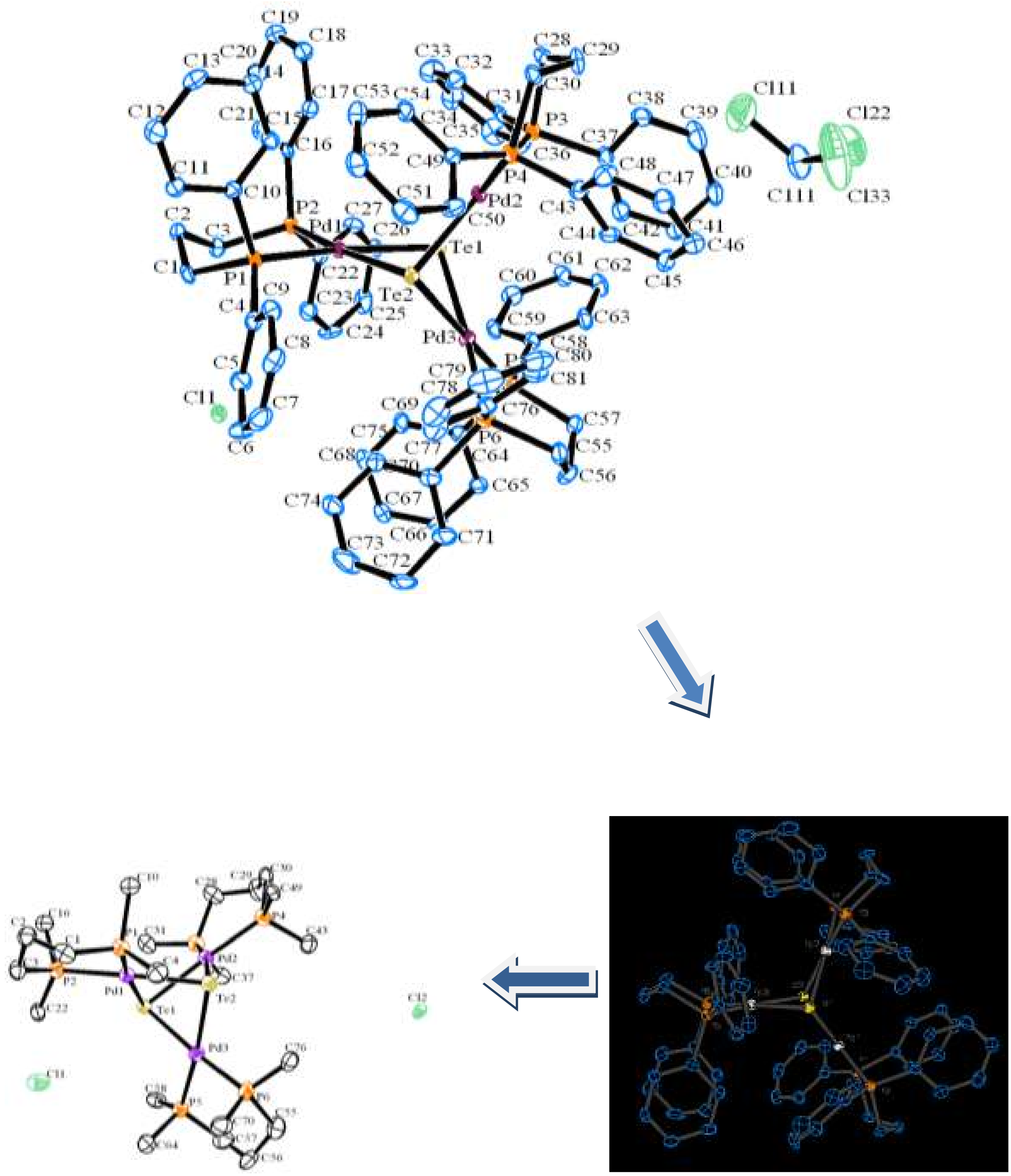


Figure 9: ORTEP diagram of $[Pd_3Te_2(dppp)_3]Cl_2$. $3CHCl_3$ (Hydrogen and sovent molecules are omitted due to clarity)

Table 28: Selected bond lengths (Å) and angles (^{o}) of $[Pd_3Te_2(dppp)_3]Cl_2 . 3CHCl_3$

Pd1–Te1	2.6061(8)	Pd1–P1	2.296(2)
Pd1–Te2	2.6044(10)	Pd1–P2	2.305(3)
Pd2–Te1	2.6023(9)	Pd2–P3	2.291(2)
Pd2–Te2	2.6022(9)	Pd2–P4	2.293(3)
Pd3–Te1	2.6024(10)	Pd3–P5	2.285(3)
Pd3–Te2	2.6005(9)	Pd3–P6	2.297(3)
P1-Pd1-Te1	171.17(8)	P5-Pd3-Te1	94.72(8)
P1-Pd1-Te2	92.09(7)	P5-Pd3-Te2	174.02(8)
P1-Pd1-P2	96.34(9)	P5-Pd3-P6	92.10(10)
P2-Pd1-Te1	92.29(6)	P6-Pd3-Te1	172.96(8)
P2-Pd1-Te2	171.48(6)	P6-Pd3-Te2	93.66(8)
Te2-Pd1-Te1	79.33(3)	Te2-Pd3-Te1	79.47(3)
P3-Pd2-Te1	92.18(7)	Pd2-Te1-Pd1	84.67(3)
P3-Pd2-Te2	171.62(8)	Pd3-Te1-Pd1	85.57(3)
P3-Pd2-P4	96.06(9)	Pd2-Te2-Pd1	84.70(3)
P4-Pd2-Te1	171.72(7)	Pd3-Te2-Pd1	85.65(3)
P4-Pd2-Te2	92.32(7)	Pd2-Te1-Pd3	80.20(3)

Various interatomic parameters involving the palladium atom in $[PdCl\{Te(Cl)_2C_5H_3(3\text{-}Me)N\}(PPh_3)]$ differ slightly from its precursor, $[PdCl\{TeC_5H_3(3\text{-}Me)N\}(PPh_3)]$ [206]. The metal square-plane defined by "TeNPCl" donor atoms forms an angle of 2^{o} with the four membered chelate ring ("PdTeCN") which lies at an angle of 7.36^{o} with the planar pyridine ring. The geometry around tellurium atom is distorted trigonal bipyramidal in which one of the equatorial sites is occupied by the stereochemically active lone pair of electrons. The chloride atoms lie at the axial position forming Cl–Te–Cl angle of 173.00(16)^{o} which is comparable to the X–Te–X angle observed in R_2TeX_2 (X = Cl, Br, I)

[263-265]. The Te–C distance is well in agreement with the value reported in literature for organotellurium compounds, e.g. (napthyl)(MesCOCH$_2$)TeCl$_2$ (Te–C – 2.121(3) Å) [263].

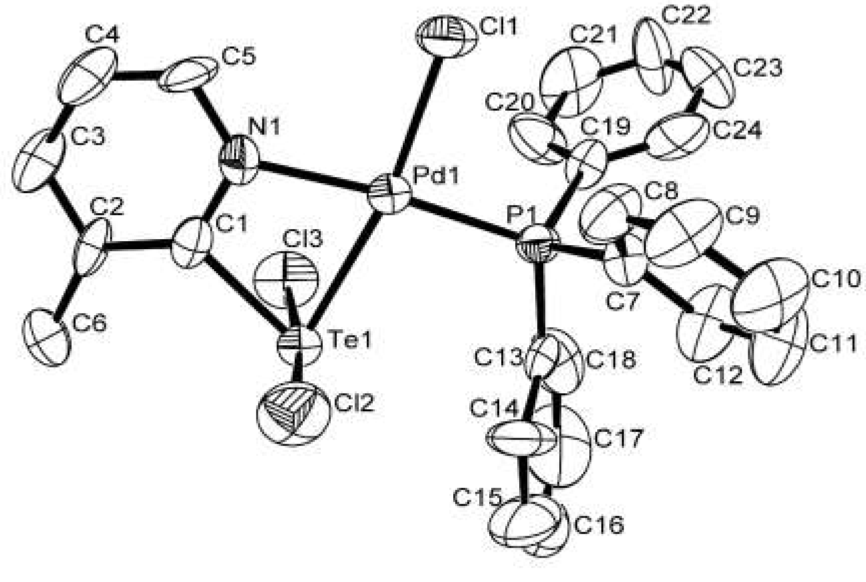


Figure 10: ORTEP diagram of [PdCl{Te(Cl)$_2$C$_5$H$_3$(3-Me)N}(PPh$_3$)]

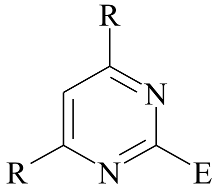
Table 29: Selected bond lengths (Å) and angles (°) of [PdCl{Te(Cl)$_2$C$_5$H$_3$(3-Me)N}(PPh$_3$)]

Te1-Pd1	2.540(2)	Te1-Cl2	2.535(5)
Pd1-N1	2.106(11)	Te1-Cl3	2.509(5)
Pd1-P1	2.242(5)	Te1-C1	2.120(13)
Pd1-Cl1	2.321(4)		
N1-Pd-P1	172.2(4)	Cl2-Te-Pd1	90.15(14)
N1-Pd1-C11	95.8(4)	Cl3-Te-Pd1	90.09(13)
P1-Pd1-C11	91.18(15)	C1-Te1-Pd1	73.5(5)
N1-Pd1-Te1	73.7(4)	Cl3-Te1-Cl2	173.00(16)
P1-Pd1-Te1	99.36(12)	C1-Te1-Cl2	88.5(4)
Cl1-Pd1-Te1	169.46(12)	C1-Te1-Cl3	84.8(4)
C5-N1-Pd1	133.5(12)		
C1-N1-Pd1	106.7(9)		

3.3 Chemistry of pyrimidylselenolate and tellurolate complexes of palladium and platnum

The chemistry of platinum group chalcogenolate complexes continues to be an active area of considerable research owing to several obvious reasons. These include their use as molecular tectons for the synthesis of high nuclearity complexes [237, 255, 266], precursors for low temperature synthesis of metal chalcogenides [241, 267, 268] and their relevance in catalysis [213, 269, 271]. Palladium catalyzed addition of E-E bond to alkyne has emerged an important strategy to prepare vinylsulfides/ selenides [213] which find numerous applications in organic synthesis, coordination chemistry and electronics [58, 272-274]. The catalytic reaction proceeds with excellent stereoselectivity and is believed to involve mononuclear *cis*-$[Pd(EAr)_2(PR_3)_2]$ (E = S or Se) complexes [275], although binuclear complexes, $[Pd_2(EAr)_2(\mu\text{-}EAr)_2(PR_3)_2]$ are generally isolated when $[Pd(PR_3)_4]$ is treated with ArEEAr (E = S or Se) [113, 116, 118, 211]. Such reactions with diaryl ditellurides, in contrast, yield several products due to competitive cleavage of Te-Te and Te-C bonds [120, 215, 216].

In view of the above and in context of sections 3.1 and 3.2 chemistry of ligand systems where chalcogen carbon is linked to two heteroatoms, e.g. 2-pyrimidyl group, has been examined. In such molecules both denticity of the ligand and basicity of the heterocyclic ring will be enhanced. Accordingly 2-chalcogenopyrimidyl ligands (**Scheme 23**) have been synthesized and their reactions with M(0) and M(II) (M = Pd or Pt) phosphine complexes, have been studied.



(R = H or Me; E= Se, Te)

Scheme 23: 2 -Chalcogenopyrimidyl ligand

Synthesis and spectroscopy

Synthesis of ligands

Treatment of 2-chloropyrimidine with Na_2E_2 (E = Se, Te) in water-ethanol mixture afforded not only a reddish diselenide but also yellow crystals of monoselenide whereas in case of tellurium only dark red (R = H) or blue crystals (R = Me) of ditellurides were obtained exclusively.

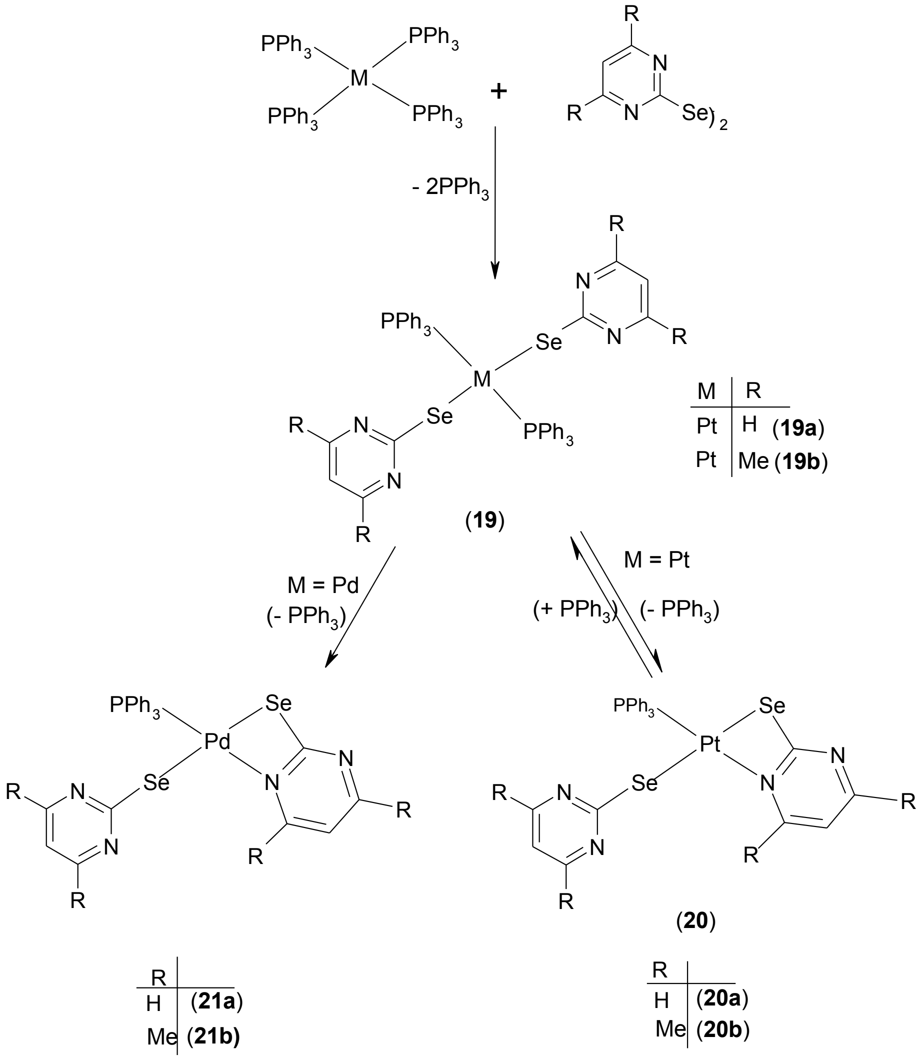
The ^1H NMR spectra of all the ligands displayed expected resonances and peak multiplicities. The ^{13}C NMR spectra of diselenides and ditellurides displayed peaks due to pyimidyl carbon in the range of 117.2-167.5 ppm. The signal due to C-4,6 carbons is significantly deshielded (~ 167 ppm) in dimethyl substituted dichalcogenides as compared to its position in unsubstituted derivatives (~ 158 ppm). The C-2 (or C-E) carbon signal in diselenided (~166 ppm) is considerably deshielded with respect to the corresponding ditellurides (~150 ppm) owing to the difference in their electronegativity and polarizabilty.

Reactions of $[M(PPh_3)_4]$ with di(2-pyrimidyl)diselenides

The oxidative addition reactions of $[M(PPh_3)_4]$ with dipyrimidyl diselenides proceed smoothly to afford complexes of the type *trans*-$[Pt\{SeC_4H(4,6\text{-}R)_2N_2\}_2(PPh_3)_2]$ (**19**) (when M = Pt) and $[Pd\{\eta^2\text{-}SeC_4H(4,6\text{-}R)_2N_2\}\{SeC_4H(4,6\text{-}R)_2N_2\}(PPh_3)]$ (**21**) (when M = Pd) (Scheme 24). Both theoretical [31] and experimental [276, 277] investigations on oxidative addition reactions of $[Pt(PR_3)_4]$ with diorgano diselenides have shown that initially a *cis*-$[Pt(SeAr)_2(PPh_3)_2]$ is formed which is subsequently isomerised to a thermodynamically stable *trans* product. Isolation of **19** as a *trans* isomer in the present study indicates that the isomerisation of *cis* form to *trans* is facile. The oxidative addition reactions of $[Pd(PPh_3)_4]$ with diorgano diselenides are known to yield binuclear complexes, $[Pd_2(SeAr)_2(\mu$-

$SeAr)_2(PPh_3)_2]$ exclusively [116, 118, 211]. However, in the present case, internal functionalization of the selenolate aids in chelation of the ligand. Based on the earlier work [116, 118, 211] and from this study it can be inferred that the oxidative addition reaction of R'_2E_2 (E = S or Se) on $[Pd(PR_3)_4]$ also yields initially a mononuclear complex, $Pd(ER')_2(PR_3)_2$, which dissociates in solution to PR_3 and a three- coordinate palladium species, "$Pd(ER')_2(PR_3)$". The latter species depending on the nature of R' group on ligand chalcogenolate ligand either dimerizes, when R' is simple alkyl or aryl group, or gives a monomeric chelate complex when R' contains an additional donor atom like nitrogen. Formation of such a three coordinate palladium species may have implication during palladium catalyzed addition of Ar_2E_2 to alkenes [275] and can be substantiated by the fact that the palladium complexes derived from chelated phosphines are inactive in these reactions [271] because of their inability to give three coordinate palladium complex.

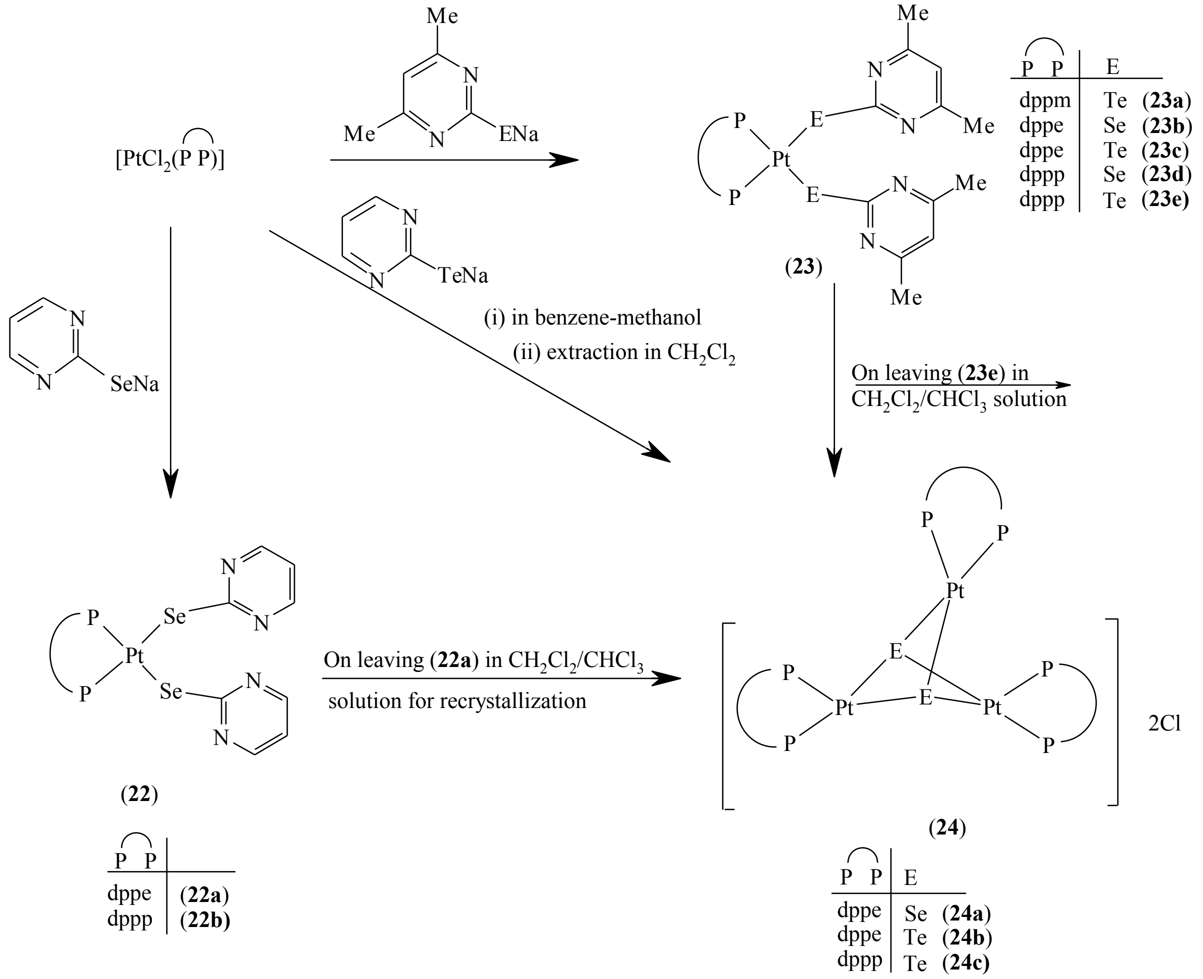
The ^{31}P NMR spectra of *trans*-$[Pt\{SeC_4H(4,6\text{-}R)_2N_2\}_2(PPh_3)_2]$ (**19**) and $[Pd\{\eta^2\text{-}SeC_4H(4,6\text{-}R)_2N_2\}\{SeC_4H(4,6\text{-}R)_2N_2\}(PPh_3)]$ (**21**) exhibited a singlet while resonances for the former were flanked by ^{195}Pt satellites (Table 30). The magnitude of $^1J(Pt\text{-}P)$ (~ 2800 Hz) is in conformity with *trans* configuration of the complexes [31, 116, 211]. The ^{195}Pt NMR spectrum of 19a showed a triplet at –5120 ppm due to coupling with two equivalent ^{31}P nuclei. The **19a** dissociated to platinum analogue (**20**) of **21** and triphenylphosphine in solution when left for a few hours. The ^{31}P NMR spectra of **20** were considerably shielded and the magnitude of $^1J(Pt–P)$ was also increased (~ 3900 Hz) with respect to **19**. The ^{195}Pt NMR spectrum of **20a** displayed a doublet due to coupling with a ^{31}P nucleus. The magnitude of $^1J(Pt–P)$ indicates that the phosphine ligand is *trans* to the nitrogen atom of the chelating selenolate ligand [206].



Scheme 24: Oxidative addition reactions of $[M(PPh_3)_4]$ (M =Pd or Pt) with 2-selenopyrimidines

Rections of $[MCl_2(P^\frown P)]$ with sodium 2-pyrimidyl chalcogenolate

Treatment of $[PtCl_2(P^\frown P)]$ with $NaSeC_4H_3N_2$ or $NaEC_4H(4,6\text{-}Me)_2N_2$ (E= Se or Te) in benzene-methanol mixture afforded mononuclear complexes of composition, $[Pt\{EC_4H(4,6\text{-}R)_2N_2\}_2(P^\frown P)]$ (**22** and **23**) (Scheme 25). However similar reaction with $NaTeC_4H_3N_2$ gave an orange powder which after extraction with dichloromethane afforded telluorido-bridged trinuclear complexes, $[Pt_3(\mu\text{-}Te)_2(P^\frown P)_3].2Cl$ (**24**) ($P^\frown P$ = dppe (**24b**) and dppp (**24c**)). When the mononuclear complexes **22a** and **23e** were left in halogenated solvents ($CDCl_3$ or CH_2Cl_2) for several hours, crystals of **24** were isolated. The ^{31}P NMR chemical shifts and $^1J(Pt–P)$ values for **24** are in conformity with the reported values [31, 237]. The formation of tellurido-bridged complex **24** either from **23e** in $CDCl_3$ or in the reaction between $PtCl_2(dppe)$ and $NaTeC_4H_3N_2$ takes place via a facile Te-C bond cleavage.



Scheme 25: Reactions of $[PtCl_2(P^{\frown}P)]$ ($P^{\frown}P$ = dppe or dppp) with sodium pyrimidyl chalcogenolate

The ^{31}P NMR spectra of **22** and **23** displayed single resonances flanked by ^{195}Pt satellites. The observed $^1J(Pt–P)$ values are consistent with the values reported for $[Pt(EAr)_2(P^{\frown}P)]$ complexes [206, 237, 278, 279]. The $^{125}Te\{^1H\}$ NMR spectrum (Figure 11) of $[Pt\{TeC_4H(4,6\text{-}Me)_2N_2\}_2(dppm)]$ displayed three lines centred at –32 ppm with platinum satellites (^{1}J(Pt–Te) = 1034 Hz). The observed pattern is in fact a second order spectrum originating due to coupling with *cis* and *trans* phosphorus nuclei.

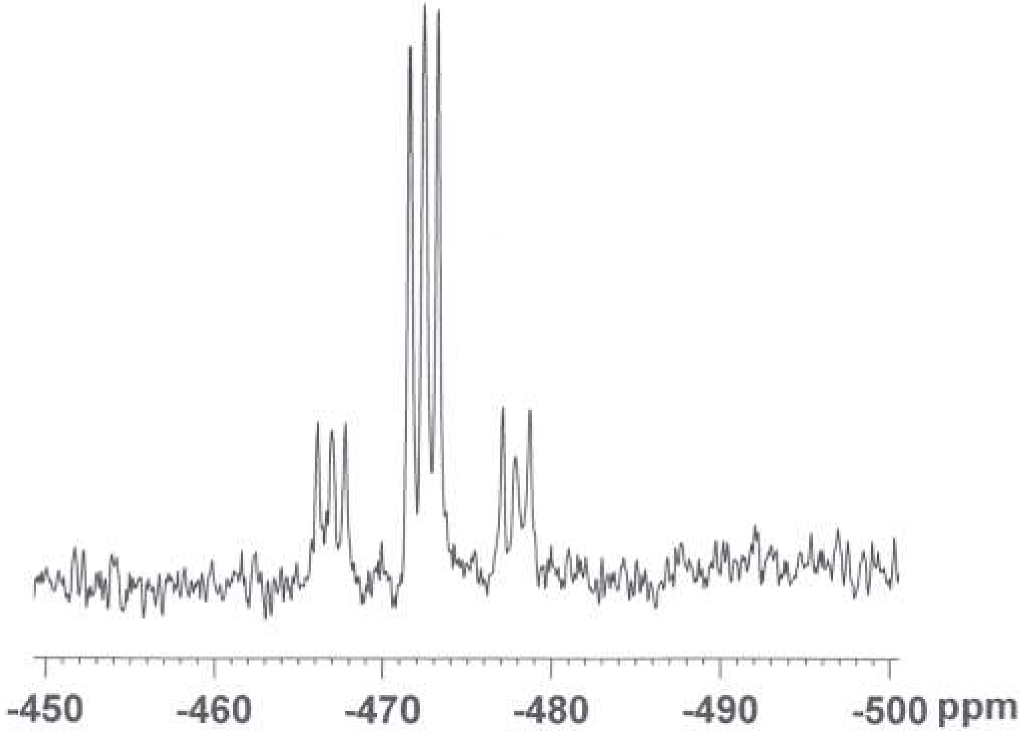
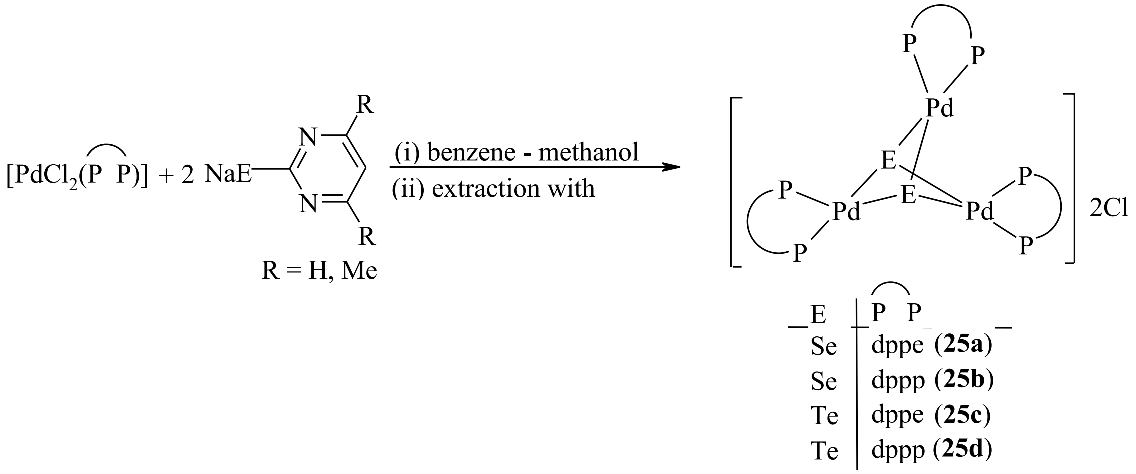


Figure 11: ^{125}Te{^{1}H} NMR spectrum of [Pt{TeC$_4$H(4,6-Me)$_2$N$_2$}$_2$(dppm)] in CDCl$_3$

The reactions between [PdCl$_2$(P$^\frown$P)] and NaEC$_4$H(4,6-R$_2$)N$_2$ (E = Se or Te; R = H or Me) in benzene-methanol mixture followed by extraction with dichloromethane invariably gave trinuclear chalcogenido-bridged palladium complexes, [Pd$_3$(μ-E)$_2$(P$^\frown$P)$_3$]2Cl (**25**) (E = Se or Te; P$^\frown$P = dppe or dppp) in 52-72% yield (Scheme 26). The ^{1}H NMR spectra were devoid of any EC$_4$H(4,6-R$_2$)N$_2$ proton resonances as expected. The ^{31}P NMR chemical shifts (Table 30) for **25** are in accordance with BPh$_4$/PF$_6$ salts of [Pd$_3$(μ-E)$_2$(P$^\frown$P)$_3$]$^{2+}$ cations reported earlier [79, 244, 280]. These complexes have been isolated in low yields by a reaction between [PdCl$_2$(P$^\frown$P)] and NaEH (E = Se or Te) in the presence of NaBPh$_4$ or NaPF$_6$ [244, 278]. The selenido- bridged complexes have been isolated in fairly good yield through unprecedented cleavage of C-Se bond of selenocarboxylate during the reaction of [Pd(SeCOAr)$_2$(P$^\frown$P)] with [PdCl$_2$(P$^\frown$P)] in the presence of NaBPh$_4$ in CH$_2$Cl$_2$-MeOH solvent mixture [280]. In an alternative route **25a** has been prepared in 52% yield by Morley *et. al.* by the reaction of [Pd(dppe)$_2$] with selenium powder in CH$_2$Cl$_2$ [246].



Scheme 26: Reactions of [PdCl$_2$(P$^\frown$P)] (P$^\frown$P = dppe or dppp) with sodium 2-pyrimidyl chalcogenolates.

X ray crystallography

The molecular structures of [Pt(SeC$_4$H$_3$N$_2$)$_2$(PPh$_3$)$_2$].2CH$_2$Cl$_2$ (Figure 12) and [Pd{η^2-SeC$_4$H$_3$N$_2$}{SeC$_4$H$_3$N$_2$}(PPh$_3$)]. CH$_2$Cl$_2$ (Figure 13) were established by X-ray diffraction analyses. Both the complexes crystallized with solvent molecule(s) (CH$_2$Cl$_2$). Selected interatomic parameters are given in Tables 31, 32.

The [Pt(SeC$_4$H$_3$N$_2$)$_2$(PPh$_3$)$_2$].2CH$_2$Cl$_2$ comprises of a distorted square planar central platinum atom. The *trans*-P$_2$Se$_2$ donor set defines the coordination environment around the platinum atom. The two selenolate groups adopt an *anti* configuration. The Pt–Se distances (2.4491(11) Å) are similar to those reported for the known [Pt(SeR')$_2$(PR$_3$)$_2$]; *trans*-[Pt(SePh)$_2$(PPh$_3$)$_2$] (2.417(3), 2.419(3) Å) [276], *trans*-[Pt(SeTh)$_2$(PPh$_3$)$_2$] (2.4629(1) Å and 2.465(1) Å) [116] and *trans*- [Pt(SePh)$_2$(PR$_3$)$_2$] (2.461(1) Å for R = Et and 2.463(3) Å for R =

Table 30: ^1H and $^{31}P\{^1H\}$ NMR data for 2-pyrimidylchalcogenolate complexes of platinum(II) and palladium(II) complex

Complex		^1H δ in ppm	$^{31}P\{^1H\}$ δ in ppm
$[Pt(SeC_4H_3N_2)_2(PPh_3)_2]$	**19a**	6.80 (br, $C_4H_3N_2$), 7.33–7.67 (m, Ph), 8.25 (br, $C_4H_3N_2$);	20.3 [(^1J (Pt–P) = 2792 Hz)]
$[Pt\{SeC_4H(4,6\text{-}Me)_2N_2\}_2(PPh_3)_2]$	**19b**	2.18 (s, Me), 6.32 (s, $C\mathit{H}$-5), 7.29 (br, Ph), 7.86 (br, C_4HN_2)	21.8 [(^1J (Pt–P) = 2831 Hz)]
$[Pt\{SeC_4H_3N_2\}\{\eta^2\text{-}SeC_4H_3N_2\}(PPh_3)]$	**20a**	—	7.4 [(^1J (Pt–P) = 3873 Hz)]
$[Pt\{SeC_4H(4,6\text{-}Me)_2N_2\}\{\eta^2\text{-}SeC_4H(4,6\text{-}Me)_2N_2\}(PPh_3)]$	**20b**	—	5.5 [(^1J (Pt–P) = 4064 Hz)]
$[Pd\{SeC_4H_3N_2\}\{\eta^2\text{-}SeC_4H_3N_2\}(PPh_3)]$	**21a**	6.73 (t, 4.8 Hz, $C_4H_3N_2$), 7.37 (br, PPh_3), 8.20 (d, 4.8 Hz, $C_4H_3N_2$);	32.9
$[Pd\{SeC_4H(4,6\text{-}Me)_2N_2\}\{\eta^2\text{-}SeC_4H(4,6\text{-}Me)_2N_2\}(PPh_3)]$	**21b**	2.23 (s, Me), 6.41 (s, C_4HN_2), 7.28 (d, Ph), 7.61 (br, Ph)	32.7
$[Pt\{SeC_4H_3N_2\}_2(dppe)]$	**22a**	2.13-2.37 (br, $-PC\mathit{H}_2$), 6.45 (br, $C_4\mathit{H}_3N_2$), 7.67-7.85 (m, Ph), 8.54 (br, pym)	46.1 [^1J(Pt–P) = 3090 Hz]
$[Pt\{SeC_4H_3N_2\}_2(dppp)]$	**22b**	1.95 (br), 2.51 (br (CH_2)$_,$ 6.79-8.48 (br, m, C_4H_3 and Ph)	–5.9 [^1J(Pt–P) = 2886 Hz]
$[Pt\{TeC_4H(4,6\text{-}Me)_2N_2\}_2(dppm)]$	**23a**	2.35 (s, Me), 4.38 (t, ^2J(P-H) = 10.2 Hz, ^3J(Pt-H) = 55 Hz, $-PC\mathit{H}_2$), 6.21 (s, $C_4\mathit{H}N_2$), 7.16-7.31 (m, Ph), 7.86 (br, Ph);	–50.1 [^1J(Pt–P) = 2512 Hz];

$[\mathrm{Pt\{SeC_4H(4,6\text{-}Me)_2N_2\}_2(dppe)}]$	**23b**	1.97 (s, Me), 2.13-2.20 (m, $-\mathrm{PC}H_2$), 6.22 (s, $\mathrm{C_4HN_2}$), 7.32 (br) 7.87 (m, $\mathrm{PPh_2}$);	45.7 [(^{1}J (Pt–P) = 3039 Hz)]
$[\mathrm{Pt\{TeC_4H(4,6\text{-}Me)_2N_2\}_2(dppe)}]$	**23c**	2.16 (m, $-\mathrm{PC}H_2$), 2.42 (s, Me), 6.22 (s, $\mathrm{C_4}H\mathrm{N_2}$), 7.31(br), 7.88 (br)(Ph);	45.8 [^{1}J(Pt–P) = 2978 Hz]
$[\mathrm{Pt\{SeC_4H(4,6\text{-}Me)_2N_2\}_2(dppp)}]$	**23d**	1.89(br), 2.49(br, $\mathrm{CH_2}$), 2.40 (s, Me), 6.33 (s, $\mathrm{C_4}H\mathrm{N_2}$), 7.33 (br), 7.83 (br, (Ph)	–5.0 [^{1}J(Pt–P) = 2887 Hz]
$[\mathrm{Pt_3Se_2(dppe)_3]Cl_2}$	**24a**	2.11-2.27(br, $-\mathrm{PC}H_2$), 7.22-7.70 (m, Ph)	38.7 [^{1}J(Pt–P) = 3244 Hz]
$[\mathrm{Pt_3(\mu\text{-}Te)_2(dppe)_3]Cl_2}$	**24b**	2.47 (m, $-\mathrm{PC}H_2$), 6.98-7.45 (m, Ph)	40.8 [^{1}J(Pt–P) = 3144 Hz]
$[\mathrm{Pt_3(\mu\text{-}Te)_2(dppp)_3]Cl_2}$	**24c**	2.51 (br, $-\mathrm{PC}H_2$), 2.95 (br, $\mathrm{C}H_2$), 7.13-7.21 (m, Ph), 7.40-744 (m, Ph), 7.78 (br, Ph);	– 13.0 [^{1}J(Pt–P) = 2980 Hz]
$[\mathrm{Pd_3(\mu\text{-}Se)_2(dppe)_3]Cl_2}$	**25a**	2.64 (br, $-\mathrm{PC}H_2$), 7.10 (t, 1.2Hz, Ph), 7.38-7.47 (m, Ph), 7.48-7.55 (m, Ph)	50.3
$[\mathrm{Pd_3(\mu\text{-}Se)_2(dppp)_3]Cl_2}$	**25b**	2.85 (br, $-\mathrm{PC}H_2$), 3.2 (br, $-\ \mathrm{C}H_2$), 6.38 -7.16 (m, Ph), 7.47 -7.59 (br, Ph), 7.77-7.84 (m, Ph)	–3.0
$[\mathrm{Pd_3(\mu\text{-}Te)_2(dppe)_3]Cl_2}$	**25c**	2.40 (m, $-\mathrm{PC}H_2$), 7.40 (br), 7.79 (br) (Ph)	46.3
$[\mathrm{Pd_3(\mu\text{-}Te)_2(dppp)_3]Cl_2}$	**25d**	2.95 (br, $-\mathrm{PC}H_2$), 2.51(br, $-\mathrm{C}H_2$), 7.14-7.77 (m, Ph)	–11.0

Bu) [118]. The Pt–P distances are in good agreement with those reported for [Pt(SeR')$_2$(PR$_3$)$_2$] complexes [31, 116, 118]. The two acute (82.74(5)°) and obtuse (97.26(5)°) P–Pt–Se angles can be compared with those observed for *trans*-[Pt(SeTh)$_2$(PPh$_3$)$_2$] (~ 83 and ~ 96°), but differ from phenylselenolate derivatives, *trans*-[Pt(SePh)$_2$(PR$_3$)$_2$] (R = Et, Bu, Ph) (~ 86 and ~ 94°) [31, 118, 277].

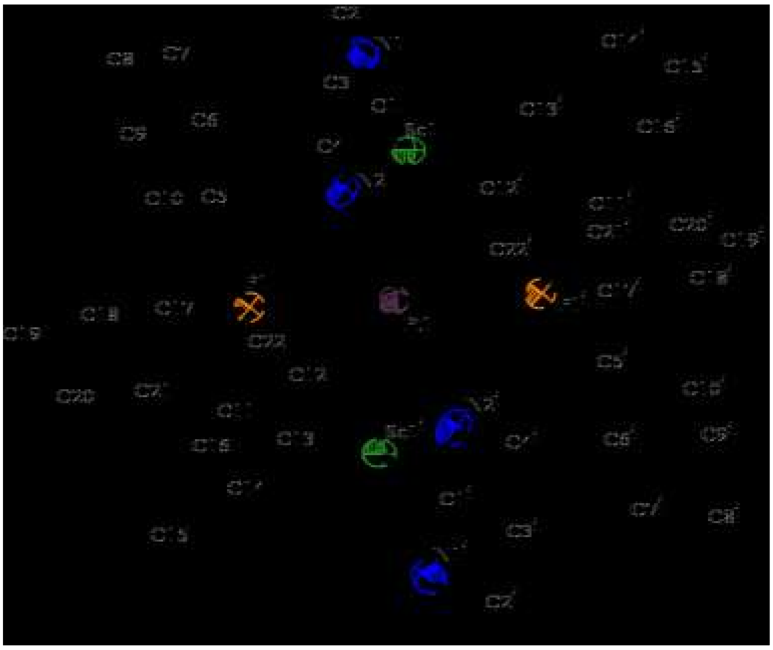


Figure12: ORTEP diagram of [Pt(SeC$_4$H$_3$N$_2$)$_2$(PPh$_3$)$_2$].2CH$_2$Cl$_2$ (Hydrogen and solvents molecules are omitted for clarity)

Table 31: Selected bond lengths (Å) and angles (°) of [Pt(SeC$_4$H$_3$N$_2$)$_2$(PPh$_3$)$_2$].2CH$_2$Cl$_2$

Pt1-P1	2.3128(19)	Pt1-P1	2.313(2)
Pt1-Se1	2.4491(11)	Pt1-Se1	2.4491
Se1-C1	1.900(7)		
P1-Pt1-P1	179.999(1)	Se1-Pt1-Se1	179.998(11)
P1-Pt1-Se1	97.26(5)	P1-Pt1-Se1	82.74(5)
P1-Pt1-Se1	82.74(5)	P1-Pt1-Se1	97.26(5)
C1-Se1-Pt1	106.9(3)		

The palladium atom in [Pd{η^2-$SeC_4H_3N_2$}{$SeC_4H_3N_2$}(PPh_3)].CH_2Cl_2 acquires distorted square planar geometry defined by P, N, Se_2 donor atoms, the neutral donor atoms (P and N) being trans. One of the selenolate ligand forms a four-membered chelate ring while the other selenolate is bound to palladium in a monodentate fashion. The four-membered chelate ring and the pyrimidyl ring are nearly co-planar. The two Pd–Se distances are similar and are in agreement with those reported in literature, e.g. [$Pd_2(SeTh)_4(PPh_3)_2$] (Pd-Se = 2.465(av)Å) [87]. The Pd–N and Pd–P distances are as expected, e.g. [PdCl(TeC_5H_3(Me)N)(PPh_3)] (Pd-P = 2.2420(15) and Pd-N = 2.085(4) Å) [206].

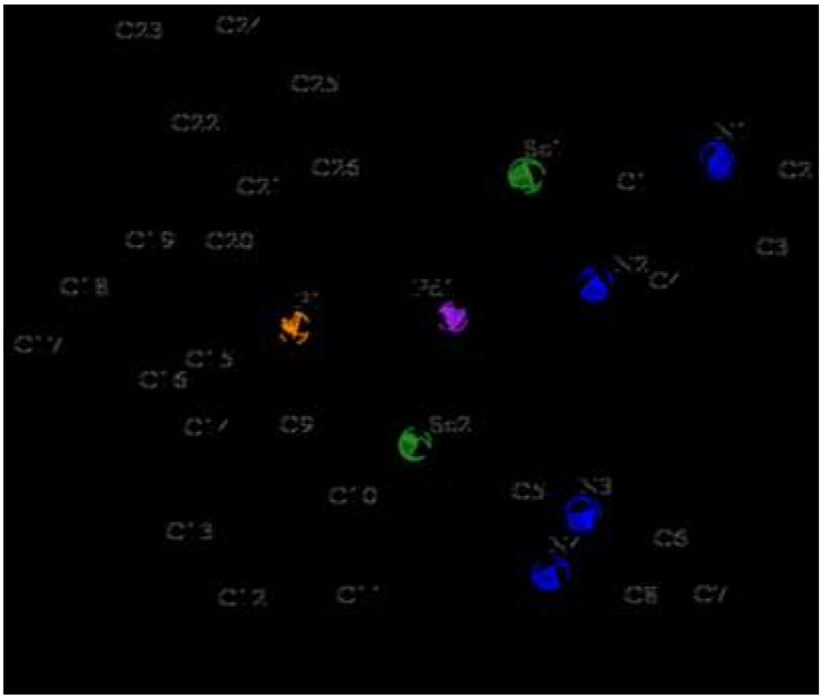


Figure 13: ORTEP diagram of [Pd{η^2-$SeC_4H_3N_2$}{$SeC_4H_3N_2$}(PPh_3)].CH_2Cl_2 (Hydrogen and solvents molecules are omitted for clarity)

Table 13: Selected bond lengths (Å) and angles (^{o}) of $[Pd\{\eta^2\text{-}SeC_4H_3N_2\}\{SeC_4H_3N_2\}(PPh_3)].CH_2Cl_2$

Pd1-P1	2.2310(13)	Se1-C1	1.891(4)
Pd1-Se1	2.4394(7)	Se2-C5	1.917(5)
Pd1-Se2	2.4341(7)	N2-C1	1.349(6)
Pd1-N2	2.118(4)		
N2-Pd1-P1	170.76(11)	C1-Se1-Pd1	77.47(14)
P1-Pd1-Se1	100.66(4)	C1-N2-Pd1	102.3(3)
P1-Pd1-Se2	90.90(4)	C5-Se2-Pd1	96.38(14)
N2-Pd1-Se1	71.01(10)	N1-C1-Se1	125.5(3)
Se2-Pd1-Se1	168.37(2)	N2-C1-Se1	109.2(3)
N2-Pd1-Se2	97.37(10)	N1-C1-N2	125.3(4)

3.5 Chemistry of nicotinamide based organoselenolate complexes of palladium and platinum

Oxidative addition reactions of diorgano-disulfides or diselenides to palladium(0) and platinum(0) complexes has received considerable recent attention [31, 212, 271, 281, 282] due to its relevance in organic synthesis [208, 212, 213] and ease to prepare metal chalcogenolate complexes which find applications in catalysis [283, 284] and materials science [214, 261]. These reactions with platinum(0) precursors afford mononuclear complexes [115, 118] while with palladium(0) species yield binuclear, $[Pd_2(\mu\text{-}ER')_2(ER')_2(PR_3)_2]$ derivatives as isolable products [113, 116, 285]. However with internally functionalized ligands, mononuclear palladium complexes are isolated [282, 286]. Unlike disulfides/ diselenides, reactions of ditellurides with Pd^0/ Pt^0 complexes often yield a mixture of products produced by competitive cleavage of Te-Te and Te-C bonds [120, 249, 257].

In the sections 3.1–3.3, reactions of 2-pyridyl/pyrimidyl dichalcogenides with palladium(0) and platinum(0) phosphine complexes [249, 257, 287] have been discussed. In these reactions several serendipitous products, e.g. $[Pt(Te)\{Te\text{-}C_5H_3(R)N\}_2(PPh_3)]$ have been isolated. The reactions of dipyridyl diselenides, in general, proceed similar to diphenyl diselenide, but dipyrimidyl diselenide shows different reactivity pattern [286]. In such reactions, besides expected products $[M(SeC_5H_3N_2)_2(P^\frown P)]$ a Se-C bond cleaved product, $[Pd_3(\mu\text{-}Se)_2((P^\frown P)_3]^{2+}$ could be isolated [286]. This led to an exploration of the reactivity pattern of N-heterocyclic selenides with additional functionalities. Thus, the reactions of nicotinoyl based selenide ligands [103] (Scheme 27), with $[M(PPh_3)_4]$ (M = Pd or Pt) have been investigated.

(R = NH_2, NHPh, NHpym, OH)

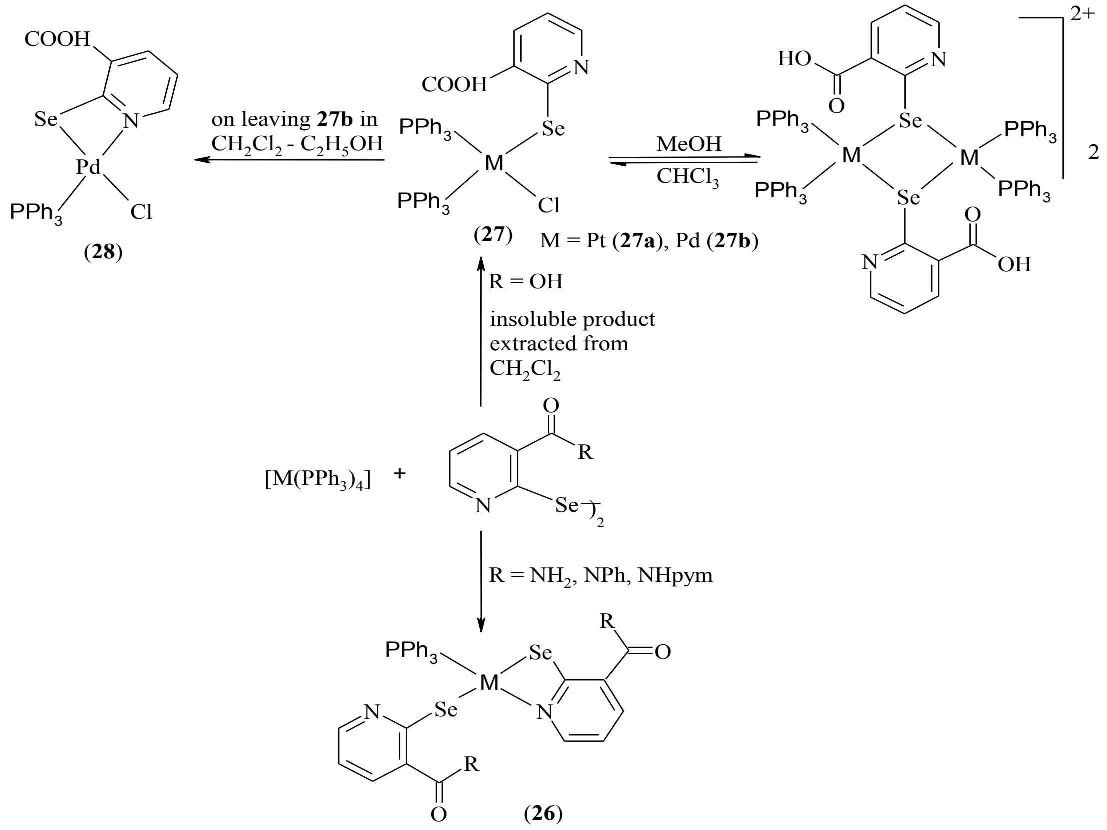
Scheme 27: Nicotinamide based organoselenium ligand

Synthesis and spectroscopy

Treatment of $[M(PPh_3)_4]$ (M = Pd or Pt) with nicotinamide based diselenides, $\{2\text{-}NC_5H_3(3\text{-}COR)Se\}_2$ (R = NH_2, NHPh, NHpym; pym = pyrimidyl), in benzene at room temperature afforded complexes of composition $[M\{\eta^2\text{-}SeC_5H_3(3\text{-}COR)N\}\{SeC_5H_3(3\text{-}COR)N\}(PPh_3)]$ (**26**) in 61-73% yield as yellow to orange/red crystalline solids (Scheme 28). The ^{31}P NMR spectra exhibited a single resonance indicating the existence of a single species in solution. The resonances for platinum complexes appeared at 6.4 ppm while the signals for the palladium complexes were considerably deshielded (δ ~32.5 ppm). The resonances for platinum complexes were flanked by ^{195}Pt satellites with $^1J(Pt\text{-}P)$ values of ~3800 Hz suggesting disposition of PPh_3 ligand *trans* to the nitrogen atom [249]. The complexes tend to decompose when left in $CDCl_3$ solution for several hours at room temperature.

Reaction of $[M(PPh_3)_4]$ with $\{2\text{-}NC_5H_3(COOH\text{-}3)Se\}_2$ in benzene methanol mixture gave an insoluble solid which after extraction with $CHCl_3/CH_2Cl_2$ afforded complexes of composition $[M(Cl)\{SeC_5H_3(COOH\text{-}3)N\}(PPh_3)_2]$ (**27**) (M = Pt (**27a**) or Pd (**27b**)). Complexes (**27**) are non-conducting in acetonitrile or chloroform solution but exhibit conducting (diionic) behavior in methanol. This suggests that a dimeric diionic species containing bridging selenolate ligand is formed in methanol (Scheme 28). The ^{31}P NMR spectra of

$[M(Cl)\{SeC_5H_3(COOH\text{-}3)N\}(PPh_3)_2]$ (**27**) displayed two resonances, as expected and can be attributed to the phosphine ligands *trans* to chloride and selenolate ligands.



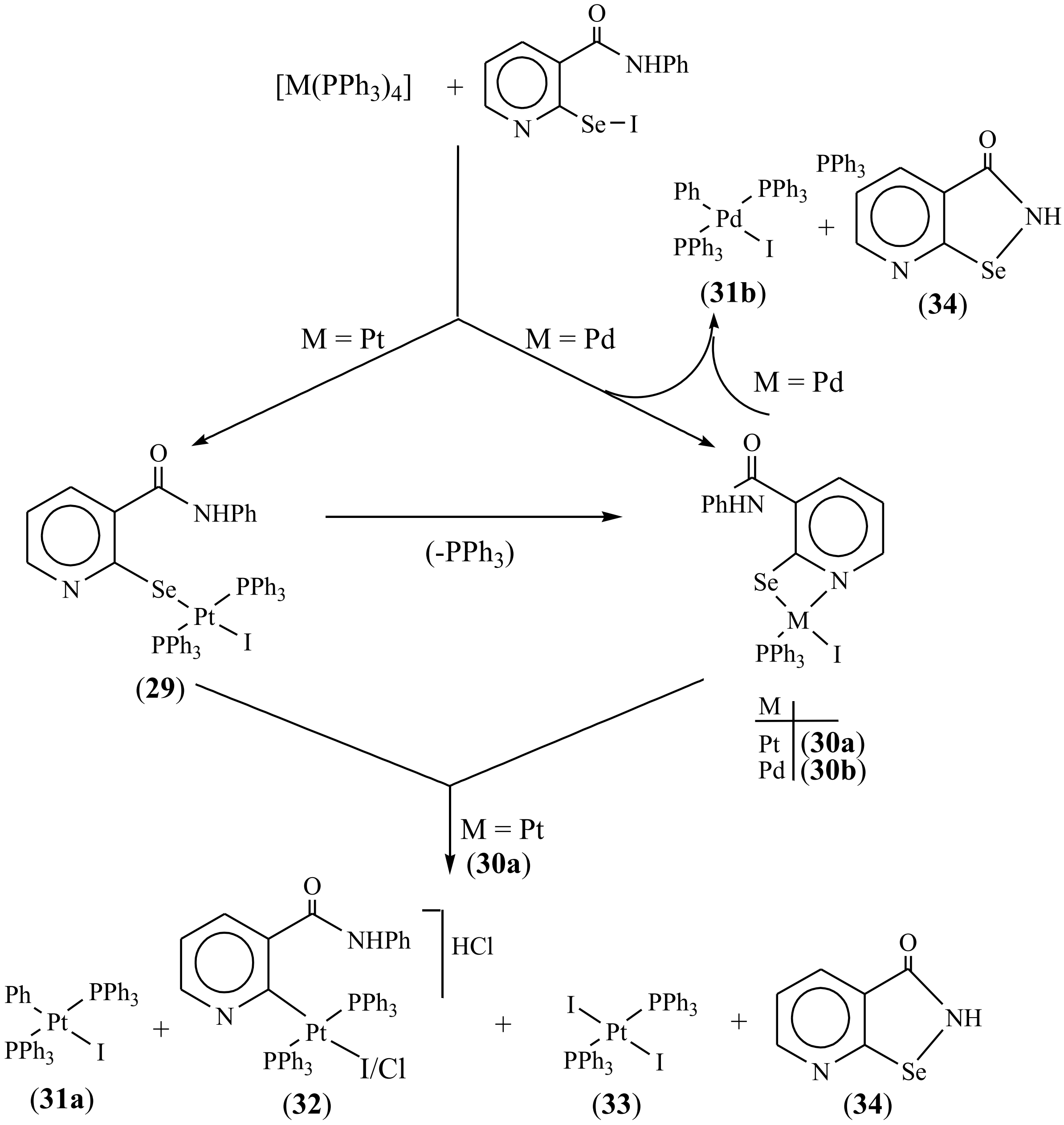
M	R	
Pt	NH_2	**26a**
Pd	NH_2	**26b**
Pt	NHPh	**26c**
Pd	NHPh	**26d**
Pd	NHpym	**26e**

Scheme 28: Reactions of $[M(PPh_3)_4]$ (M = Pt, Pd) with $[2\text{-}NC_5H_3(3\text{-}COR)Se]_2$

The ^1J(Pt-P) values (2750 (*trans* to selenolate) and 3586 Hz (*trans* to Cl)) for **27a** are also in accordance with this configuration. The complex **27b**, when left in CH_2Cl_2-EtOH solution for several hours at room temperature, gave a brown powder of composition $[Pd(Cl)\{\eta^2\text{-}SeC_5H_3(COOH\text{-}3)N\}(PPh_3)]$ (**28**). The latter showed only a single ^{31}P NMR resonance at 31.8 ppm. Recently Singh and co-workers [282] have reported a similar complex, $[Pd(Cl)\{\eta^2\text{-}SeC_6H_4\text{-}C(O)CH_2CMe_2N\}(PPh_3)]$ which was isolated from the reaction of $[Pd(PPh_3)_4]$ with bis{2-(4,4-dimethyl-2-oxazolinyl)phenyl}diselenide in dichloromethane.

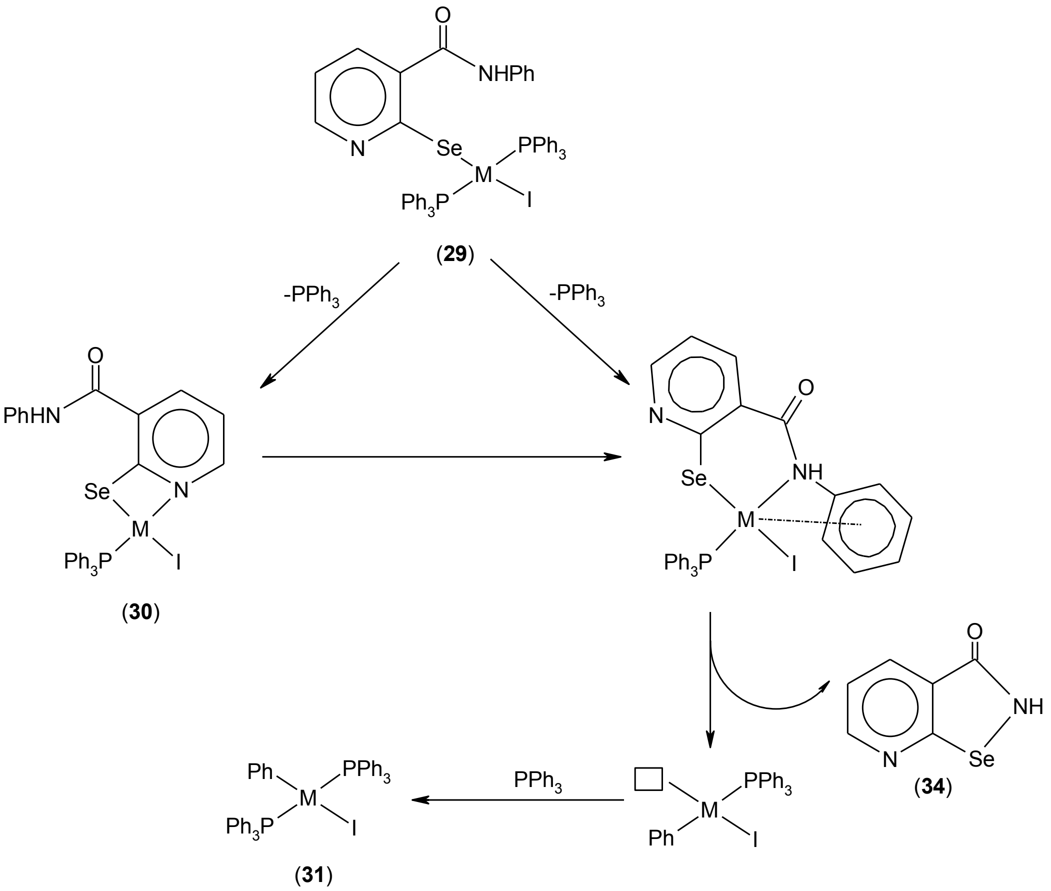
The reaction of $[M(PPh_3)_4]$ with $2\text{-}NC_5H_3(3\text{-}CONHPh)SeI$ in benzene at room temperature is quite complex giving several products formed by dissociation and/or decomposition of initially produced oxidative addition complex, $[M(I)\{SeC_5H_3(3\text{-}CONHPh)N\}(PPh_3)_2]$ (**29**) (Scheme 29) (M = Pt (**29a**), Pd (**29b**)). In the case of platinum, **29a** could be isolated in 74% yield as a yellow powder. The magnitude of $^1J(Pt\text{-}P)$ suggests that the phosphine ligands are mutually *trans*. The **29a** slowly loses triphenylphosphine in $CDCl_3$ solution to yield a new selenolate complex, $[Pt(I)\{\eta^2\text{-}SeC_5H_3(3\text{-}CONHPh)N\}(PPh_3)]$ (**30a**). The ^{31}P and ^{195}Pt NMR data for **30a** are consistent with the phosphine ligand *trans* to the nitrogen atom of the chelating ($Se^\frown N$) selenolate ligand [286]. When **29a** was left in CH_2Cl_2 solution for more than two days, at least four compounds, $[Pt(I)Ph(PPh_3)_2]$ (**31a**), $[Pt(Cl_{0.5}I_{0.5})\{C_5H_3(CONHPh)N\}(PPh_3)_2].HCl$ (**32**), *trans*-$[PtI_2(PPh_3)_2]$ (**33**) and $[2\text{-}NC_5H_3(3\text{-}CO)SeNH]$ (**34**) could be isolated. They were separated from each other based on their differences in solubilities in different solvents and by repeated crystallization. The NMR and analytical data are consistent with the suggested formulations. The former two, **31** and **32**, have been structurally characterized (see later).

When M is palladium, **29b** could not be isolated instead a brown powder of $[Pd(I)\{\eta^2\text{-}SeC_5H_3(3\text{-}CONHPh)N\}(PPh_3)]$ (**30b)** was precipitated out from the reaction. From the supernatant of this reaction or even leaving **30b** in $CDCl_3$ solution for several hours, at least two compounds, $[PdI(Ph)(PPh_3)_2]$ (**31b**) and [2- $NC_5H_3(3\text{-}CO)SeNH]$ (**34**), were separated. Singh *et. al.* have isolated complexes similar to **30b** in the reaction of $[Pd(Ph_3)_4]$ with {2-(4,4-dimethyl-2-oxazolinyl)phenyl}seleneyl halides (halide = Cl, Br, I) or {2-(N, N-dimethylaminomethyl)phenyl}selenyl halide (halide = Br or I) [282].



Scheme 29: Oxidative addition of [M(PPh_3)$_4$] (M = Pd, Pt) with [2-NC_5H_3(3-CONHPh)SeI]

The formation of **31** and **34** from **29/30** is rather intriguing and a plausible route for their formation is depicted in Scheme 30. During the oxidative addition reaction between [M(PPh_3)$_4$] and seleneyl iodide the expected oxidative product of composition **29** is formed and is isolated in case of platinum. This product loses a molecule of phosphine, rapidly in case of palladium to give isolable **30b**, and slowly (over a period of few hrs) in case of platinum to afford **30a**, which contains bidentate chelating four-membered selenolate (Se⌒N) ligand. Alternatively, the selenolate can also function as a six-membered Se⌒N chelating lignd via amide nitrogen atom coordination (Scheme 30). This species may have resonance interaction between filled metal dπ orbital and the phenyl ring as described in the literature [288]. This species on decomposition gives **34** and three coordinated "$[M(I)(Ph)(PPh_3)]$" which after coordination with liberated PPh_3 yield **31**. It is interesting to note that **34** is N-heterocyclic derivative of a well studied antioxidant organoselenium compound, ebselen [289].



Scheme 30: A possible path way involved in the formation of $[Pt(I)(Ph)(PPh_3)_2]$ **(31)** and $[2\text{-}NC_5H_3(3\text{-}CO)Se\text{-}NH]$ **(34)**

From the results discussed above and from recent reported work on oxidative addition reactions of $M(PR_3)_4$ with organoslenium ligands, it is evident that, in addition to expected complexes, some other products may also form depending on the nature of M, tertiary phosphine ligand and the organic groups attached to selenium atom. The role of the latter has marked influence on the overall reactivity of the complex. While the phenylselenolate complexes are stable in halogenated solvents for several days, the corresponding $SeC_5H_3(3\text{-}R)N$ derivatives tend to dissociated to give $Se^\frown N$ chelated products [19, 20]. In contrast, the pyrimidylselenolate complexes, in addition to $Se^\frown N$ chelation, also undergo Se-C bond cleavage [17]. Additional functionalization, as in the present case, leads to the formation of several products formed by the cleavage of C-Se (e.g. **31**)/ C-N (e.g. **34**) bonds. It appears that additional bonding sites bind the metal atom in solution to give transient species which undergo dissociation/ decomposition to give other products.

X-ray crystallography

The molecular structures of $[Pt\{\eta^2\text{-}SeC_5H_3(3\text{-}CONH_2)N\}\{SeC_5H_3(3\text{-}CONH_2)N\}(PPh_3)]$, $[Pd\{\eta^2\text{-}SeC_5H_3(3\text{-}CONHPh)N\}\{SeC_5H_3(3\text{-}CONHPh)N\}(PPh_3)]$, $[PtI(Ph)(PPh_3)_2]$ and $[Pt(Cl_{0.5}I_{0.5})\{C_5H_3(3\text{-}CONHPh)N\}(PPh_3)_2].HCl$ were established by X-ray diffraction analyses. The molecular structures are shown in Figures 14-17 while selected interatomic parameters are summarized in Tables 34-36.

The coordination environments around central metal atom in $[Pt\{\eta^2\text{-}SeC_5H_3(3\text{-}CONH_2)N\}\{SeC_5H_3(3\text{-}CONH_2)N\}(PPh_3)]$ and $[Pd\{\eta^2\text{-}SeC_5H_3(3\text{-}CONHPh)N\}\{SeC_5H_3(3\text{-}CONHPh)N\}(PPh_3)]$ are similar and are defined by PPh_3, monodentate and chelating bidentate ($Se^\frown N$) selenolate ligands. There are six independent molecules in the crystal lattice of $[Pd\{\eta^2\text{-}SeC_5H_3(3\text{-}CONHPh)N\}\{SeC_5H_3(3\text{-}CONHPh)N\}(PPh_3)]$ which differ marginally from each other in various bond lengths, angles and torsion angles. Two of these independent molecules are highly disordered. The four-membered "PdSeNC" and $SeC_5H_3(3\text{-}CONR)N$ rings are coplanar. The two M–Se distances in each complex are slightly different and the one

Table 33: ^{1}H, $^{31}P\{^{1}H\}$ and $^{77}Se\{^{1}H\}$NMR data for nicotinamide based organoselenium complexes of platinum(II) and palladium(II) complex

Complex		^{1}H δ in ppm	$^{31}P\{^{1}H\}$ δ in ppm	^{77}Se δ in ppm
$[Pt\{SeC_5H_3(3\text{-}CONH_2)N\}_2(PPh_3)]$	**26a**	5.83 (br, NH_2), 6.89-6.95 (m, py, CH-5), 7.11-7.73 (m, Ph), 8.07 (d, 6.6 Hz, CH-4), 8.23 (d, 7.8 Hz, CH-4), 8.73 (d, 3.6 Hz, CH-6), 9.05 (br, CH-6)	6.4 ($^{1}J(Pt–P)$ = 3806 Hz)]	232
$[Pd\{SeC_5H_3(3\text{-}CONH_2)N\}_2(PPh_3)]$	**26b**	5.81 (br, NH_2), 6.88 (t, 6.3 Hz, C_5H_4N), 7.22-7.72 (m, Ph+ C_5H_4N), 8.07 (d, 6.6 Hz, C_5H_4N)	32.6	213
$[Pt\{SeC_5H_3(3\text{-}CONHPh)N\}_2(PPh_3)]$	**26c**	6.71 (br, C_5H_4N), 7.32–7.47 (m, Ph+C_5H_4N), 7.50–7.67 (m, Ph+ C_5H_4N)	6.4 ($^{1}J(Pt–P)$ = 3775 Hz)]	
$[Pd\{SeC_5H_3(3\text{-}CONHPh)N\}_2(PPh_3)]$	**26d**	6.95 (dd, 5.1 Hz, C_5H_4N), 7.11 (t, 7.5 Hz, Ph), 7.30–7.75 (m, Ph), 8.12 (d, 8 Hz), 8.18 (br, d, C_5H_4N), 9.27 (s, –CON*H*)	51.1	203
$[Pt\{SeC_5H_3(3\text{-}CONHpym)N\}_2(PPh_3)]$	**26e**	7.43 (dd, 3.6 Hz, 6.3 Hz, $C_5H_3N_2$), 7.44–7.50 (m, Ph), 7.68–7.75 (m), 7.90 (t, 6.6 Hz), 8.05 (d, 6.3 Hz, C_5H_4N), 8.61 (d, 3 Hz, $C_5H_3N_2$), 9.15 (br), 9.79 (S, –CON*H*)	32.3	255

[Pt(Cl){SeC$_5$H$_3$(3-COOH)N}(PPh$_3$)$_2$]	**27a**	4.56 (br, –COO*H*), 6.40 (br, C$_5$H$_3$N), 6.70 (br, C$_5$H$_3$N), 7.37–7.49 (m, Ph), 8.29 (d, 7.2 Hz, C$_5$H$_4$N)	14.3 [^{1}J(Pt–P) = 2750 Hz)], 10.3 [^{1}J(Pt–P) = 3586 Hz)]	243
[Pd(Cl){SeC$_5$H$_3$(3-COOH)N}(PPh$_3$)$_2$]	**27b**	7.39-7.48 (m, Ph), 7.51-7.57 (m), 7.62-7.70(m)	34.7, 15.4	259
[Pd(Cl){SeC$_5$H$_3$(3-COOH)N}(PPh$_3$)]	**28**	6.89–7.15 (m), 7.43-7.48 (m), 7.71-7.76 (q, 6.6 Hz), 8.46 (d, 6.3 Hz)	31.8	
[Pt(I){SeC$_5$H$_3$(3-CONHPh)N}(PPh$_3$)$_2$]	**29**	7.09-7.68 (m), 8.37 (br), 8.57 (br, py), 8.92 (s, NH)	13.5 [^{1}J(Pt–P) = 2925 Hz)]	235
[Pt(I){SeC$_5$H$_3$(3-CONHPh)N}(PPh$_3$)]	**30a**	7.15 (t, 7.2 Hz, C$_5$H$_4$N), 7.34 (t, 7.5 Hz, Ph), 7.46–7.73 (m, Ph), 8.21 (d, 7.8 Hz, C$_5$H$_4$N), 8.32 (br, C$_5$H$_4$N), 8.94 (s, CON*H*)	4.0 [^{1}J(Pt–P) = 3668 Hz)]	201
[Pd(I){SeC$_5$H$_3$(3-CONHPh)N}(PPh$_3$)]	**30b**	7.04 (m, Ph), 7.15 (t, 7.5 Hz, C$_5$H$_4$N), 7.34 (t, 7.5 Hz, Ph), 7.53 (br, Ph), 7.74 (m, Ph), 8.22 (d, 8.1 Hz, C$_5$H$_4$N), 8.80 (d, 5.1 Hz, C$_5$H$_4$N)	31.7	204
[Pt(I)(Ph)(PPh$_3$)$_2$]	**31a**	7.36–7.48 (m, Ph), 7.64–7.73 (m), 7.74–7.76 (m)	21.7 [^{1}J(Pt–P) = 3092 Hz)]	
[Pd(I)(Ph)(PPh$_3$)$_2$]	**31b**	6.91 (t, 6 Hz, C$_5$H$_4$N), 7.04 (m, Ph), 7.14–7.36 (m, Ph), 7.49 (br, Ph), 7.59 (t, 7.8 Hz), 7.75 (m, Ph)	20.0	
[Pt(I){C$_5$H$_3$(3-CONHPh)N}(PPh$_3$)$_2$]	**32**	6.65 (t, 8 Hz, py), 6.78 (t, 7.5 Hz), 7.16–7.69(m, Ph), 8.04 (d), 8.19 (d, 7.8 Hz, py), 8.50 (s, NH)	9.4 [^{1}J(Pt–P) = 3564 Hz)]	

with chelating selenolate ligand is longer than the monodentate selenolate. The M–Se distances are well in agreement to those reported in $[Pd(\mu\text{-}SeCH_2CH_2COOEt)(\eta^3\text{-}C_3H_5)]_3$ [290] and other related derivatives [282, 291, 292]. The M–N distances are as expected [87, 206, 292]. The short bite of the chelating selenolate ligands leads to an acute N–M–Se angle (~70°) as a consequence adjacent angles are opened up.

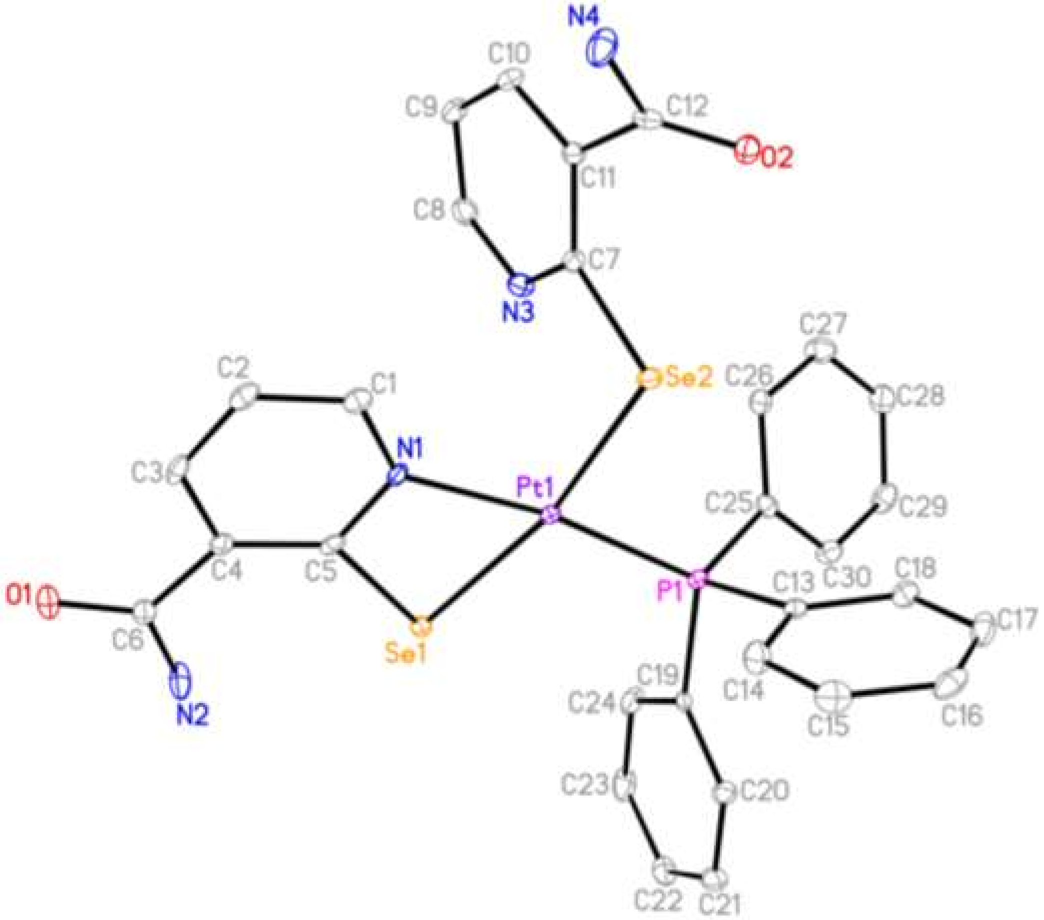


Figure 14: ORTEP diagram of $[Pt\{\eta^2\text{-}SeC_5H_3(3\text{-}CONH_2)N\}\{SeC_5H_3(3\text{-}CONH_2)N\}(PPh_3)]$, (Hydrogen atoms are omitted for clarity)

Table 34: Selected bond lengths (Å) and angles (^{o}) of [Pt{SeC_5H_3(3-$CONH_2$)N}$_2$(PPh_3)]

Pt(1)-P(1)	2.2016(9)	Pt(1)-N(1)	2.086(3)
Pt(1)-Se(1)	2.4437(4)	Pt(1)-Se(2)	2.4231(4)
Se(1)-C(5)	1.902(3)	Se(2)-C(7)	1.907(3)
P(1)-Pt(1)-N(1)	171.24(8)	P(1)-Pt(1)-Se(1)	103.58(3)
P(1)-Pt(1)-Se(2)	90.13(3)	Se(1)-Pt(1)-N(1)	69.99(8)
Se(1)-Pt(1)-Se(2)	166.119(13)	N(1)-Pt(1)-Se(2)	96.14(8)
N(1)-C(5)-Se(1)	105.8(2)	Pt(1)-Se(2)-C(7)	95.71(11)
Pt(1)-Se(1)-C(5)	78.33(11)	Pt(1)-N(1)-C(5)	105.9(2)

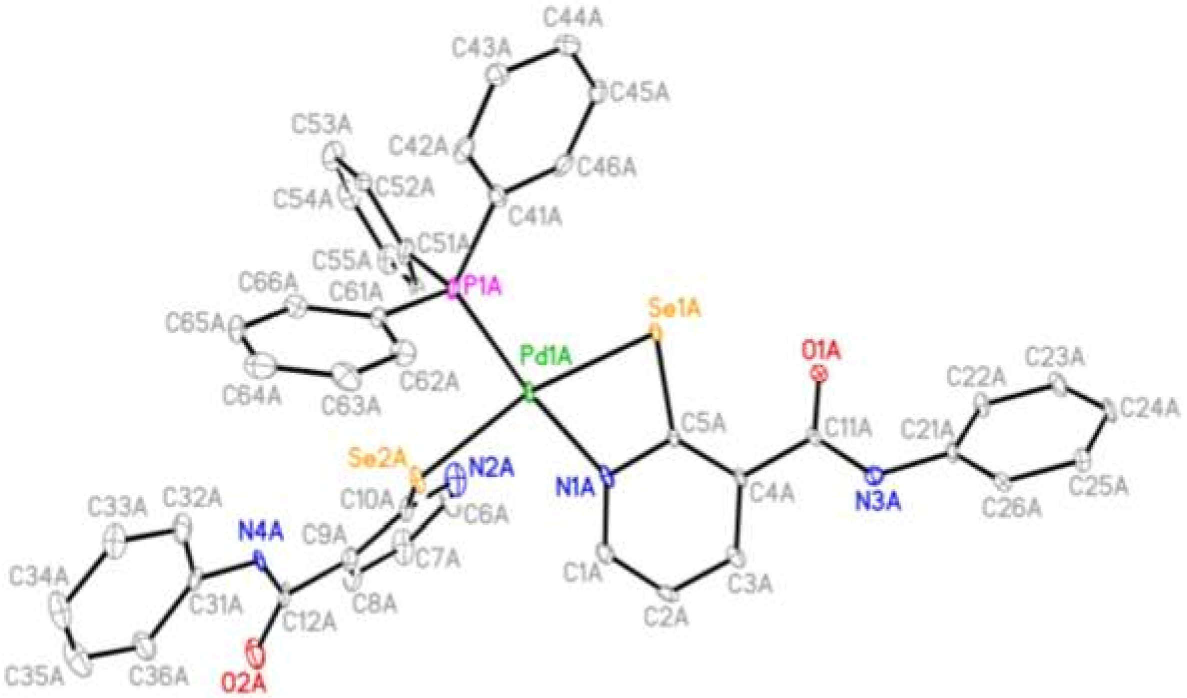


Figure 15: ORTEP diagram of [Pd{η^2-SeC_5H_3(3-CONHPh)N}{SeC_5H_3(3-CONHPh)N}(PPh_3)] (Hydrogen atoms are omitted for clarity)

Table 35: Selected bond lengths (Å) and angles (^{o}) of $[Pd\{\eta^2\text{-}SeC_5H_3(3\text{-}CONHPh)N\}\{SeC_5H_3(3\text{-}CONHPh)N\}(PPh_3)]$

	Molecule A	Molecule B	Molecule C	Molecule D	Molecule E	Molecule F
	X = A	X = B	X = C	X = D	X = E	X = F
Pd1X-P1X	2.252(2)	2.242(2)	2.243(2)	2.242(2)	2.267(3)	2.243(2)
Pd1X-N1X	2.079(7)	2.088(7)	2.102(7)	2.081(7)	2.028(8)	2.091(7)
Pd1X-Se1X	2.4411(9)	2.4352(10)	2.4322(11)	2.4478(10)	2.4467(10)	2.4621(10)
Pd1X-Se2X	2.4383(10)	2.4169(11)	2.4259(11)	2.4294(10)	2.4335(16)	2.4256(10)
Se1X-C5X	1.887(8)	1.902(9)	1.886(9)	1.896(8)	1.908(10)	1.918(9)
Se2X-C10X	1.932(8)	1.919(9)	1.911(9)	1.893(8)	1.890(9)	1.919(9)
P1X-Pd1X-N1X	173.63(18)	172.4(2)	172.0(2)	174.0(2)	172.4(2)	172.4(2)
P1X-Pd1X-Se1X	102.35(6)	101.92(6)	102.67(6)	103.37(6)	101.57(7)	103.69(6)
P1X-Pd1X-Se2X	89.61(6)	89.25(6)	89.41(6)	87.89(6)	90.30(7)	88.17(6)
Se1X-Pd1X-N1X	71.33(17)	71.19(19)	70.6(2)	70.85(19)	71.9(2)	71.30(19)
Se1X-Pd1X-Se2X	166.96(4)	168.15(4)	167.65(4)	168.10(4)	166.43(5)	167.23(4)
N1X-Pd1X-Se2X	96.76(17)	97.87(19)	97.5(2)	97.99(19)	96.6(2)	97.36(19)
N1X-C5X-Se1X	108.4(5)	107.7(6)	109.1(6)	108.0(6)	107.3(7)	107.4(6)
Pd1X-Se2X-C10X	104.8(2)	102.8(3)	101.7(3)	104.0(3)	106.9(3)	105.7(3)
Pd1X-Se1X-C5X	77.1(2)	77.4(3)	77.1(3)	77.0(3)	75.9(3)	77.1(3)
Pd1X-N1X-C5X	103.1(5)	103.7(5)	103.1(5)	104.1(5)	104.8(6)	104.0(5)

The complex, [PtI(Ph)(PPh_3)$_2$] adopts a distorted square planar configuration around platinum as observed for *trans*-[PtCl(Ph)(PPh_3)$_2$] [293] and [PtCl(C_4H_3S)(PPh_3)$_2$] [216]. The Pt–C distance is in agreement with the one reported for [PtCl(Ph)(PPh_3)$_2$] (Pt–C = 2.01(1) Å) [293], but slightly longer than that found in *trans*-[PtI($C_6H_4CF_3$-4)(PPh_3)$_2$] (1.963(9) Å) [294]. The Pt–I distance (2.6979(9) Å) is similar to the one reported in *trans*-[PtI($C_6H_4CF_3$-4)(PPh_3)$_2$] (2.7011(9) Å) [294], but is slightly longer than [PtI_2(PPh_3)$_2$] (2.6647(6), 2.6448(5) Å) [295] owing to the strong trans influence of the phenyl group.

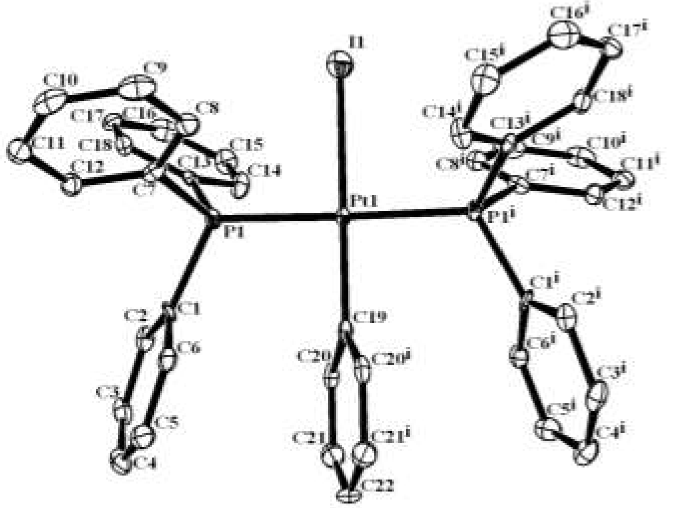


Figure 16: ORTEP diagram of [Pt(I)(Ph)(PPh_3)$_2$] [Interatomic parameters : bond lengths (Å) : Pt(1)-C(19), 2.015(9); Pt(1)-I(1), 2.6979(9); Pt(1)-P(1), 2.2903(16); bond angles (^{o}) : P(1)#-Pt(1)-P(1), 178.27(9); C(19)-Pt(1)-P1, 90.86(4); P(1)-Pt(1)-I(1), 89.14(4); C(19)-Pt(1)-I(1), 180.00(1)

The overall molecular structure of [Pt($Cl_{0.5}I_{0.5}$){C_5H_3(3-CONHPh)N}(PPh_3)$_2$].HCl is similar to [Pt(I)(Ph)(PPh_3)$_2$]. Distorted square planar platinum atom is coordinated to two trans triphenylphosphine ligands and Cl/I and C atom of the C1 carbon atom of the nicotinyl ring of the C_5H_3(3-CONHPh)N fragment. One of the nitrogen atoms is protonated and chloride is found at two positions both of which are 50% occupied. The Pt–C and Pt–P distances are as expected [293, 295].

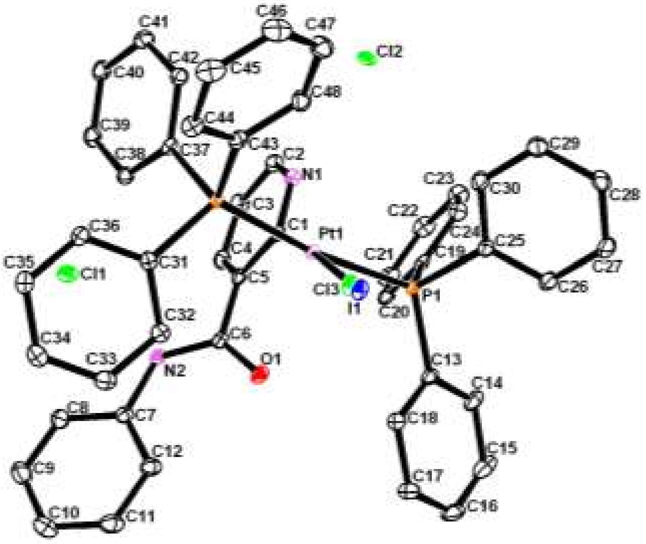


Figure 17: ORTEP diagram of $[Pt(Cl_{0.5}I_{0.5})\{C_5H_3(3\text{-}CONHPh)N\}(PPh_3)_2].HCl$ (Hydrogen atoms are omitted for clarity so the solvent molecule (CH_3CN))

Table 36: Selected bond lengths (Å) and angles (°) of $[Pt(Cl_{0.5}I_{0.5})\{C_5H_3(3\text{-}CONHPh)N\}_2(PPh_3)_2].HCl$

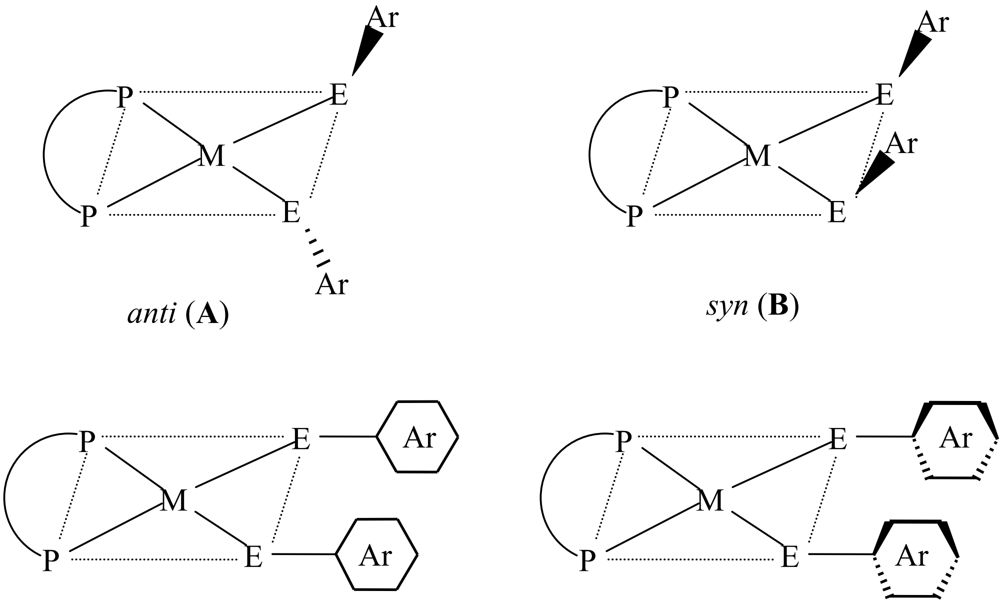
Pt(1)-C(1)	1.997(3)	Pt(1)-I(1)	2.6672(6)
Pt(1)-Cl(3)	2.390(3)	Pt(1)-P(1)	2.3221(7)
Pt(1)-P(2)	2.3057(7)	O(1)-C(6)	1.226(4)
N(2)-C(6)	1.361(4)	N(2)-C(7)	1.413(4)
N(1)-C(1)	1.348(4)	N(1)-C(2)	1.350(4)
P(2)-Pt(1)-P(1)	171.51(3)	C(1)-Pt(1)-P(1)	91.24(8)
P(1)-Pt(1)-I(1)	88.36(3)	P(1)-Pt(1)-Cl(3)	90.63(13)
C(1)-Pt(1)-P(2)	90.34(8)	P(2)-Pt(1)-I(1)	90.68(3)
P(2)-Pt(1)-Cl(3)	88.49(13)	C(1)-Pt(1)-I(1)	175.79(9)
C(1)-Pt(1)-Cl(3)	175.01(16)	Cl(3)-Pt(1)-I(1)	2.31(15)

3.5 Chemistry of arylchalcogenolate complexes of palladium and platinum

Mononuclear cis configured palladium and platinum organochalcogenolate complexes, *cis*-$[M(ER')_2(PR_3)_2]$ are of considerable interest as they are used as molecular tectons for constructing a variety of bi- and high-nuclearity complexes [237, 255, 296] and are believed to be catalytically active species in metal catalyzed C–E (E = S or Se) bond formation [113, 275]. In the case of monodentate ER' and PR_3 ligands, isomerization to the thermodynamically more stable *trans* form [297] and polymerization to R'E-bridged species [298] are usually encountered. To circumvent these problems, chelating phosphines [278, 279], and/or chelating [291, 299]/bulky [291] chalcogenolate ligands are employed. The aryl groups on chalcogenolate ligands can mutually adopt different orientations with respect to the metal square plane, *viz.*, *anti* form (A), *syn* form (B), aryl-rings coplanar with the metal plane(C) and aryl planes perpendicular to metal plane(D) (Scheme 31). In general distortions from these idealized conformations are usually encountered in the solid state (from X-ray crystallography). The two Pt–E distances in *cis*-$Pt(EAr)_2(P^\frown P)$ are often non-equivalent as a consequence the two Pt–P distances are also differ slightly from each other, although complexes with the same two Pt–E distances are also reported. The difference in the two Pt–E distances, irrespective of the nature of chalcogen atom, can be as large as 0.07 Å. Such differences are, however, not evident from the ^{31}P and ^{195}Pt NMR spectra in solution and are indicative of equivalence of the two ^{31}P nuclei.

The coordination chemistry of small bite heterocyclic chalcogenolate ligands, combining soft (E) and hard (N) donor atoms, is of considerable interest as these ligands show several binding possibilities, viz. terminal E bonding, E-bridging, N,E-chelating, N,E-bridging, N,E-chelating-cum-E bridging or N,E-bridging-cum-E-bridging modes (E = S, Se, Te). The ligand chemistry of thio ligands is fairly well explored [300, 301], the interest in higher homologues is gaining momentum and quite often shows remarkable difference in reactivity [87, 257, 286].

In the light of the above and to gain further insight on the structural features of *cis*-$[Pt(EAr)_2(P^\frown P)]$ complexes, a sterically hindered Ar (mesityl) and also heterocyclic (pyridyl and pyrimidyl) groups have been chosen.



anti (**A**)

syn (**B**)

Coplanar with the metal plane (**C**)

Perpendicular to metal plane (**D**)

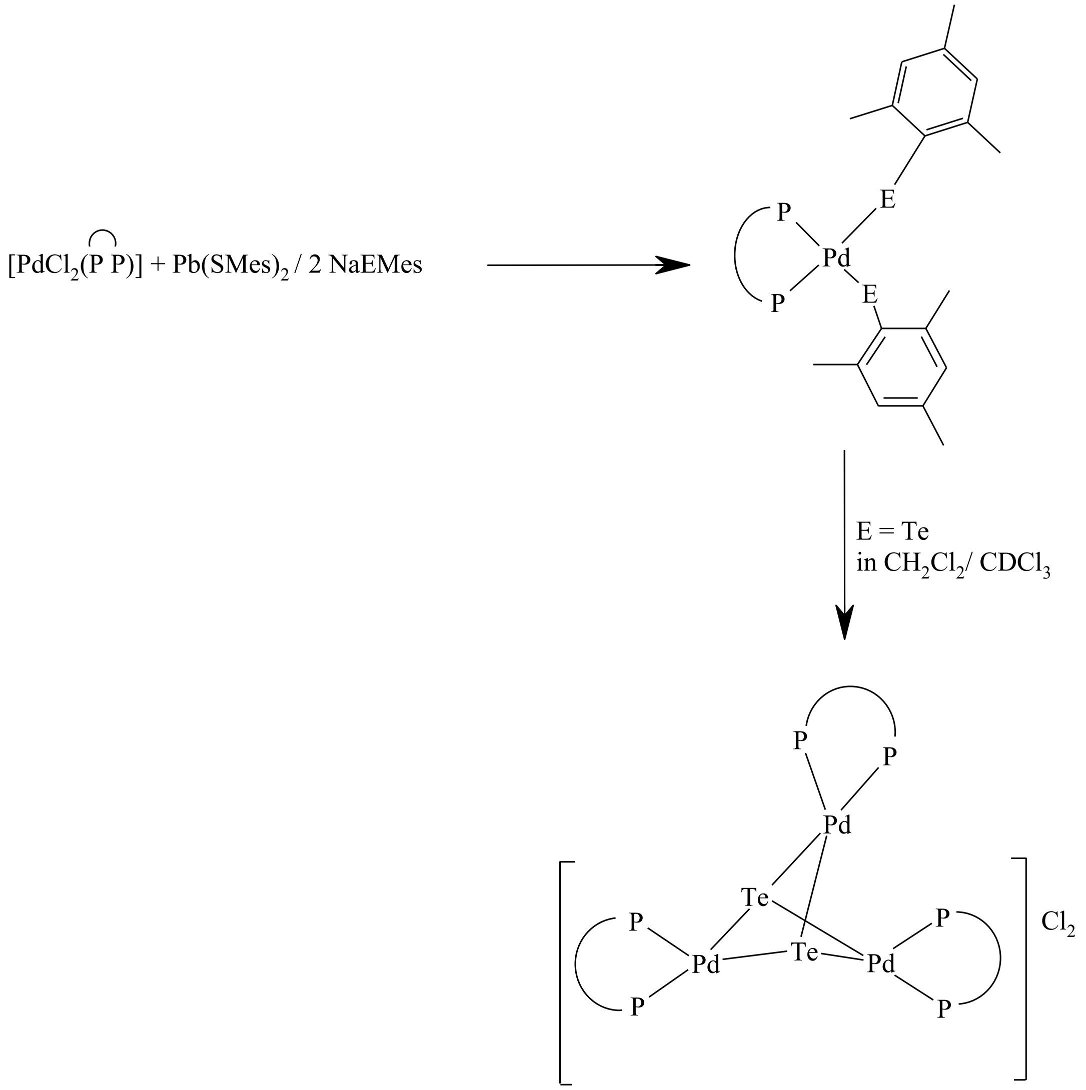
(M = Pd, Pt)

Scheme 31: Different orientations of aryl group with respect to metal square plane

3.5.1 Palladium chalcogenolate complexes

Synthesis and spectroscopy

Treatment of $[PdCl_2(P^\frown P)]$ with mesitylchalcogenolate group in benzene / benzene-methanol afforded bis chalcogenolate complexes of palladium(II) (Scheme 32). However, the reaction of $[PdCl_2(dppp)]$ with NaTeMes, after extraction with dichloromethane, gave a tellurido-bridged trinuclear complex, $[Pd_3(\mu\text{-}Te)_2(dppp)_3]Cl_2$ in 50% yield. It appears that initially a bis tellurolate complex, ‘[Pd(TeMes)$_2$(dppp)]’ is formed which during extraction from dichloromethane is transformed in to a trinuclear tellurido-bridged derivative. To ascertain this transformation, mononuclear tellurolate complex, [Pd(TeMes)$_2$(dppe)] was left in CDCl$_3$ solution for a few hours. From this solution a tellurido-bridged complex, [Pd$_3$(μ-Te)$_2$(dppe)$_3$]Cl$_2$ could be isolated. The telluoride-bridged complexes seem to be formed via Te–C bond cleavage in chlorinated solvents. The cleavage of Te–C bond in tellurolate complexes in halogenated solvent is well documented [246, 286, 287].



Scheme 32: Reactions of [PdCl$_2$(P$^\frown$P)] with lead/sodium mesityl chalcogenolate

The NMR spectra showed expected resonances (Table 37). Shielding of ^{31}P NMR resonance with increasing size of the chalcogen atom is evident from Table 18 and is in conformity with the trend reported earlier [287]. The ^{31}P NMR chemical shifts for tellurido-bridged complexes $[Pd_3(\mu\text{-}Te)_2(P^\frown P)_3]^{2+}$ are well in agreement with the values reported in the literature [244, 287].

Table 37: Physical, analytical and ^{1}H NMR data for $[Pd(EMes)_2(P^\frown P)]$

Complex	^{1}H NMR data	$^{31}P\{^1H\}$ NMR data
$[Pd(SMes)_2(dppe)]$	2.10 (s, Me), 2.20 (s, 2Me), 2.25 (s, Me), 2.33 (s, Me), 2.55 (br, CH_2); 6.73, 6.83 (s), 7.33-7.81 (m, Ph)	49.2
$[Pd(SeMes)_2(dppe)]^a$	2.05 (s, 4-Me), 2.16 (s, 2,6-Me), 2.32-2.60 (m, -CH_2), 6.39 (s, 3,5-H), 7.26-7.34 (m, Ph), 7.41-7.43 (m, Ph), 7.57-7.63 (m, Ph).	47.2
$[Pd(TeMes)_2(dppe)]$	2.32 (s, 4-Me), 2.36 (s, 2,6-Me), 2.32-2.60 (m, -CH_2), 6.87 (s, 3,5-H), 7.34-7.57 (m, Ph), 7.84-7.90 (m, Ph).	46.3
$[Pd_3(\mu\text{-}Te)_2(dppe)_3]Cl_2$	–	45.9
$[Pd(SMes)_2(dppp)]$	2.09 (s, Me), 2.33 (s, Me), 2.00 (br, CH_2), 2.54 (br, PCH_2), 6.73, 6.83 (each s), 7.30-7.80 (m, Ph)	4.4
$[Pd(SeMes)_2(dppp)]$	2.09(s, 2Me), 2.24 (s, Me), 2.04 (br, CH_2), 2.38 (br, PCH_2), 6.68 (s), 7.30-7.67 (m, Ph)	−3.0
$[Pd_3(\mu\text{-}Te)_2(dppp)_3]Cl_2$	–	−11.1

X-ray crystallography

Molecular structures of $[Pd(SeMes)_2(dppe)].CHCl_3$ was established by single crystal X-ray diffraction analyses. ORTEP drawings with atomic numbering scheme are depicted in Figure 18 while selected inter-atomic parameters are given in Table 38.

The complex [Pd(SeMes)$_2$(dppe)] crystallizes with a molecule of chloroform. There are two independent molecules (Figure 18) in the crystal lattice which differ slightly in various inter atomic parameters. The two selenium atoms in molecule **a** lie out of the PdP2Se2 mean plane by 0.343 (Se1) and 0.273 Å (Se2) while in molecule **b** they lie within the mean plane defined by PdP2Se2.The mesityl rings on selenolate ligands in molecule **a** are at an angle of 79.63 (Se1Mes) and 66.77° (Se2Mes) from the mean plane of PdP2Se2 and are mutually at an angle of 79.73°. While in molecule **b** these rings lie at 79.53 (Se3Mes) and 77.39° (Se4Mes) angles with the mean plane of PdP2Se2 and are mutually at an angle of 79.43°.

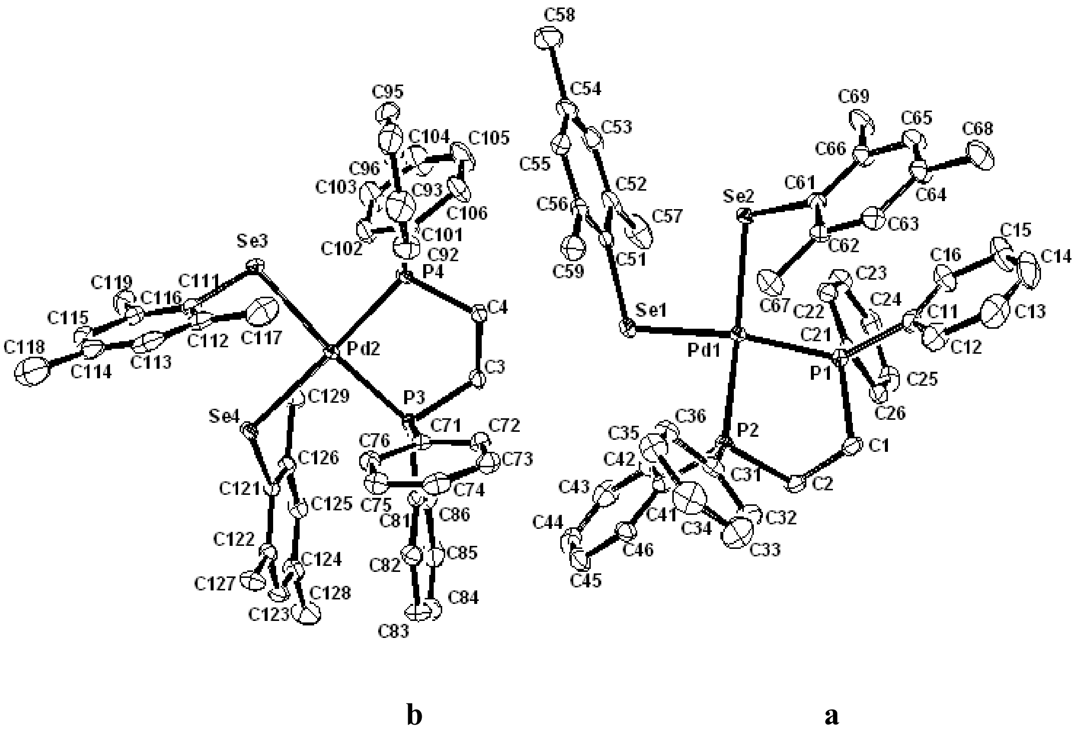


Figure **18**: ORTEP drawing of [Pd(SeMes)$_2$(dppe)] (Hydrogen atoms are omitted for clarity so the solvent molecule)

The Pd–Se and Pd–P distances in molecule **a** differ marginally while in molecule **b** they are essentially similar (Table 38). These distances can be compared with those reported in [Pd(SePh)$_2$(dppe)] (Pd-Se = 2.444 (1), 2.480(1) Å) [279] and [Pd(SeTh)$_2$(dppe)] (Pd–Se =

2.455 (1), 2.480(1) Å) [227]. The Se–Pd–Se angle in the molecule **a** is opened up from the ideal value of 90°. The observed angles are much smaller than the reported in [Pd(SePh)$_2$(dppe)] (99.11 (4)°). The E–M–E angle in cis-[M(EAr)$_2$(PR$_3$)$_2$] (M = Pd or Pt; E = S, Se, Te) complexes varies between 78 and 101° [227, 278, 279, 301] and appears to be influenced by the orientation of aryl ring with respect to the M–E bond [227].

Table **38:** Selected bond lengths (Å) and angles (^{o}) of [Pd(SeMes)$_2$(dppe)].CHCl$_3$

Molecule a		**Molecule b**	
Pd1-Se1	2.4542(3)	Pd2-Se3	2.4712(3)
Pd1-Se2	2.4652(3)	Pd2-Se4	2.4714(3)
Pd1-P1	2.2826(6)	Pd2-P3	2.2807(6)
Pd1-P2	2.2638(6)	Pd2-P4	2.2823(6)
Se1-C51	1.920(2)	Se3-C111	1.929(2)
Se2-C61	1.932(2)	Se4-C121	1.929(2)
P1-Pd1-P2	85.11(2)	P3-Pd2-P4	85.06(2)
P1-Pd1-Se1	157.183(17)	P3-Pd2-Se3	168.543(17)
P1-Pd1-Se2	99.773(16)	P3-Pd2-Se4	97.550(16)
P2-Pd1-Se1	86.594 (17)	P4-Pd2-Se3	88.247(17)
P2-Pd1-Se2	166.794(18)	P4-Pd2-Se4	177.360(17)
Se1-Pd1-Se2	93.058 (10)	Se3-Pd2-Se4	89.235(10)
Pd1-Se1-C51	107.09(7)	Pd2-Se3-C111	103.01(7)
Pd1-Se2-C61	106.83(7)	Pd2-Se4-C121	107.71(7)
P1-Pd1-Se1-C51	-120.96(8)	P3-Pd2-Se3-C111	-89.68(11)
P1-Pd1-Se2-C61	-43.99(8)	P3-Pd2-Se4-C121	-50.05(8)
P2-Pd1-Se1-C51	170.96(8)	P4-Pd2-Se3-C111	-143.92(8)
P2-Pd1-Se2-C61	66.83(11)	P4-Pd2-Se4-C121	121.7(4)
C51-Se1-Pd1-Se2	4.18(8)	C111-Se3-Pd2-Se4	36.87(8)
C61-Se2-Pd1-Se1	154.95(8)	C121-Se4-Pd2-Se3	139.21(8)

3.5.2. Platinum chalcogenolate complexes

Synthesis and spectroscopy

Reactions of [PtCl$_2$(P$^\frown$P)] with either Pb(SMes)$_2$ or two equivalents of NaEAr (E = Se or Te) (prepared by reductive cleavage of E–E bond in Ar$_2$E$_2$ by NaBH$_4$ in methanol-benzene) gave mononuclear platinum chalcogenolate complexes, [Pt(EAr)$_2$(P$^\frown$P)] (E = S, Se, Te; Ar = Ph, Mes, py, pyMe, pym or Me$_2$pym; P$^\frown$P = dppm, dppe or dppp) as yellow crystalline solids.

The ^{31}P{^{1}H} NMR spectra of these complexes displayed single resonances which appeared in the expected range of the respective chelating phosphine complexes of platinum [302]. The resonances were flanked by ^{195}Pt couplings. The magnitude of ^{1}J(Pt–P) lies in the range 2419-3090 Hz (Table 39) and depends on the nature of the chelating phosphine ligand, chalcogen atom and to a some extent on the nature of Ar group on chalcogen. The observed magnitude of ^{1}J(Pt–P) is reduced significantly as compared to the values for the corresponding [PtCl$_2$(P$^\frown$P)] indicating strong trans influence of the organochalcogenolate ligand.

The order of coupling constant for each chalcogen atom of EAr group follows the trend dppm<dppp<dppe. The observed trend of coupling is in conformity with the earlier reports [278, 302, 303]. On keeping the bis phosphine ligand fixed, the coupling constant followed the trend Se>S≥Te. Interestingly the π-acidity (nucleophilicity) of chalcogenolate ligand follows the sequence Te>Se >>S. The variation of group on chalcogen atom resulted into a slight change in coupling constant (less than 150 Hz). Attempts to correlate these values with respect to the nature of Ar group (electronic effect) were inconclusive as the contributions from steric effect of different Ar groups could not be rationalized.

Table 39: ^{1}H and ^{31}P{^{1}H}NMR data of [Pt(EAr)$_2$(P$^\frown$P)]

Complex	^{1}H NMR (δ in ppm)	^{31}P{^{1}H}NMR δ (^{1}J(Pt–P) in Hz)
[Pt(TePh)$_2$(dppm)]	—	−55.1 (2436)
[Pt(Tetol)$_2$(dppm)]	—	−55.3 (2419)
[Pt(SMes)$_2$(dppm)]	—	−46.4 (2641)
[Pt(SeMes)$_2$(dppm)]	2.03 (s, 4-Me), 2.23 (d, 9.6Hz, -CH$_2$), 2.40 (s, 2,6-Me), 6.28 (s, 3,5-H), 7.28-7.31 (m, Ph), 7.40-7.49 (m, Ph)	−52.5 (2522)
[Pt(TeMes)$_2$(dppm)]	2.03 (s, 4-Me), 2.17 (d, 0.9Hz, -CH$_2$), 2.22 (s, 2,6-Me), 6.46 (s, 3,5-H), 7.31-7.36 (m, Ph), 7.39-7.48 (m, Ph), 7.66(m, Ph), 7.82-7.86(m)	−57.4 (2422)
[Pt(SeC$_4$H$_3$N$_2$)$_2$(dppm)]	—	−50.8 (2770)
[Pt{SeC$_4$H(4,6-Me$_2$)N$_2$}$_2$(dppm)]	—	−49.9 (2685)
[Pt(Tetol)$_2$(dppe)]	—	45.7 (2894)
[Pt(SMes)$_2$(dppe)]	2.07 (s, 4-Me), 2.15 (s, 2,6-Me), 2.23-2.51 (m, -CH$_2$), 6.39 (s, 3,5-H), 7.34-7.43 (m, Ph), 7.63-7.70 (m, Ph)	47.3 (2346)
[Pt(SeMes)$_2$(dppe)]	—	43.8 (2935)
[Pt(TeMes)$_2$(dppe)]	2.18 (s, 4-Me), 2.22-2.31 (m, -CH$_2$), 2.34 (s, 2,6-Me), 6.28 (s, 3,5-H), 7.38-7.41 (m, Ph), 7.79-7.86 (m, Ph).	47.9 (2810)

[Pt(TePh)$_2$(dppp)]	—	−8.6 (2744)
[Pt(Tetol)$_2$(dppp)]	—	−8.3 (2894)
[Pt(SMes)$_2$(dppp)]	2.09 (s, Me), 2.33 (m, -PCH$_2$), 2.48 (br, -CH$_2$), 6.37 (s, 3,5-H), 7.32-7.38 (m, Ph), 7.74 (br, Ph)	−2.9 (2743)
[Pt(SeMes)$_2$(dppp)]	2.10 (s, Me), 2.46 (br, -CH$_2$), 6.45 (s, 3,5-H), 7.30-7.37 (m, Ph), 7.73 (br, Ph).	−6.6 (2775)
[Pt(TeMes)$_2$(dppp)]	2.17 (s, 4-Me), 2.22-2.42 (m, -CH$_2$), 2.57 (s, 2,6-Me), 6.78 (s, 3,5-H), 7.39-7.59 (m, Ph), 7.75-7.81 (m, Ph).	−6.8 (2469)
[Pt(SeC$_5$H$_4$N)$_2$(dppp)]	—	−4.8 (2811)
[Pt{SeC$_5$H$_3$(3-Me)N}$_2$(dppp)]	—	−7.7 (2869)

X-ray crystallography

Molecular structures of [Pt(SeMes)$_2$(dppp)], [Pt(TeMes)$_2$(dppp)], [Pt(SeC$_4$H$_3$N$_2$)$_2$(dppm)] and [Pt{SeC$_4$H(4,6-Me$_2$)N}$_2$(dppm)] were established by single crystal X-ray diffraction analyses. ORTEP drawings with atomic numbering scheme are depicted in Figures 19-22 while selected inter-atomic parameters are given in Tables 40-43.

Except [Pt(SeC$_4$H$_3$N$_2$)$_2$(dppm)], these complexes crystallized with the solvent of crystallization. There are two independent molecules of [Pt(SeC$_4$H$_3$N$_2$)$_2$(dppm)] in the crystal lattice which differ slightly in inter-atomic parameters from each other. The other complexes comprised of discrete monomeric units.

The platinum atom in these complexes adopts a distorted square planar geometry defined by two chalcogenolate ligands and the chelating phosphine ligand in a *cis* configuration. The Pt–Se (2.4182(5) – 2.4914(5) Å), Pt–Te (2.6394(3) Å) and Pt–P (2.238(2)

– 2.2710(8) Å) distances can be compared with mononuclear platinum chalcogenolate complexes, [Pt(EAr)$_2$(P$^{\frown}$P) (E = Se or Te) [91, 107, 127, 29]. The two Pt–Te distances in [Pt(TeMes)$_2$(dppp)] are essentially the same, whereas these are distinctly different in [Pt(TeTh)$_2$(dppe)] (Pt–Te = 2.6594(9), 2.607 (1) Å) [29].

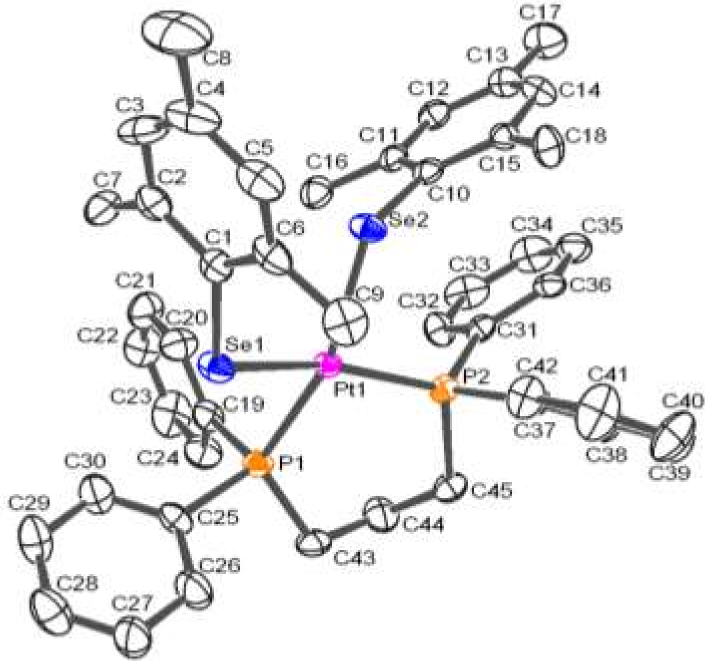


Figure 19: ORTEP drawing of [Pt(SeMes)$_2$(dppp)] (Hydrogen atoms and the solvent molecule are omitted for clarity)

Table 40: Selected bond lengths (Å) and angles (°) of [Pt(SeMes)$_2$(dppp)].½C$_6$H$_6$

Pt1-P1	2.246(2)	Pt1-P2	2.238(2)
Pt1-Se1	2.4251(11)	Pt1-Se1	2.4353(13)
Se1-C1	1.887(9)	Se2-C10	1.914(8)
P1-Pt1-P2	97.14(9)	Se1-Pt1-Se2	88.65(4)
P1-Pt1-Se1	85.18(7)	P2-Pt1-Se1	159.95(7)
P1-Pt1-Se2	161.68(7)	P2-Pt1-Se2	94.56(7)
C1-Se1-Pt1	111.0(3)	C10-Pt1-Se2	113.4(2)
P1-Pt1-Se1-C1	-164.5(3)	P2-Pt1-Se1-C1	97.9(4)
P1-Pt1-Se2-C10	-89.4(4)	P2-Pt-Se2-C10	40.2(3)
C1-Se1-Pt1-Se2	-1.7(3)	C10-Se2-Pt1-Se1	-159.7(3)

The Pt–P distance in [Pt(TeMes)$_2$(dppp)] (2.2710(8) Å) is marginally longer than the selenium analogue, [Pt(SeMes)$_2$(dppp)] (av. 2.242 Å) indicating stronger *trans* influence of the tellurolate group. The E–Pt–E angle in these complexes lies in the range 79.633(17) – 94.673 (13)°. The E–M–E angle in *cis*-[M(EAr)$_2$(PR$_3$)$_2$] (M = Pd or Pt; E = S, Se, Te) complexes varies between 78 and 101° [29, 91, 92, 107,127] and is influenced by the orientation of the aryl group on the chalcogen atom with respect to the M–E bond [29].

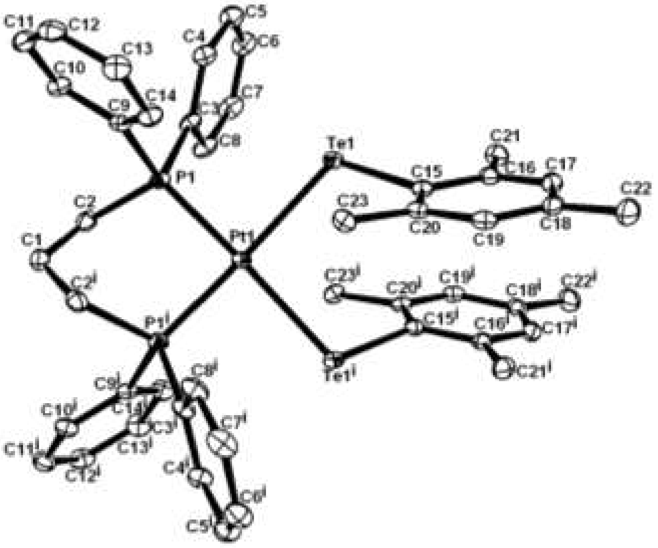


Figure 20: ORTEP drawing of [Pt(TeMes)$_2$(dppp)] (Hydrogen atoms and the solvent molecule are omitted for clarity.

Table 41: Selected bond lengths (Å) and angles (°) of [Pt(TeMes)$_2$(dppp)].3C$_6$H$_6$

Pt1-P1	2.2710(8)	Te1-C15	2.141(3)
Pt1-Te1	2.6394(3)		
P1-Pt1-P1	91.17(4)	Te1-Pt1-Te1	94.673(13)
P1-Pt1-Te1	169.734(19)	C15-Te1-Pt1	108.15(8)
P1-Pt1-Te1	87.97 (2)		
P1-Pt1-Te1-C15	152.40(8)	C15-Te1-Pt1-Te1’	-37.54(8)
P1-Pt1-Te1’-C15’	67.03(14)		

Each of the two Pt−Se and two Pt−P distances, except molecule **b** of [Pt($SeC_4H_3N_2$)$_2$(dppm)] are distinctly different in selenolate complexes while in molecule **b** of [Pt($SeC_4H_3N_2$)$_2$(dppm)] the two Pt−Se and Pt−P distances are the same.The P−Pt−P and Se−Pt−Se angles in [Pt($SeC_4H_3N_2$)$_2$(dppm)] [73.85(4), 85.559(16)° (molecule **a**) and 74.09(6), 80.27(2)° (molecule **b**)] and [Pt{SeC_4H(4,6-Me_2)N}$_2$(dppm)] (73.54(5), 79.633(17)°) can be compared with the sulfur analogue, [Pt($SC_4H_3N_2$)$_2$(dppm)] (73.73(3); S−Pt−S = 79.35(3)°) [124] and [Pt(SC_5H_4N)$_2$(dppm)] (74.01(4); S−Pt−S = 78.56(4)°) [123].

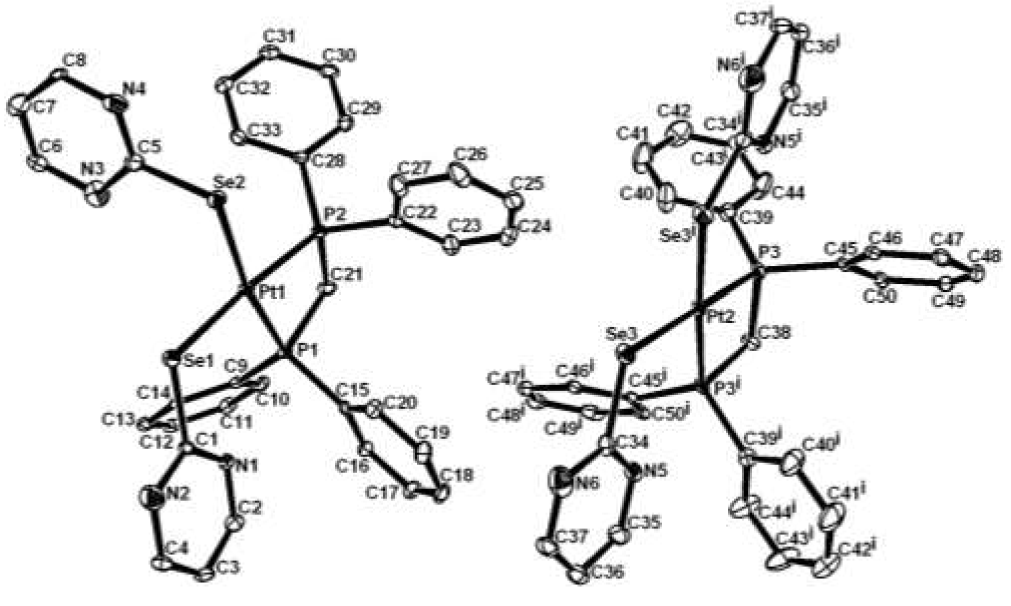


Figure 21: ORTEP drawing of [Pt($SeC_4H_3N_2$)$_2$(dppm)] (Hydrogen atoms and the solvent molecule are omitted for clarity)

The relative orientation of the aryl groups attached to the chalcogen atom is a distinguishing feature among the several structures reported here and in the literature. Attempts to rationalize their features in terms of either by electronic (C_6H_5, $C_4H_3N_2$, C_6F_5) factors or steric (mesityl or *o*-caborane) effects of the aryl group remain inconclusive. The observed different orientations of the Ar group in the solid state may possibly due to subtle crystal packing energy requirements.

Table 42: Selected bond lengths (Å) and angles (°) of [Pt($SeC_4H_3N_2$)$_2$(dppm)]

Molecule a		**Molecule b**	
Pt1-P1	2.2642(10)	Pt2-P3	2.2603(11)
Pt1-P2	2.2488(11)	Pt2-Se3	2.4537(5)
Pt1-Se1	2.4182(5)	Se3-C34	1.908(5)
Pt1-Se2	2.4914(5)		
Se1-C1	1.903(4)		
Se2-C5	1.920(5)		
P1-Pt1-P2	73.85(4)	P3-Pt2-P3′	74.09(6)
P1-Pt1-Se1	104.83(3)	P3-Pt2-Se3	176.25(4)
P1-Pt1-Se2	169.50(3)	P3-Pt2-Se3′	102.86(3)
P2-Pt1-Se1	175.11(3)	Se3-Pt2-Se3	80.27(2)
P2-Pt1-Se2	95.67(3)	C34-Se3-Pt2	111.71(14)
Se1-Pt1-Se2	85.559(16)		
C1-Se1-Pt1	110.62(13)		
C5-Se2-Pt1	106.96(13)		
P1-Pt1-Se1-C1	15.01(14)	P3-Pt2-Se3-C34	8.82(15)
P1-Pt1-Se2-C5	106.2(2)	C34-Se3-Pt2-Se3	-169.08(15)
P2-Pt1-Se1-C1	-58.7(4)	C34-Se3-Pt2-P3	44.1(5)
P2-Pt1-Se2-C5	102.60(14)		
C1-Se1-Pt1-Se2	-163.41(13)		
C5-Se2-Pt1-Se1	-82.10(14)		

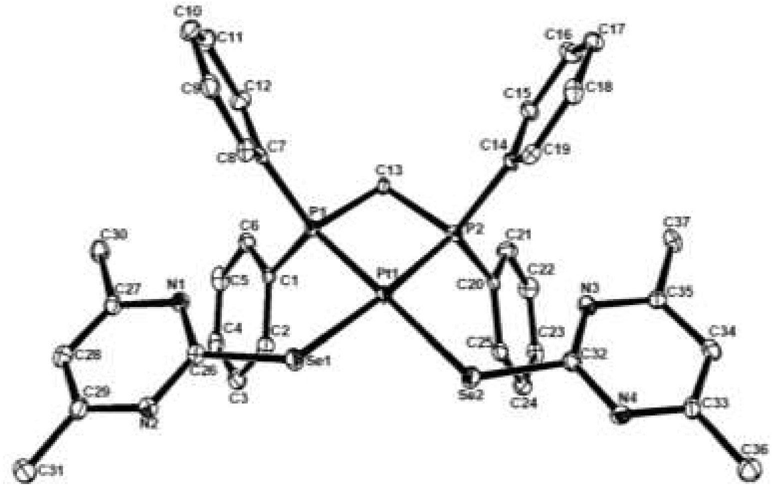


Figure 22: ORTEP drawing of [Pt{$SeC_5H(4,6\text{-}Me)N_2$}$_2$(dppm)].CH_2Cl_2 (Hydrogen atoms and the solvent molecule are omitted for clarity)

Table 43: Selected bond lengths (Å) and angles (^{o}) of [Pt{$SeC_5H(4,6\text{-}Me)N_2$}$_2$(dppm)].CH_2Cl_2

Pt1-P1	2.2550(12)	Pt1-P2	2.2523(13)
Pt1-Se1	2.4568(6)	Pt1-Se2	2.4445(5)
Se1-C26	1.910(5)	Se2-C32	1.908(5)
P1-Pt1-P2	73.54(5)	Se1-Pt1-Se2	79.633(17)
P1-Pt1-Se1	102.85(3)	P2-Pt1-Se1	175.81(4)
P1-Pt1-Se2	174.99(4)	P2-Pt1-Se2	104.14(3)
C26-Se1-Pt1	111.96(15)	C32-Se2-Pt1	113.64(14)
P1-Pt1-Se1-C26	17.10(17)	P2-Pt1-Se1-C26	47.0(5)
P1-Pt1-Se2-C32	64.3(4)	P2-Pt1-Se2-C32	2.48(17)
C26-Se1-Pt1-Se2	-158.45(16)	C32-Se2-Pt1-Se1	-175.66(16)

The present thesis consists of four chapters, *viz* Introduction, Experimental, Results and Discussion and Summary and Conclusion followed by references.

Chapter 1 deals with general introduction of platinum group metals, brief coverage on palladium and platinum complexes, organochalcogen as ligands which is followed by application of platinum group metal chalcogenolate complexes. The scope of the present work is discussed at the end of the chapter.

Chapter 2, "Experimental", describes different experimental techniques and synthetic methods employed during the course of present work. Details of synthesis and characterization of various ligands, metal precursors, metal chalcogenolates, are included. The complexes were characterized by elemental analyses, IR, NMR, UV/Vis spectroscopy and single crystal X-ray analysis. The physical and analytical data of all the complexes and structure refinement details of the complexes studied by crystallography are given in this chapter.

Chapter 3 deals with the results obtained during the present investigation and discussion on the present work. This chapter is further divided onto five sections.

Section 3.1.1 deals with the chemistry of various non-chelating phosphine complexes of platinum with pyridyl and 3-methylpyridyl tellurolate ligands. The complexes of the type $[Pt\{TeC_5H_3(3\text{-}R)N\}_2(PPh_3)_2]$ as a major and $[Pt\{TeC_5H_3(3\text{-}R)N\}_2Te(PPh_3)]$ (R = H, Me) as minor product, have been isolated through an oxidative addition reaction of $[Pt(PPh_3)_4]$ with $\{C_5H_3(3\text{-}R)N\}_2Te_2$. The above complexes can also be obtained by substitution reaction of $[PtCl_2(PR'_3)_2]$ ($PR'_3 = PPh_3$ or $PPh_2(2\text{-}py)$) with two equivalents of $Na\{TeC_5H_3(3\text{-}R)\}$. The molecular structures of $[Pt(TeC_5H_4N)_2Te(PPh_3)]$ and $[Pt\{TeC_5H_3(Me)N\}_2Te(PPh_3)]$ were established by single crystal X-ray diffraction. Both complexes exhibit a distorted square-planar configuration at the platinum(II) center. The two mutually trans 2-pyridinetellurolate ligands $[TeC_5H_3(R)N]$ coordinate to the central platinum atom in a monodentate fashion through the tellurium atoms. The tellurium(0) atom adopts a "bent T" configuration as it is bridging the $TeC_5H_3(R)N$ fragments via N-Te-N bonds (166° angle), and coordinates to Pt^{II} in trans position to PPh_3. The novel bis(pyridine)tellurium arrangement resembles the bis(pyridine)iodonium structure.

Section 3.1.2 describes the reaction of dipyridyl ditellurides with various chelating paltinum(0) phosphine compound. Oxidative addition reaction of dipyridyl ditellurides to $[Pt_2(dppm)_3]$ gave two types complexes, $[Pt\{TeC_5H_3(3\text{-}R)N\}_2(dppm)]$ and $[Pt\{PPh_2C(TeC_5H_3(3\text{-}R)N)PPh_2\}_2]$ (R = H or Me) in ~65 and ~20% yield, respectively. Both these complexes are also formed in the substitution reaction between $[PtCl_2(dppm)]$ and $NaTeC_5H_3(3\text{-}R)N$. Treatment of $[Pt(dppe)_2]$ with dipyridyl ditellurides yielded an oxidative addition product, $[Pt\{TeC_5H_3(3\text{-}R)N\}_2(dppe)]$ (R = H or Me) exclusively. In a substitution reaction of $[PtCl_2(dppe)]$ with $NaTeC_5H_3(3\text{-}Me)N$ a complex of composition, $Pt\{TeC_5H_3(3\text{-}Me)N\}(dppe)Cl$ was formed. The reaction between either $[Pt(dppp)_2]$ and $Te_2(C_5H_3(3\text{-}Me)N)_2$ or $[PtCl_2(dppp)]$ and $NaTeC_5H_3(3\text{-}R)N$, afforded a mixture of $[Pt\{TeC_5H_3(3\text{-}Me)N\}_2(dppp)]$ and $[Pt_3Te_2(dppp)_3]^{2+}$ which were seperated by column chromatography. All the complexes were characterized by elemental analyses and NMR (^1H, ^{31}P, ^{195}Pt) spectroscopy. The molecular structures of $[Pt\{PPh_2C(TeC_5H_4N)PPh_2\}_2]$ and $[Pt_2\{TeC_5H_3(3\text{-}Me)N\}_2(dppe)_2][BPh_4]_2$ were established by single crystal X-ray diffraction analyses. The bonding, charge transfer and geometry of compounds $[Pt\{TeC_5H_3(3\text{-}R)N\}_2(dppm)]$, $[Pt\{PPh_2C(TeC_5H_3(3\text{-}R)N)PPh_2\}_2]$ and $[Pt_3Te_2(dppp)_3]^{2+}$ have been analyzed through relativistic density functional calculations.

Section 3.2 discusses the reactions of either palladium(0) phosphine complexes with dipyridyldichalcogenides or $[PdCl_2(P^\frown P)]$ ($P^\frown P$ = dppe, dppp) with sodium pyridylchalcogenolate. A variety of Pd(II) complexes have been isolated and characterized. Oxidative addition of $\{SeC_5H_3(3\text{-}R)N\}_2$ (R = H or Me) to $[Pd(P^\frown P)_2]$ ($P^\frown P$ = dppe, dppp) gave either a mononuclear complex, [Pd{SeC_5H_3(3-R)N}$_2$(P$^\frown$P)] (for P$^\frown$P/R: dppe/H or Me ; dppp/H) or a cationic binuclear complex, [Pd_2{μ-SeC_5H_3(3-Me)N}$_2$(dppp)$_2$]$^{2+}$ (R = Me) whereas reactions involving the tellurium analogue exclusively afforded trinuclear complexes, [Pd_3(μ-Te)$_2$(P$^\frown$P)$_3$]Cl_2 (P$^\frown$P = dppe or dppp). The reactions resulted in the formation of mono-, bi- and tri- nuclear complexes depending on the nature of the chalcogen atom (E = S, Se or Te) and the substituent on the pyridyl ring (R = H or Me). Treatment of dipyridyl ditellurides, {TeC_5H_3(3-R)N}$_2$ (R = H or Me), with [Pd(PPh_3)$_4$] gave expected tellurolate complexes, [Pd{TeC_5H_3(3-R)N}$_2$(PPh_3)$_2$] which on prolonged standing in $CDCl_3$ solution gave green crystals of [PdCl{Te(Cl)$_2C_5H_3$(3-Me)N}(PPh_3)].

In **Section 3.3** oxidative addition reactions of (4,6-$R_2C_4HN_2$)$_2Se_2$ with [M(PPh_3)$_4$] (M = Pt or Pd) in benzene have been described. In these reactions complexes of composition, [Pt{SeC_4H(4,6-R)$_2N_2$}$_2$(PPh_3)$_2$] and [Pd{Se-C_4H(4,6-R)$_2N_2$}{η^2-Se-C_4H(4,6-R)$_2N_2$}(PPh_3)] (R = H or Me) have been isolated. The former when left in solution dissociated to [Pt{SeC_4H(4,6-R)$_2N_2$}{η^2-SeC_4H(4,6-R)$_2N_2$}(PPh_3)] and PPh_3. Treatment of [$PtCl_2$(P$^\frown$P)] (P$^\frown$P = dppe or dppp) and $NaEC_4H$(4,6-R)$_2N_2$ (for E/R = Se/H/Me or Te/Me) gave mono-nuclear complexes [Pt{EC_4H(4,6-R)$_2N_2$}$_2$(P$^\frown$P)] (R = H or Me, P$^\frown$P = dppe or dppp) which on leaving for recrystallization in dichloromethane/ $CDCl_3$ solution resulted in tri-nuclear chalcogenido-bridged complexes [Pt_3(μ-E)$_2$(P$^\frown$P)$_3$].2Cl (E = Se or Te). The latter were also formed when [$PtCl_2$(P$^\frown$P)] (P$^\frown$P = dppe or dppp) was treated with sodium salt of 2-pyrimidyltellurolate. The substitution reactions between [$PdCl_2$(P$^\frown$P)] (P$^\frown$P = dppe or dppp) and $NaEC_4H$(4,6-R)$_2N_2$ (E = Se or Te; R = H or Me) afforded chalcogenido-bridged tri-nuclear complexes, [Pd_3(μ-E)$_2$(P$^\frown$P)$_3$]2Cl (P$^\frown$P = dppe or dppp). Distorted square-planar configuration has been adopted around the metal atom in complexes [Pt($SeC_4H_3N_2$)$_2$(PPh_3)$_2$] and [Pd($SeC_4H_3N_2$)$_2$(PPh_3)]

Section 3.4 describes oxidative addition reactions of nicotinamide bsed organoselenium compounds of composition $[2\text{-}NC_5H_3(3\text{-}COR)Se]_2$ (R = NH_2, NHPh, or NHpym (pym = pyrimidine)) with $[M(PPh_3)_4]$ (M = Pd, Pt). Complexes of the type, $[M\{\eta^2\text{-}SeC_5H_3(3\text{-}COR)N\}\{SeC_5H_3(3\text{-}COR)N\}(PPh_3)]$ (M = Pt, Pd; R = NH_2, NHPh, or NHpym) have been isolated. A similar reaction with $[2\text{-}NC_5H_3(3\text{-}COOH)Se]_2$ gave an insoluble product which after extraction with dichloromethane gave $[M(Cl)\{SeC_5H_3(3\text{-}COOH)N\}(PPh_3)_2]$. The former complex, in methanolic solution is transformed into a dimeric ionic complex, but on prolonged standing in CH_2Cl_2 or $CHCl_3$ is converted into $[M(Cl)\{\eta^2\text{-}SeC_5H_3(3\text{-}COOH)N\}(PPh_3)]$. Treatment of $[M(PPh_3)_4]$ with $[2\text{-}NC_5H_3(3\text{-}CONHPh)SeI]$ initially yielded the expected oxidative addition product $[M(I)\{SeC_5H_3(3\text{-}CONHPh)N\}(PPh_3)_2]$ which loses a molecule of PPh_3 to give $[M(I)\{\eta^2\text{-}SeC_5H_3(3\text{-}CONHPh)N\}(PPh_3)]$. Both the complexes on prolonged standing in dichloromethane gave several product such as $[M(I)(Ph)(PPh_3)_2]$, $[2\text{-}NC_5H_3(3\text{-}CO)Se\text{-}NH]$.

Section 3.5 deals with the reactions of $[MCl_2(P^\frown P)]$ (M = Pd, Pt ; $P^\frown P$ = dppm, dppe, dppp) with various sodium arylchalcogenolates. Mononuclear complexes of the type, $[M(EAr)_2(P^\frown P)]$ (Ar = Ph, tol, Mesityl ; E = S, Se or Te) have been isolated. An attempt has been made to rationalize the NMR data in terms of the nature of bonding, chelated bis phosphine ligand, chalcogen atom and aryl substituent on chalcogen atom. Structures of $[Pt(SeC_4H_3N_2)_2(PPh_3)_2].2CH_2Cl_2$ and $[Pd\{\eta^2\text{-}SeC_4H_3N_2\}\{SeC_4H_3N_2\}(PPh_3)].CH_2Cl_2$ have been established by single crystal X ray diffraction analyses.

From the forgoing discussion the following conclusions can be drawn:

- Oxidative addition reactions between bis(2-pyridyl)ditellurides and platinum(0) compounds give several products in addition to expected products, $[Pt\{TeC_5H_3(3\text{-}R)N\}_2(PR'_3)_2]$. These reactions also gave serendipitous complex $[Pt\{TeC_5H_3(3\text{-}R)N\}_2Te(PR'_3)]$ (R = H, Me). In the latter complex, formally zero-valent tellurium bridges two pyridine nitrogen rings of two trans-situated Te-coordinated 2-pyridyltellurolates.

- The oxidative addition reactions of (diphosphine)Pt^{o} with dipyridyl ditellurides and substitution reactions of $[PtCl_2(P^{\frown}P)]$ ($P^{\frown}P$ = dppm, dppe, dppp) with 2-pyridyltellurolate ions, afforded not only expected products but also gave serendipitous derivatives e.g. $[Pt\{TeC_5H_3(3\text{-}R)N\}_2(dppe)]$ (R = H or Me). Mono to trinuclear complexes are formed depending on the nature of chelating phosphine and the substituent in the pyridyl ring.
- Depending on the nature of phosphine and the chalcogen atom, variety of the complexes has been isolated in the reactions of 2-chalcogenpyridines with palladium phosphine precursors. The tellurolate complexes are highly susceptible to halogenated solvents and undergo facile Te-C bond cleavage.
- The reactivity of tellurium ligands is markedly different from those of sulfur/ selenium lignads. The tellurium ligands also undergo Te-C bond cleavage leading to the formation of tellurido-bridged derivatives, $[M_3(\mu\text{-}E)_2(P^{\frown}P)_3]^{2+}$.
- In case of pyrimidyl dichalcgenides, E-C (E = Se, Te) bond is weaker than pyridine analog which leads facile conversion of mononuclear complexes of composition $[M\{EC_4H(4,6\text{-}R_2)N_2\}_2(P^{\frown}P)]$ to trinuclear $[M_3(\mu\text{-}E)_2(P^{\frown}P)_3].2Cl$ (M= Pd, Pt) complex in halogenated solvent.
- Oxidative addition reactions of nicotinoyl based selenides with $[M(PPh_3)_4]$ (M = Pt, Pd) give a variety of complexes. The complexes of the type $[M(I)\{SeC_5H_3(3\text{-}CONHPh)N\}(PPh_3)_2]$ in $CH_2Cl_2/CHCl_3$ undergo, initially dissociation of PPh_3 ligand, followed by decomposition to several other novel products including $[M(I)(Ph)(PPh_3)_2]$ and $[(C_5H_3N)SeC(NH)CO]$.

- The mononuclear chalcogenolate complexes, $M(EAr)_2(P^\frown P)$ show different orientation of the aryl group with respect to metal square plane, whereas in solution at room temperature (by NMR) such differences are not noticed. The observed different orientation of the aryl group in the solid state may possibly be due to subtle crystal energy packing requirements.

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List of Publications

1. Tellurium(0) as a ligand: Synthesis and characterization of 2-pyridyltellurolates of platinum (II) and structures of [Pt{2-Te-3-(R)C_5H_3N}$_2$Te(PR'$_3$)] (R = H or Me).

   R. S. Chauhan, G. Kedarnath, A. Wadawale, A. M. Castro, R. A. Perez, V. K. Jain, W. Kaim

   Inorg. Chem., 49 (2010) 4179-4185.

2. Reactions of 2-telluropyridine ligands with (diphosphine)Pt^{o} and (diphosphine)$PtCl_2$ complexes and isolation of different structural motifs of platinum(II)complexes.

   R. S. Chauhan, G. Kedarnath, A. Wadawale, A. L. Rheingold, A. M.Castro, R. A. Perez, V. K. Jain

   *Organometallic*s, 31 (2012) 1743-1750.

3. Reactivity of dipyrimidyldiselenides with [M(PPh_3)$_4$] and 2-pyrimidylchalcogenolates with [MCl_2(diphosphine)] (M = Pd or Pt)

   R. S. Chauhan, R. K. Sharma, G. Kedarnath, D. B. Cordes, A. M. Z. Slawin, V. K. Jain

   J. Organomet. Chem., 717 (2012) 180-186.

4. Reactivity of 2-chalcogenopyridines with palladium-phosphine complexes: Isolation of different complexes depending on the nature of chalcogen atom

   R. S. Chauhan, G. Kedarnath, A. Wadawale, A. M. Z. Slawin, V. K. Jain

   Dalton Trans., 42 (2013) 259-269.

5. Oxidative addition reactions of nicotinamide based organoselenium compounds on $[M(PPh_3)_4]$ (M = Pd or Pt) : An insight study for the formation of several isolable products

   R. S. Chauhan, C. P. Prabhu, P. P. Phandis, G. Kedarnath, J. A. Golen, A. L. Rheingold, V. K. Jain

   J. Organomet. Chem., 723 (2013) 163-170.

6. Bis phosphine palladium(II) mesityl chalcogenolate complexes: Synthesis and structure of [Pd(SeMes)2(dppe)]

   R. S. Chauhan, G. Kedarnath, A. Wadawale, J. A. Golen, A. L. Rheingold, V. K. Jain

   *Ind. J. Chem.,*52 A (2013) 42-44.

7. Cis configured bis phosphine platinum(II) chalcogenolate complexes: Structures and a comparative NMR study

   R. S. Chauhan, G. Kedarnath, A. Wadawale, J. A. Golen, A. L. Rheingold, V. K. Jain

   J. Organomet. Chem. (submitted)

Conferences/Symposia

1. Structural and spectroscopic characterization of platinum complex with C-substituted (pyridyltelluro)-bis(diphenylphosphino)methane,

   R. S. Chauhan, G. Kedarnath, A. Wadawale, V. K. Jain

   “3rd International Conference on Materials Chemistry”, 7-10 December 2010, BARC, Mumbai.

2. Reactions of 2-Chalcogenopyridine with palladium phosphine complexes,

   R. S. Chauhan, G. Kedarnath, A. M. Z. Slawin, V. K. Jain

   “3rd Asian Conference on Coordiantion Chemistry” 17-20 October 2011, Indian Habitate Centre, New Delhi.

3. Main group metal chalcogenolate complexes and their utility as molecular precursors for metal chalcogenides,

   R. K. Sharma, **R. S. Chauhan**, G. Kedarnath, A. Wadawale, V. K. Jain

   “National symposium on Frontier in Main-Group and Organometallic chemistry”, 19-20 December 2011, IISC, Bangalore.

4. Organometallic chemistry of platinum group metal chalcogenolates : Syntheis, Structures and Spectroscopy,

   R. S. Chauhan, G. Kedarnath, V. K. Jain

   “24th Research Scholar Meet-2012”, 17-18 February, 2012, SIES College of Arts, Science and Commerce, Mumbai.

5. Organometallic chemistry of platinum group metal complexes derived from various hemilabile chalcogenolate ligands : Synthesis, spectroscopy and structures,

   R. S. Chauhan, G. Kedarnath, V. K. Jain

   “GECOM CONCOORD 2012” 3-8 June 2012, Metabief, France