

**HYBRID LIGANDS OF (Te, N), (Te, N_x, O_y), (Te, N, S) AND
(O, N, S/P) TYPE: DESIGNING, METAL COMPLEXES
AND APPLICATIONS IN ORGANIC SYNTHESIS**

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*DEDICATED TO
MY PARENTS, SISTERS AND BROTHERS*

CERTIFICATE

This is to certify that the thesis entitled, “**HYBRID LIGANDS OF (Te, N), (Te, N_x, O_y), (Te, N, S) AND (O, N, S/P) TYPE: DESIGNING, METAL COMPLEXES AND APPLICATIONS IN ORGANIC SYNTHESIS**” being submitted by **Mr. RAGHAVENDRA KUMAR P** 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. Raghavendra Kumar P 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: 24.4.06


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ABSTRACT

The derivatives of tellurated alkyl amines, 4-CH₃OC₆H₄Te(CH₂)₂NH₂·HCl (**1**), 4-CH₃OC₆H₄Te(Cl₂)(CH₂)₃NH₂·HCl (**2**), Cl₂Te[(CH₂)₂NH₂·HCl]₂ (**3**) and Cl₂Te[(CH₂)₃NH₂·HCl]₂ (**4**) have been synthesized by reacting appropriate organic halide with nucleophile 4-CH₃OC₆H₄Te⁻(ArTe⁻) or Te²⁻ generated in-situ by borohydride reduction of (4-CH₃OC₆H₄Te)₂ or Te powder, followed by treatment with HCl of appropriate concentration. The zwitterionic species [Cl₄Te(CH₂)_nNH₃⁺] (**2a**) was generated when single crystals of **2** were grown. The Pd(II) and Ru(II) complexes of tellurated 1° alkyl amines, [Pd(ArTeCH₂CH₂NH₂)Cl₂] (**5**), [RuCl(*p*-cymene)(ArTeCH₂CH₂NH₂)]Cl·H₂O (**6**) and [RuCl(*p*-cymene)(ArTeCH₂CH₂CH₂NH₂)]Cl (**7**) have been synthesized. When **5** was treated with PPh₃ in presence of AgNO₃, [Pd(ONO₂)₂(PPh₃)₂] (**8**) resulted. Single crystal structures of **1-6**, **8** and **2a** have been determined by X-ray diffraction. The Te···Cl, C-H···π and/or N-H···O secondary interactions were observed in **1-6** and **2a**. The **5** and **6** are the first examples of structurally characterized Pd(II) and Ru(II) complexes of a tellurated alkyl amines.

2-(4-Methoxyphenyltelluro)ethyl/propylamine and bis(2-aminoethyl/propyl) telluride on reaction with *o*-hydroxyacetophenone in dry ethanol gave Schiff bases ArTeCH₂CH₂N=C(CH₃)C₆H₄-2-OH (**L**¹), [2-HO-C₆H₄-(CH₃)C=NCH₂CH₂]₂Te (**L**³), ArTeCH₂CH₂CH₂N=C(CH₃)C₆H₄-2-OH (**L**⁵) and [2-HO-C₆H₄-(CH₃)C=NCH₂CH₂CH₂]₂Te (**L**⁷) respectively. Reduction of **L**¹, **L**³, **L**⁵ and **L**⁷ with NaBH₄ results in ArTeCH₂CH₂NHCH(CH₃)C₆H₄-2-OH (**L**²), [2-HO-C₆H₄-(CH₃)CHNHCH₂CH₂]₂Te (**L**⁴), ArTeCH₂CH₂CH₂NHCH(CH₃)C₆H₄-2-OH (**L**⁶) and [2-HO-C₆H₄-(CH₃)CHNHCH₂CH₂CH₂]₂Te (**L**⁸) respectively which contain 1 or 2 chiral centers. The Pd(II), Ru(II) and

Hg(II) complexes of L^1 to L^4 viz., $[PdCl(L^1-H)]$ (9), $[HgBr_2(L^1)_2]$ (10), $[PdCl(L^2-H)]$ (11) and $[RuCl(L^2-H)]$ (12), $[HgBr_2(L)_2]$ (13-15) (where $L = L^2-L^4$) were synthesized. The ligands L^1 , L^3 , L^5 and L^7 and the complexes 9, 11 and 12 were structurally characterized by single crystal X-ray diffraction. These are the first structurally characterized acyclic tellurated Schiff bases and complexes of (Te, N, O^-) type ligands. In 11 the Te $\cdots$ Cl secondary interactions bring two Pd atoms of two neighboring molecules closer than sum of the Van der Waals radii. The 12 was formed by the substitution of *p*-cymene by a hybrid organotellurium ligand (L^2) for the first time. There exist Te $\cdots$ Cl secondary interactions and NH $\cdots$ O intermolecular hydrogen bonds in 12 which remain stable even in solution. The Ru-Ru distance has been found to be 3.247(3) Å, which is less than sum of van der Waals radii (4.0 Å)

2-Methylthiobenzaldehyde was reacted with 2-ethanolamine and 2-(4-methoxyphenyltelluro)ethylamine to give Schiff bases 2-MeSC₆H₄-CH=NCH₂CH₂OH (L^9) and 2-MeSC₆H₄CH=NCH₂CH₂TeAr (L^{11}) respectively. Borohydride reduction of L^9 and L^{11} resulted in 2-MeSC₆H₄CH₂NCH₂CH₂OH (L^{10}) and 2-MeSC₆H₄CH₂NHCH₂CH₂TeAr (L^{12}) respectively. The ligands L^{11} and L^{12} are the first (Te, N, S) type tridentate hybrid organotellurium ligands. Pd(II), Pt(II) and Ru(II) complexes of L^9 to L^{12} have been synthesized. The single crystal structures of $[PdCl_2(L^9)]$ (17), $[PdCl(L^{11})]PF_6$ (18), $[PdCl(L^{12})]ClO_4$ (20) and $[Ru(p\text{-cymene})(L^{12})](PF_6)_2$ (22) have been determined by X-ray diffraction. The L^{10} acts as a bidentate (S, N) donor in 17 whereas L^{11} and L^{12} behave as tridentate (S, N, Te) donors. The geometry around Pd has been found to be square planar whereas for Ru it is octahedral. In 18 the Te $\cdots$ Cl and Pd $\cdots$ Te secondary interactions are interesting and the later one is rare.

(2-Aminoethyl)phenylsulfide and (2-aminoethyl)diphenylphosphine were prepared and reacted with *o*-hydroxyacetophenone to give the Schiff bases 2-[1-(2-phenylsulfanylethylimino)ethyl]phenol (L^{13}), 2-[1-(2-diphenylphosphanylethylimino)ethyl]phenol (L^{16}) respectively. 2-[1-(2-Phenylsulfanylethylamino)ethyl]phenol (L^{15}) and 2-[1-(2-diphenylphosphanylethylamino)ethyl]phenol (L^{17}) were obtained by borohydride reduction of L^{13} and L^{16} respectively. The ligand L^{14} has been synthesized by condensation of 2,4-dihydroxyacetophenone with (2-aminoethyl)phenylsulfide.

The complexes $[PdCl(L-H)]$ ($L = L^{13}, 23; L^{14}, 24; L^{15}, 25; L^{16}, 26; L^{17}, 27$) and $[NiCl(L-H)]$ ($L^{16}, 28; L^{17}, 29$) have been synthesized. The single crystal structures of $[PdCl(L^{13}-H)]$ (23), $[PdCl(L^{15}-H)]$ (25) and $[NiCl(L^{16}-H)]$ (28) were determined by X-ray diffraction.

Immobilization of complex $[PdCl(PhSCH_2CH_2N=C(CH_3)C_6H_3-2-O^-4-OH)]$ (24) on silica gel has been made. The resulting matrix has been characterized by IR and ^{13}C CPMAS NMR spectroscopy and used as catalyst for C-C coupling reactions (Suzuki-Miyaura coupling). The catalytic activity has been found to be promising.

TABLE OF CONTENTS

Sl. No.	Contents	Page No.
1	Certificate	i
2	Acknowledgements	ii
3	Abstract	iii
4	List of figures	ix

CHAPTER 1 INTRODUCTION

Sl. No.	Contents	Page No.
1.1	Monodentate and Bidentate telluroethers	2
1.2	Tridentate telluroethers	3
1.3	Hybrid telluroethers of (Te, X) type (X = N, P, As, Sb, O and S)	4
1.4	Hybrid Telluroether Ligands of (X, Te, Y) (X/Y= N/N, O/N, Te/S, N/Te) type	13
1.5	Polydentate Hybrid Telluroethers	19
1.6	Cyclic Telluroethers	20
1.7	Tellurated Schiff bases	24
1.8	Polydentate Hybrid Ligands Containing Nitrogen and Oxygen Donors and either Sulfur or Phosphorus	27
1.9	Polymer Supported Heterogeneous Catalysis	41
1.10	Silica gel Based Heterogeneous Catalysts and their Applications	43
1.11	Objectives and Scope of the Present Work	51
	References	54

CHAPTER 2 MATERIALS AND METHODS

Sl. No.	Contents	Page No.
2.1	Chemicals	65
2.2	Synthesis of precursors	65
2.3	Elemental analyses	68
2.4	Melting point	69
2.5	Molecular weight determination	69
2.6	Conductance measurements	69
2.7	Infrared spectra	70
2.8	Nuclear magnetic resonance spectra	70
2.9	Single crystal X-ray diffraction studies	70
	References	71

CHAPTER 3 TELLURATED ALKYL AMINES AND THEIR Pd(II) AND Ru(II) COMPLEXES

Sl. No.	Contents	Page No.
3.1	Introduction	72
3.2	Experimental	73
3.3	X-ray diffraction analysis	78
3.4	Results and discussion	79
3.5	Conductance and Molecular Weight measurements	81
3.6	IR spectra	83
3.7	^1H NMR spectra	84
3.8	$^{13}\text{C}\{^1\text{H}\}$ NMR spectra	85
3.9	Crystal Structures of 1-6, 2a and 8	94
3.10	Conclusions	121
	References	122

**CHAPTER 4 HYBRID LIGANDS OF (Te, N_x, O_y) TYPE AND THEIR
METAL COMPLEXES**

Sl. No.	Contents	Page No.
4.1	Introduction	125
4.2	Experimental	126
4.3	X-ray diffraction analysis	130
4.4	Results and discussion	132
4.5	Conductance and Molecular Weight measurements	134
4.6	IR spectra	134
4.7	¹ H NMR spectra	138
4.8	¹³ C{ ¹ H} NMR spectra	141
4.9	Crystal Structures of L ¹ , L ³ , L ⁵ , L ⁷ , 9, 11 and 12	166
4.10	Conclusions	186
	References	187

**CHAPTER 5 HYBRID LIGANDS OF (O, N, S) AND (Te, N, S) TYPE AND
THEIR METAL COMPLEXES**

Sl. No.	Contents	Page No.
5.1	Introduction	190
5.2	Experimental	191
5.3	X-ray diffraction analysis	197
5.4	Results and discussion	197
5.5	Conductance measurement	198
5.6	IR spectra	199
5.7	¹ H NMR spectra	203
5.8	¹³ C{ ¹ H} NMR spectra	216
5.9	Crystal Structures of 16, 17, 18, 20 and 22	223
5.10	Conclusions	240
	References	241

**CHAPTER 6A HYBRID LIGANDS OF (O, N, S/P) TYPE AND THEIR Pd(II)
AND Ni(II) COMPLEXES**

Sl. No.	Contents	Page No.
6.1	Introduction	244
6.2	Experimental	245
6.3	X-ray diffraction analysis	249
6.4	Results and discussion	250
6.5	Conductance measurement	251
6.6	IR spectra	255
6.7	¹ H NMR spectra	255
6.8	¹³ C{ ¹ H} NMR spectra	271
6.9	³¹ P{ ¹ H} NMR spectra	272
6.10	Crystal Structures of L¹³, L¹⁴, 23, 25 and 28	281

**CHAPTER 6B: APPLICATIONS OF Pd(II) COMPLEXES OF (O, N, S)
LIGANDS IN ORGANIC SYNTHESIS (C-C COUPLING)**

Sl. No.	Contents	Page No.
6.11	Introduction	292
6.12	Experimental	293
6.13	Results and discussion	294
6.14	Characterization of heterogenized palladium complex (30) immobilized silica gel	295
6.15	Conclusions	299
	References	300

CHAPTER 7:

Sl. No.	Contents	Page No.
1.	Concluding Comments and Further Scope of the Work	302
2.	Curriculum Vitae	306