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

By

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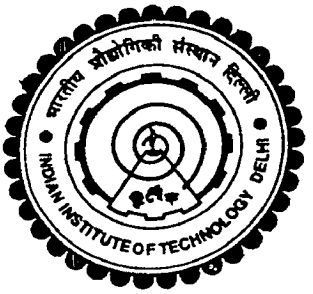
Submitted

in fulfillment of the requirements of the degree of

DOCTOR OF PHILOSOPHY

To The



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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 Indain 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-$CH_3OC_6H_4Te(CH_2)_2NH_2 \cdot HCl$ (**1**), 4-$CH_3OC_6H_4Te(Cl_2)(CH_2)_3NH_2 \cdot HCl$ (**2**), $Cl_2Te[(CH_2)_2NH_2 \cdot HCl]_2$ (**3**) and $Cl_2Te[(CH_2)_3NH_2 \cdot HCl]_2$ (**4**) have been synthesized by reacting appropriate organic halide with nucleophile 4-$CH_3OC_6H_4Te^-$($ArTe^-$) or Te^{2-} generated in-situ by borohydride reduction of $(4\text{-}CH_3OC_6H_4Te)_2$ or Te powder, followed by treatment with HCl of appropriate concentration. The zwitterionic species [$^-Cl_4Te(CH_2)_nNH_3^+$] (**2a**) was generated when single crystals of **2** were grown. The Pd(II) and Ru(II) complexes of tellurated 1° alkyl amines, [$Pd(ArTeCH_2CH_2NH_2)Cl_2$] (**5**), [RuCl(*p*-cymene)($ArTeCH_2CH_2NH_2$)]$Cl \cdot H_2O$ (**6**) and [RuCl(*p*-cymene)($ArTeCH_2CH_2CH_2NH_2$)]Cl (**7**) have been synthesized. When **5** was treated with PPh_3 in presence of $AgNO_3$, $[Pd(ONO_2)_2(PPh_3)_2]$ (**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 $ArTeCH_2CH_2N{=}C(CH_3)C_6H_4\text{-}2\text{-}OH$ ($\mathbf{L^1}$), $[2\text{-}HO\text{-}C_6H_4\text{-}(CH_3)C{=}NCH_2CH_2]_2Te$ ($\mathbf{L^3}$), $ArTeCH_2CH_2CH_2N{=}C(CH_3)C_6H_4\text{-}2\text{-}OH$ ($\mathbf{L^5}$) and $[2\text{-}HO\text{-}C_6H_4\text{-}(CH_3)C{=}NCH_2CH_2CH_2]_2Te$ ($\mathbf{L^7}$) respectively. Reduction of $\mathbf{L^1}$, $\mathbf{L^3}$, $\mathbf{L^5}$ and $\mathbf{L^7}$ with $NaBH_4$ results in $ArTeCH_2CH_2NHCH(CH_3)C_6H_4\text{-}2\text{-}OH$ ($\mathbf{L^2}$), $[2\text{-}HO\text{-}C_6H_4\text{-}(CH_3)CHNHCH_2CH_2]_2Te$ ($\mathbf{L^4}$), $ArTeCH_2CH_2CH_2NHCH(CH_3)C_6H_4\text{-}2\text{-}OH$ ($\mathbf{L^6}$) and $[2\text{-}HO\text{-}C_6H_4\text{-}(CH_3)CHNHCH_2CH_2CH_2]_2Te$ ($\mathbf{L^8}$) respectively which contain 1 or 2 chiral centers. The Pd(II), Ru(II) and

Hg(II) complexes of $\mathbf{L^1}$ to $\mathbf{L^4}$ viz., [PdCl($\mathbf{L^1}$-H)] (**9**), [$HgBr_2$($\mathbf{L^1}$)$_2$] (**10**), [PdCl($\mathbf{L^2}$-H)] (**11**) and [RuCl($\mathbf{L^2}$-H)] (**12**), [$HgBr_2$(L)$_2$] (**13-15**) (where L = $\mathbf{L^2}$-$\mathbf{L^4}$) were synthesized. The ligands $\mathbf{L^1}$, $\mathbf{L^3}$, $\mathbf{L^5}$ and $\mathbf{L^7}$ 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···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 ($\mathbf{L^2}$) for the first time. There exist Te···Cl secondary interactions and NH···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-$MeSC_6H_4$-CH=NCH_2CH_2OH ($\mathbf{L^9}$) and 2-$MeSC_6H_4CH$=NCH_2CH_2TeAr ($\mathbf{L^{11}}$) respectively. Borohydride reduction of $\mathbf{L^9}$ and $\mathbf{L^{11}}$ resulted in 2-$MeSC_6H_4CH_2NCH_2CH_2OH$ ($\mathbf{L^{10}}$) and 2-$MeSC_6H_4CH_2NHCH_2$ CH_2TeAr ($\mathbf{L^{12}}$) respectively. The ligands $\mathbf{L^{11}}$ and $\mathbf{L^{12}}$ are the first (Te, N, S) type tridentate hybrid organotellurium ligands. Pd(II), Pt(II) and Ru(II) complexes of $\mathbf{L^9}$ to $\mathbf{L^{12}}$ have been synthesized. The single crystal structures of [$PdCl_2$($\mathbf{L^9}$)] (**17**), [PdCl($\mathbf{L^{11}}$)]PF_6 (**18**), [PdCl($\mathbf{L^{12}}$)]ClO_4 (**20**) and [Ru(*p*-cymene)($\mathbf{L^{12}}$)]$(PF_6)_2$ (**22**) have been determined by X-ray diffraction. The $\mathbf{L^{10}}$ acts as a bidentate (S, N) donor in **17** whereas $\mathbf{L^{11}}$ and $\mathbf{L^{12}}$ 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···Cl and Pd···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 ($\mathbf{L^{13}}$), 2-[1-(2-diphenylphosphanylethylimino) ethyl]phenol ($\mathbf{L^{16}}$) respectively. 2-[1-(2-Phenylsulfanylethylamino)ethyl]phenol ($\mathbf{L^{15}}$) and 2-[1-(2-diphenylphosphenylethylamino)ethyl]phenol ($\mathbf{L^{17}}$) were obtained by borohydride reduction of $\mathbf{L^{13}}$ and $\mathbf{L^{16}}$ respectively. The ligand $\mathbf{L^{14}}$ has been synthesized by condensation of 2,4-dihydroxyacetophenone with (2-aminoethyl)phenylsulfide.

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

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