

**COMPLEXES OF METALLIC AND
ORGANOMETALLIC HALF SANDWICH SPECIES
WITH ORGANOCHALCOGEN LIGANDS AND
CATALYTIC ORGANIC REACTIONS**

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HALF SANDWICH SPECIES WITH
ORGANOCHALCOGEN LIGANDS AND CATALYTIC
ORGANIC REACTIONS**

by

OM PRAKASH

Department of Chemistry

Submitted

in fulfillment of the requirements of the degree of

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CERTIFICATE

This is to certify that the thesis entitled, “**Complexes of Metallic and Organometallic Half Sandwich Species with Organochalcogen Ligands and Catalytic Organic Reactions**” being submitted by **Mr. Om Prakash** 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. Om Prakash 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.

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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 thus mainly focused on designing of bidentate, terdentate and tetradentate ligands containing S and Se donor sites along with / without N and O and exploring their co-ordination chemistry with Ag(I), Pd(II), (η^6 -benzene)Ru(II) and (η^5 -pentamethylcyclopentadiene) Rh(III)/Ir(III). The exploration on resulting complexes for a variety of catalytic organic reactions such as C–C cross-couplings, three component coupling reaction of aldehyde, amine and alkyne (A^3 reaction), oxidation of alcohols, Oppenauer-type oxidation of alcohols and transfer hydrogenation reaction of carbonyl compounds.

The (2-arylchalcogenomethyl)pyridine ligands (**L1–L3**) were synthesized by the reaction of *in situ* generated ArE^- ($E = S$ or Se ; $Ar = Ph / 2$ -pyridyl for S , Ph for Se) with (2-chloromethyl)pyridine in N_2 atmosphere. The reactions of S^{2-} and Se^{2-} with (2-chloromethyl)pyridine result in bis(2-pyridylmethyl)chalcogenide (**L4** and **L5** respectively). Half-sandwich complexes $[(\eta^6-C_6H_6)Ru(L)Cl][PF_6]$ (**1–3**) $[(\eta^5-Cp^*)Rh(L)Cl][PF_6]$ (**4** and **6**), $[(\eta^5-Cp^*)Rh(L2)CH_3CN][PF_6]_2$ (**5**), $[(\eta^5-Cp^*)Ir(L)Cl][PF_6]$ (**7–9**), $[(\eta^6-C_6H_6)Ru(L)][2PF_6]$ (**10** and **11**), $[(\eta^5-Cp^*)Rh(L)][2PF_6]$ (**12** and **13**) and $[(\eta^5-Cp^*)Ir(L)][2PF_6]$ (**14** and **15**) ($L = L1–L5$) have been synthesized by reacting **L** with $[(\eta^6-C_6H_6)RuCl(\mu-Cl)]_2$, $[(\eta^5-Cp^*)RhCl(\mu-Cl)]_2$, and $[(\eta^5-Cp^*)IrCl(\mu-Cl)]_2$ respectively. The ligands and complexes have been characterized by IR, HR-MS, 1H , $^{13}C\{^1H\}$ and $^{77}Se\{^1H\}$ NMR spectra. The single crystal structures of complexes **1–13** and **15** have been determined with X-Ray crystallography. Each metal has pseudo-octahedral half sandwich “Piano–Stool” geometry. The complexes **1–15** have been explored for catalysis of transfer

hydrogenation reaction of ketones with 2-propanol and found very efficient as revealed by TON values which are up to 9.8×10^3 . The Ru(II) complexes **1–3**, **10** and **11** are promising for catalytic oxidation of primary and secondary alcohols in the presence of *N*-methylmorpholine-*N*-oxide (NMO). The TON values are found upto 9.9×10^3 . The complexes of Se ligands have been found more efficient than their sulphur analogues. These orders of efficiency are supported by DFT calculations. DFT calculations also indicate reactivity order for complexes as Rh > Ir. The calculated bond lengths/angles by DFT are generally consistent with the experimental ones.

The half-sandwich complexes $(\eta^5\text{-Cp}^*)\text{Rh}(\text{L})\text{Cl}[\text{PF}_6]$ (**16–18**), and $(\eta^5\text{-Cp}^*)\text{Ir}(\text{L})\text{Cl}[\text{PF}_6]$ (**19–21**), have been prepared by reacting **L = L6–L8** [1,2-bis(phenylthio)ethane (**L6**), (1-phenylseleno)-2-(phenylthio)ethane(**L8**) and 1,2-bis(phenylseleno)ethane (**L9**) with $(\eta^5\text{-Cp}^*)\text{RhCl}(\mu\text{-Cl})_2$ and $(\eta^5\text{-Cp}^*)\text{IrCl}(\mu\text{-Cl})_2$ respectively at room temperature followed by treatment with NH_4PF_6 . The HR-MS, ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{77}\text{Se}\{^1\text{H}\}$ NMR spectra have authenticated them. The single crystal structures of **16–21** have been established by X-Ray crystallography. The complexes **16–21** have been explored for catalytic Oppenauer-type oxidation of alcohols and TH of ketones with 2-propanol. The **18** and **21** are most efficient for the two catalytic reactions [TON values up to 9.9×10^2 and 9.8×10^3 respectively] and therefore investigated in detail. In transfer hydrogenation it appears that one of the catalytic species is without Cp* ring. DFT calculations indicate higher reactivity for Rh complexes in comparison to Ir ones. The calculated bond lengths/angles by DFT are generally consistent with the experimental values.

Ligands 1,2-bis(phenylthiomethyl)benzene (**L9**), 1,2-bis(phenylselenomethyl)benzene (**L10**), 1,2,4,5-tetrakis(phenylthiomethyl)benzene (**L11**), and 1,2,4,5-tetrakis(phenylseleno

methyl)benzene (**L12**), react with $[(\eta^5\text{-Cp}^*)\text{MCl}(\mu\text{-Cl})]_2$ ($\text{M} = \text{Rh}$ or Ir) at room temperature, followed by treatment with NH_4PF_6 have resulted in half-sandwich monometallic $[(\eta^5\text{-Cp}^*)\text{M}(\text{L})\text{Cl}][\text{PF}_6]$ and bimetallic complexes $[(\eta^5\text{-Cp}^*)\text{M}(\text{L})\text{Cl}][\text{PF}_6]_2$, (Rh : **22**, **23**; Ir : **24**, **25**; $\text{L} = \text{L9}$ or **L10** and Rh : **26**, **27**; Ir : **28**, **29**; $\text{L} = \text{L11}$ or **L12**). Their HR-MS, ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{77}\text{Se}\{^1\text{H}\}$ NMR spectra were found characteristic. The crystal structures of **22–25**, **27** and **29** have been established by X-Ray crystallography. The complexes **22–29** have been found efficient for catalytic transfer hydrogenation (TH) of aldehydes and ketones in glycerol which acts as a green solvent and hydrogen source. The complexes of (Se, Se) ligand are marginally efficient than the corresponding complexes of (S, S) ligand. The reactivity of Rh complexes in comparison to those of Ir also appears to be somewhat more. The results of DFT calculations appear to be generally consistent with experimental catalytic efficiencies and bond lengths/angles.

The Pd(II) complexes (**30** and **31**) have been synthesized by reaction of $\text{Pd}(\text{CH}_3\text{CN})\text{Cl}_2$ and 2-(pyridine-2-ylmethylsulfanyl)benzoic acid(**L13**). The complex **31** appears to be formed by intramolecular cyclization within complex **30** via C–H activation of thiophene. The reactions of **L13** with $[(\eta^5\text{-Cp}^*/\eta^6\text{-C}_6\text{H}_6)\text{MCl}(\mu\text{-Cl})]_2$, [C_6H_6 : $\text{M} = \text{Ru}$; Cp^* : $\text{M} = \text{Rh}$ or Ir] at room temperature followed by treatment with NH_4PF_6 result in water soluble half-sandwich complexes $[(\eta^5\text{Cp}^*/\eta^6\text{-benzene})\text{M}(\text{L})\text{Cl}][\text{PF}_6]$ [**32–34** for $\text{M} = \text{Ru}$, Rh and Ir]. Their HR-MS, ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra have been found characteristic. The single crystal structures of **30–31** have been established with X-Ray crystallography. The COOH group increases the solubility of complex **30–31**, in water. Pd(II) complexes **30** and **31** have been found to be efficient catalysts for Suzuki–Miyaura coupling reactions in

water and DMF-water adduct respectively. The Hg/PPh₃ poisoning experiments, two phase test and TEM analysis of black residue formed during catalysis have shown that [Pd(0)–Pd(II)] process is involved in catalysis. Nano-particles with a narrow size distribution (size of 80-85% particles ~3–5.5 nm) formed with the starting of these reactions; appear to be important for catalytic coupling. The complexes **32–34** have been found efficient for catalytic transfer hydrogenation (TH) of carbonyl compounds in water with glycerol as a hydrogen donor. The catalysis with glycerol as a hydrogen source is pH-independent. Higher reactivity for Rh complex in comparison to Ru and Ir ones has been observed. DFT calculations are generally consistent with the experimental values of bond lengths/angles and catalytic reactivity order.

The (ENE) Pincer Ligands (E = S, Se) ligands **L14–L15** have been synthesized by reaction of *in situ* generated PhE[−] (E = S or Se) with 4,5-bis (bromomethyl)acridine in N₂ atmosphere. The Ru(II) complexes (**35** and **36**) and Ag(I) complexes (**37–40**) are formed by reaction of [(RuCl₂(PPh₃)₃] and AgNO₃ with ligands **L14–L15**. All the ligands and complexes have shown characteristic ¹H, ¹³C{H}, and ⁷⁷Se{H} NMR spectra. The structures of complexes (**37, 39**) have been established with X-Ray crystallography. In the complexes **37** and **39**, Ag has a distorted pyramidal geometry and is encapsulated by 10 membered chelate ring in **37**. The ligand is in pincer coordination mode in **39**. The complexes **35** and **36** have been used in Oppenauer-type oxidation of alcohols in which acetone acts as an oxidant (TON upto 9.9×10²). The Ag(I) complexes **37–40** have been used in three-component coupling of aldehyde, alkyne, and amine. The complex of Se containing ligand is more efficient catalyst than its sulphur analogue.

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