PLATINUM GROUP METAL COMPLEXES OF HYBRID ORGANOCHALCOGEN LIGANDS AND CATALYTIC ORGANIC SYNTHESIS

By

PRADHUMN SINGH

Department of Chemistry

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CERTIFICATE

This is to certify that the thesis entitled, **"PLATINUM GROUP METAL COMPLEXES OF HYBRID ORGANOCHALCOGEN LIGANDS AND CATALYTIC ORGANIC SYNTHESIS"** being submitted by **Mr. PRADHUMN SINGH** to the Indian Institute of Technology, Delhi for the award of the degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by him. Mr. Pradhumn Singh has worked under my guidance and supervision. He has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this dissertation have not been submitted, in part or in full, to any other university or institute for award of any degree or diploma.

Date:

Dr. AJAI K. SINGH

Professor & Head
Department of Chemistry
Indian Institute of Technology,
Delhi, New Delhi-110016, India

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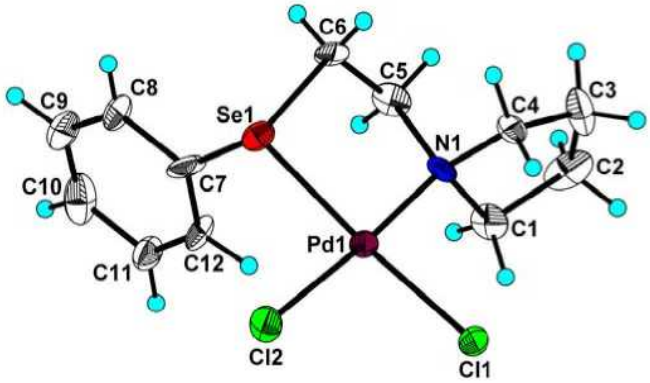
PRADHUMN SINGH

ABSTRACT

The chemistry of hybrid organochalcogen ligands is of current interest due to their potential for several applications including catalytic ones. The present thesis is focused on designing of bi- and tridentate compounds containing S, Se and Te donor sites along with N and exploring their coordination chemistry with platinum group metals i.e. including Pd(II), Pt(II), Ru(II)/(III) and Rh(III) species. The Pd(II), (η^6-arene)Ru(II)/(III) and Rh(III) complexes of these chalcogenated ligands have been studied for catalytic C–C, C–N and Negishi cross-couplings, oxidation of alcohols and transfer hydrogenation reaction of ketones. Half sandwich complexes of Ru(II) having (η^6-benzene / *p*-cymene) units also show important promising anticancer activity as such species are now a days targeted for anticancer research programme.

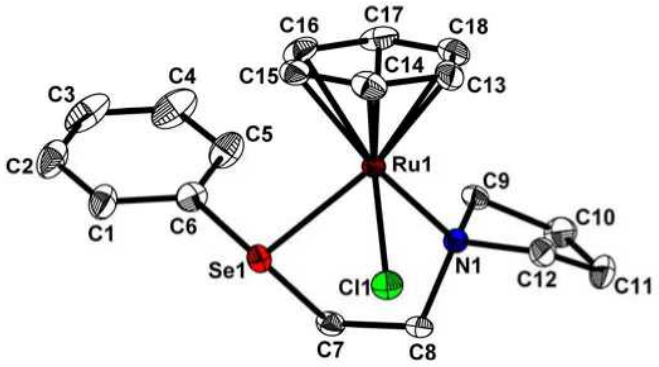
The reactions of PhS^-, $PhSe^-$ and Se^{2-} with *N*-{2-(chloroethyl)}pyrrolidine result in *N*-{2-(phenylthio)ethyl}pyrrolidine (**L1**), *N*-{2-(phenylseleno)ethyl}pyrrolidine (**L2**) and bis{2-(pyrrolidene-*N*-yl)ethyl} selenide (**L3**) respectively. The **L3** is unstable. The Pd(II) and Pt(II) form complexes with **L1**–**L2** type $[MCl_2(\mathbf{L})]$ (M = Pd, **L** = **L1**–**L2**: **1**–**2** and M = Pt, **L** = **L1**–**L2**: **3**–**4**). The molecular structure of $[PdCl_2(\mathbf{L2})]$ is shown below.



ORTEP diagram of $[PdCl_2(\mathbf{L2})]$ (**2**)

The complexes $[(\eta^6\text{-}C_6H_6)RuCl(\mathbf{L})][PF_6]$ (**L** = **L1**–**L2**: **5**–**6**) and $[(\eta^6\text{-}p\text{-cymene})RuCl(\mathbf{L})][PF_6]$ (**L** = **L1**–**L2**: **7**–**8**) have been synthesized by the reaction of

L1–**L2** with chloro-bridged dimmers $[\{(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)\}_2]$ and $[\{(\eta^6\text{-}p\text{-cymene})RuCl(\mu\text{-}Cl)\}_2]$, treatment with NH_4PF_6. The $[(\eta^6\text{-}p\text{-cymene})RuCl(\mathbf{NH_3})][PF_6]$ (**9**), is also formed unexpectidly due to reaction of unreacted chloro-bridged dimeric compound of ruthenium with NH_4PF_6. The $[(\eta^6\text{-}p\text{-cymene})Ru(CH_3CN)(\mathbf{L2})][PF_6]_2.CH_3CN$ (**10**) was formed by reaction of **8** with CH_3CN and AgOtf. The ligands **L1**–**L3** and complexes **1**–**10** were characterized by ^1H, $^{13}C\{^1H\}$, $^{77}Se\{^1H\}$ NMR and FT–IR spectroscopy. The crystal structures of **2** and **5**–**10** have been solved by X-ray diffraction. In **5**–**10**, the cations exhibit the pseudo-octahedral half sandwich "Piano-Stool" disposition around ruthenium (see ORTEP diagram of **6**). The ligands are coordinated in bidentate mode to the metal.

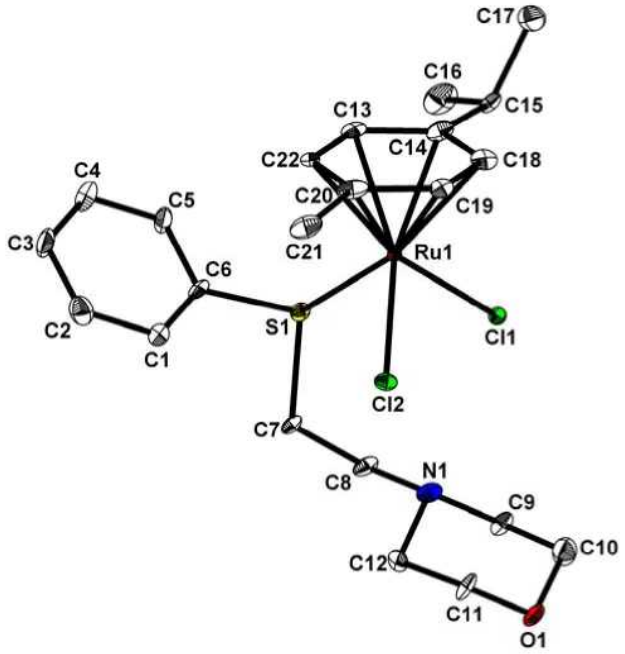


ORTEP diagram of cation of $[(\eta^6\text{-}C_6H_6)RuCl(\mathbf{L2})][PF_6]$ (**6**)

The Pd(II)-complexes have been explored for catalytic Heck and Suzuki–Miyaura coupling reactions. The TON values for both catalytic reactions have been found up to 83000 and 85000 respectively. The efficiency of **2** is marginally better than **1**. The Ru-complexes **5**–**6** are promising for catalytic oxidation of primary and secondary alcohols in the presence of *N*-methylmorpholine-*N*-oxide (NMO). The TON value found upto 9.7×10^4. The **6** is somewhat more efficient catalyst than **5** (sulfur analogue).

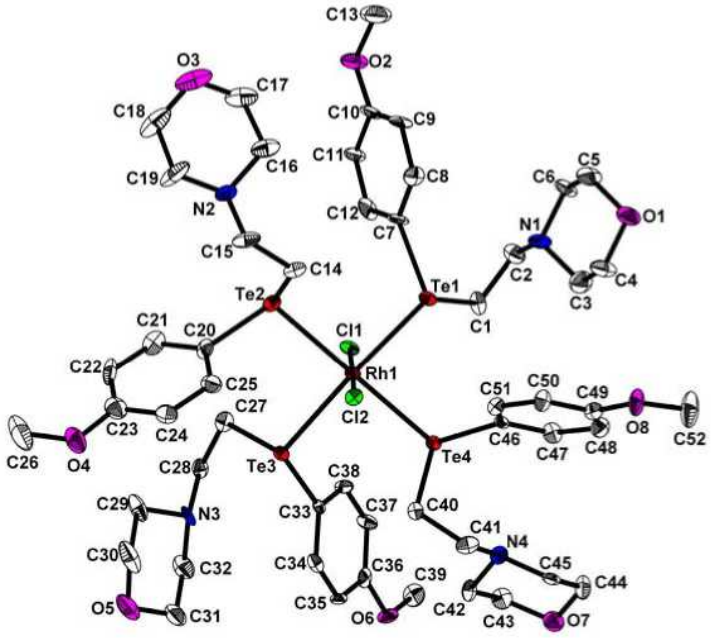
The reactions of *N*-{2-(chloroethyl)}morpholine with in-*situ* generated PhS^- / PyS^-, $PhSe^-$ and $ArTe^-$ result in *N*-{2-(phenylthio)ethyl}morpholine (**L4**), *N*-{2-

(pyridylthio)ethyl}morpholine (**L5**), *N*-{2-(phenylseleno)ethyl}morpholine (**L6**) and *N*-{2-(aryltelluro)ethyl}morpholine (**L7**) respectively. The complexes $[PdCl_2(\mathbf{L})]$, $[(\eta^6\text{-}C_6H_6)RuCl(\mathbf{L})][PF_6]$ (**L** = **L4**–**L7**: **15**–**18**) and $[(\eta^6\text{-}p\text{-cymene})RuCl(\mathbf{L})][PF_6]$ (**L** = **L4**: **19**; **L** = **L6**: **20**) have been synthesized. The $[\{(\eta^6\text{-}p\text{-cymene})RuCl(\mu\text{-}Cl)\}_2]$ reacts with **L4** and excess NH_4PF_6 in MeOH at room temperature (24 h), resulting unexpectedly $[(\eta^6\text{-}p\text{-cymene})RuCl_2(\mathbf{L4})][PF_6]$ (**21**) and $[(\eta^6\text{-}p\text{-cymene})RuCl(\mathbf{NH_3})_2][PF_6]$ (**22**). The **21** (see ORTEP diagram) is a 17 e^- half sandwich complex of η^6-*p*-cymene with Ru(III) formed due to oxidation of Ru(II) with NH_4PF_6. The complexes $[RhCl_2(\mathbf{L})_4][ClO_4]$ (**L** = **L6**–**L7**: **23**–**24**), result on reacting $RhCl_3.3H_2O$ with **L6**–**L7** and treatment of $AgClO_4$.



ORTEP diagram of cation of $[(\eta^6\text{-}p\text{-cymene})RuCl_2(\mathbf{L4})][PF_6]$ (**21**)

The ligands **L4**–**L7** and complexes **11**–**24** were characterized by ^1H, $^{13}C\{^1H\}$, $^{77}Se\{^1H\}$, $^{125}Te\{^1H\}$ NMR and FT–IR spectroscopy. The crystal structures of **11**–**18**, **21**–**22** and **24** have been solved. The geometry around palladium is slightly distorted square planar. The geometry around Rh in **24** (see ORTEP diagram) is distorted octahedral.

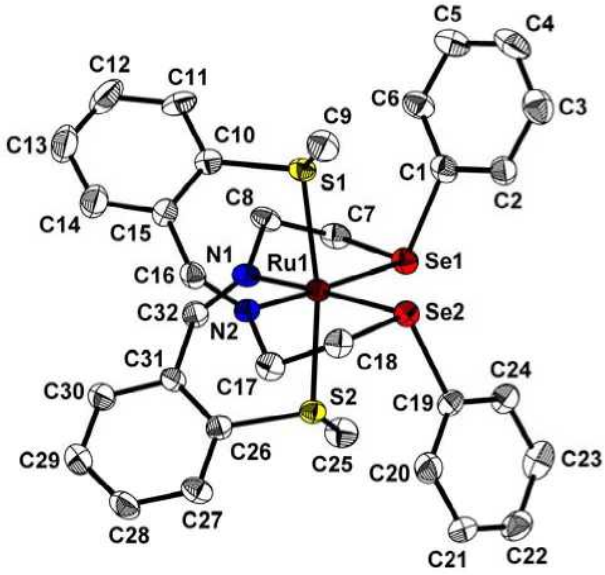


ORTEP diagram of cation of $[RhCl_2(\mathbf{L7})_4][ClO_4]\cdot C_2H_5OH\cdot 2H_2O$ (**24**)

The TON value was upto 9700 when Pd-complexes **11**–**14** have been explored for catalytic C–N cross-coupling reaction. The order of catalytic efficiency is Te > Se > S. The complexes **15**–**20** have been used for catalytic oxidation of primary and secondary alcohols in presence of *N*-methylmorpholine-*N*-oxide (NMO), *t*-butyl hydroperoxide (*t*-BuOOH), sodium oxychloride (NaOCl), and sodium periodate ($NaIO_4$). For all four oxidants **18** appears to be most efficient among all six Ru-species. The TON value was found upto 9.8×10^4. The complexes **21** and **23**–**24** catalyze transfer hydrogenation reaction of ketones in presence of 2-propanol and the TON values were found upto 9.8×10^4. In comparison to catalyst **23**, the performance of **24** is somewhat better.

2–(Arylchalcogeno)ethylamine (NH_2–CH_2CH_2–EAr) on reaction with 2–methylthiobenzaldehyde gives Schiff bases: 2–$MeSC_6H_4CH{=}NCH_2CH_2$–EAr (where **L8**: E = S, Ar = C_6H_4; **L9**: E = Se, Ar = C_6H_4; **L10**: E = Te, Ar = C_6H_4–OMe). The complexes $[PdCl(\mathbf{L})][PF_6/ClO_4]$ (**L** = **L8**: **25**; **L** = **L9**: **26**–**27**; **L** = **L10**: **28**) were synthesized by the reaction of $PdCl_2$ in CH_3CN with **L8**–**L10**, followed by treatment

with $AgPF_6$ / $AgClO_4$. The reaction of $[\{(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)\}_2]$ with **L8**–**L10** and subsequent treatment with NH_4PF_6 give *fac*-$[(\eta^6\text{-}C_6H_6)Ru(\mathbf{L})][PF_6]_2$ (**L** = **L8**: **29**; **L** = **L9**: **30**; **L** = **L10**: **31**). The $[Ru(\mathbf{L9})][PF_6]_2$ (**32**), is formed by the reaction of chloro-bridged dimmer $[\{(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)\}_2]$ with **L9** and subsequent treatment with NH_4PF_6. This is the first example in which chloro as well benzene ring of $[\{(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)\}_2]$ are successively substituted by controlling metal:ligand ratio and of reaction time. The ligands **L8**–**L10** and complexes **25**–**32** were characterized by ^1H, $^{13}C\{^1H\}$, $^{77}Se\{^1H\}$, $^{125}Te\{^1H\}$ NMR and FT–IR spectroscopy. The crystal structures of **25**–**32** have been solved.



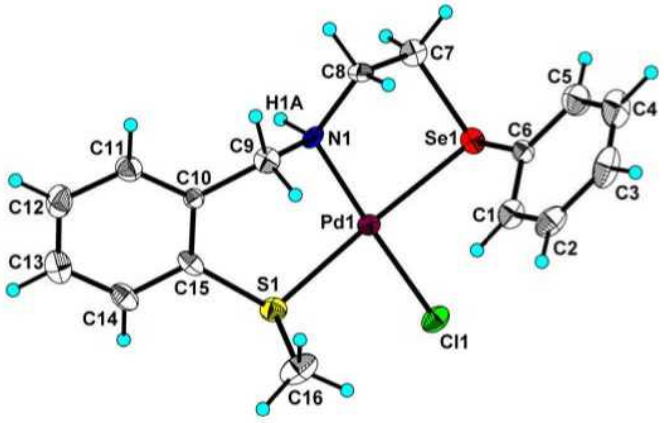
ORTEP diagram of $[Ru(\mathbf{L9})][PF_6]_2$ (**32**)

The geometry around palladium is distorted square planar. In Ru-complexes (**29**–**31**), the cations exhibit the pseudo-octahedral half sandwich "Piano-Stool" geometry. The geometry around ruthenium in **32** is distorted octahedral (see ORTEP diagram).

The Pd-complexes **25**–**28** have been explored for catalytic Negishi cross-coupling reaction with the maximum yields upto 91 %. The order of catalytic efficiency is Te > Se > S. The complexes **29**–**31** were explored for catalytic oxidation

of alcohols with NMO (*N*-methylpyrrolidine-*N*-oxide), *t*-BuOOH, NaOCl and $NaIO_4$ and transfer hydrogenation of ketones with maximum TON value of 9.9×10^4 and 9.7×10^4 respectively. The catalytic efficiency varies with chalcogen ligands in the order of Te > Se > S for catalytic oxidation as well as transfer hydrogenation which may be tailored to some extent by strong electron donating methoxy group present on tellurium.

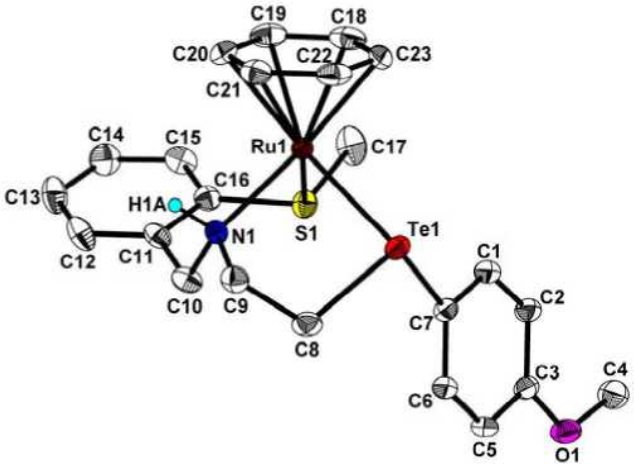
The Schiff base ligands **L8**–**L10** on reduction with sodium borohydride in dry ethanol resulted in 2–$MeSC_6H_4CH_2$–$NHCH_2CH_2$–EAr (**L11**: E = S, Ar = C_6H_4; **L12**: E = Se, Ar = C_6H_4; **L13**: E = Te, Ar = C_6H_4–OMe) secondary amines. The complexes [PdCl(**L**)][PF_6/ClO_4] (**L** = **L11**: **33**; **L** = **L12**: **34**; **L** = **L13**: **35**), *fac*-[(η^6-C_6H_6)Ru(**L**)][PF_6][X] (**L** = **L11**: **36**; **L** = **L12**: **37**; **L** = **L13**: **38**. X = PF_6 or Cl) have been synthesized as for parent Schiff bases of **L11**–**L13**.



ORTEP diagram of cation of [PdCl(**L9**)][PF_6] (**34**)

The ligands **L11**–**L13** and complexes **33**–**38** were characterized by ^1H, $^{13}C\{^1H\}$, $^{77}Se\{^1H\}$, $^{125}Te\{^1H\}$ NMR and FT–IR spectroscopy. The crystal structures of **33**–**38** were solved. The geometry around palladium is distorted square planar (see ORTEP diagram of **34**). In Ru-complexes (**36**–**38**), the cations exhibit the pseudo-octahedral half sandwich "Piano-Stool" geometry (see ORTEP diagram of **38**).

The Pd-complexes **33**–**35** have been explored for catalytic Negishi cross-coupling reaction (yields up to 94 %). The order of catalytic efficiency is Te > Se > S.



ORTEP diagram of cation of $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{L13})][PF_6]_2.CH_3CN$ (**38**)

The complexes **36**–**38** were explored for catalytic oxidation of alcohols with NMO (*N*-methylpyrrolidine-*N*-oxide), *t*-BuOOH, NaOCl and $NaIO_4$ and transfer hydrogenation of ketones with maximum TON values are similar to those of **29**–**31**. The results were found to be promising and the catalytic efficiency varies with chalcogen ligands in the order of Te > Se > S which may be tailored to some extent by strong electron donating methoxy group present on tellurium.

TABLE OF CONTENTS

Chapter 1 Introduction

Chapter 2 Materials and Methods

Chapter 3 Pyrrolidine based Chalcogen Ligands and their Metal Complexes

Chapter 4 Morpholine based Chalcogen Ligands and their Metal Complexes

Chapter 5 Chalcogenated Schiff bases and their Metal Complexes

Chapter 6 Chalcogenated Secondary Amine and their Metal Complexes

Chapter 7 Concluding Comments and Future Scope of the Work

Curriculum Vitae