METAL COMPLEXES OF GROUP 15 AND 16 DONORS: SYNTHESIS, STRUCTURES AND APPLICATIONS IN ORGANIC SYNTHESIS

By

SUMIT BALI

Department of Chemistry

Submitted

in fulfilment of the requirements of the degree of

DOCTOR OF PHILOSOPHY

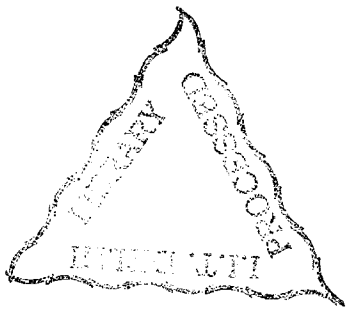
to the

INDIAN INSTITUTE OF TECHNOLOGY, DELHI

INDIA

AUGUST, 2005

Organic Synthesis



CERTIFICATE

This is to certify that the thesis entitled **"METAL COMPLEXES OF GROUP 15 AND 16 DONORS: SYNTHESIS, STRUCTURES AND APPLICATIONS IN ORGANIC SYNTHESIS"**, being submitted by **Mr. SUMIT BALI**, 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. Sumit Bali 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 thesis have not been submitted, in part or in full, to any other university or institute for award of any degree or diploma.

Date: 31.8.05

Dr. AJAI K. SINGH
Professor
Department of Chemistry
Indian Institute of Technology, Delhi
New Delhi -110016

ACKNOWLEDGEMENTS

I wish to express my sincere regards from the depth of my heart to my guide, Professor Ajai K. Singh, whose generosity, faith and superb guidance cannot be described in simple words. A source of constant encouragement, he motivated me with the keen interest in my progress that inspired me to complete this work.

My sincere thanks to the Head, Department of Chemistry, for providing all the departmental facilities. I also wish to thank the supporting staff members for the help they provided during the research.

I express my gratitude to all foreign collaborators for providing crystallographic support.

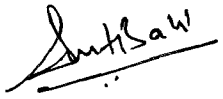
This work could not have been carried out without the support of my wife Garima. I thank her for being so understanding, supportive and helpful.

I am thankful to my lab seniors Dr. M. Kadarkaraisamy, Dr. Parbati Sengupta, Dr Anupama Datta, Dr. Vibha Gurnani, Dr. Ashu Chaudhary for their support and help. I am thankful to my lab colleague Mr G. Venkatesh for being so helpful, supportive and caring. I am also thankful to my labmates Raghvendra K. P., Arun and Neetu for their kind contribution.

I have no words to express my gratitude to my dear friends Mukesh and Sanjay Kathait for being always there at time of need. It would have been impossible for me to complete this work without there support and help. My sincere thanks to Prosenjit for always being around to help, support and keep my spirits high. I would also like to acknowledge the support of my friends Amit, Adil, Khatri, Pravin, Sokhi.

It was constant endearment, wholehearted moral support and love of my parents, my sister Himani and my brother Sourabh that I am able to see this day. I shall always remain indebted to them. I owe a great deal to my parents-in-law and Chikki, Sonal, Monal for being ever supportive.

Last but not least I am thankful to the ALMIGHTY.

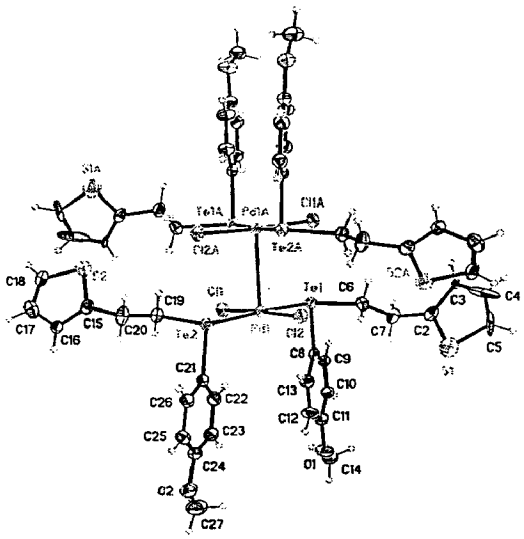


SUMIT BALI

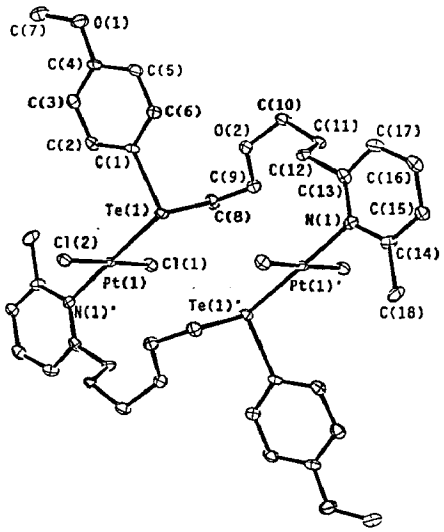
ABSTRACT

Hybrid organotellurium ligands 2-[2-(4-methoxyphenyltelluro)ethyl]thiophene ($\mathbf{L^1}$) and 1-(4-methoxyphenyltelluro)-2-[3-(6-methyl-2-pyridyl)propoxy]ethane ($\mathbf{L^3}$) are synthesized by reacting $ArTe^-$ (generated in situ by borohydride reduction of Ar_2Te_2) with 2-(2-chloroethyl)thiopene and [3-2-(chloroethoxy)propyl]-6-methylpyridine respectively under N_2 atmosphere. Bis[2-(2-thienyl)ethyl] telluride ($\mathbf{L^2}$) and bis-{2-[3-(6-methyl-2pyridyl)propoxy]ethyl} telluride ($\mathbf{L^4}$) are synthesized by the reaction of Na_2Te with 2-(2-chloroethyl)thiopene and [3-2-(chloroethoxy)propyl]-6-methylpyridine respectively under N_2 atmosphere. Ligands Tetrahyro-2-furanylmethyl(2-thienyl) telluride ($\mathbf{L^5}$) and tetrahydro-2H-2-pyranylmethyl(2-thienyl) telluride ($\mathbf{L^6}$) are synthesized by reacting ThTeLi with tetrahydrofurfuryl chloride and 2-(bromomethyl)tetrahydro-2H-pyran respectively under nitrogen atmosphere. $\mathbf{L^1}$ and $\mathbf{L^3}$ are stable under ambient conditions for two months while $\mathbf{L^2}$ and $\mathbf{L^4}$ start decomposing when stored under ambient conditions for four to eight days. $\mathbf{L^5}$ and $\mathbf{L^6}$ are also stable but start decomposing after two weeks under ambient conditions. The ^1H and $^{13}C\{^1H\}$ NMR of $\mathbf{L^1}$–$\mathbf{L^6}$ are characteristic. The complexes $[AgNO_3(\mathbf{L^1})]$ **(1)**, $[PdCl_2(\mathbf{L^1})_2]_2$ **(2)**, $[PtCl_2(\mathbf{L^1})_2]$ **(3)**, $[HgBr_2(\mathbf{L^1})]_2$ **(4)**, [Ru(*p*-cymene)$Cl_2(\mathbf{L^1})$] **(5)**, [Ru(*p*-cymene)$Cl_2(\mathbf{L^2})$] **(6)**, $[PdCl_2(\mathbf{L^2})_2]$ **(7)**, $[PdCl_2(\mathbf{L^3})]_2$ **(8)**, $[PtCl_2(\mathbf{L^3})]_2$ **(9)**, $[HgBr_2(\mathbf{L^3})]$ **(10)**, $[PdCl_2(\mathbf{L^4})]_2$ **(13)**, $[PtCl_2(\mathbf{L^4})]_2$ **(14)**, $[(PdCl_2)_3(\mathbf{L^4})_2]$ **(15)**, $[PdCl_2(\mathbf{L^5})_2]$ **(16)**, $[PtCl_2(\mathbf{L^5})_2]$ **(17)**, $[HgBr_2(\mathbf{L^5})_2]$ **(18)**, [Ru(*p*-cymene)Cl_2 $(\mathbf{L^5})$] **(19)**, $[CuBr_2(\mathbf{L^5})]$ **(20)**, $[PdCl_2(\mathbf{L^6})_2]$ **(21)**, $[PtCl_2(\mathbf{L^6})_2]$ **(22)**, $[HgBr_2(\mathbf{L^6})_2]$ **(23)**, [Ru(*p*-cymene)$Cl_2(\mathbf{L^6})$] **(24)** are synthesized and characterized by IR, ^1H, $^{13}C\{^1H\}$ NMR spectroscopy along with elemental analyses, conductance and molecular weight measurements. $MeOC_6H_4HgBr$ **(11)** and $[RTe^+\text{-}HgBr_2]Br$ (R = $-CH_2CH_2OCH_2CH_2CH_2$-(2-(6-CH_3-C_5H_3N))) **(12)** have been formed by decomposition of **11** during its

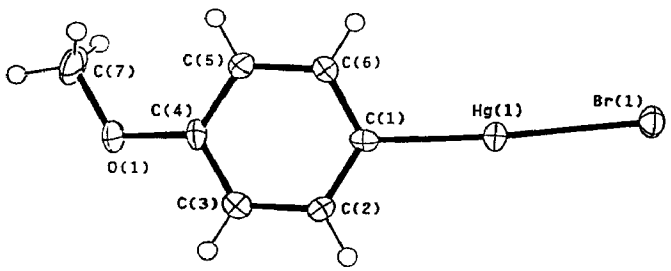
crystallization. Both **11** and **12** have been characterized by spectroscopic methods (IR, ^{1}H and $^{13}C\{^{1}H\}$ NMR along with elemental analyses. The CH_2-Te signal in the ^{1}H (except in case of **1** and **20**) and $^{13}C\{^{1}H\}$ NMR spectra of all the complexes appears deshielded as compared to free ligands thereby indicating the binding of ligands $\mathbf{L^1}$ – $\mathbf{L^6}$ through Te. The single crystal structures of complexes $[PdCl_2(\mathbf{L^1})_2]_2$ (**2**), [Ru(*p*-cymene)$Cl_2(\mathbf{L^2})$] (**6**), $[PdCl_2(\mathbf{L^2})_2]$ (**7**), $[PdCl_2(\mathbf{L^3})]_2$ (**8**), $[PtCl_2(\mathbf{L^3})]_2$ (**9**), [Ru (*p*-cymene)Cl_2 ($\mathbf{L^5}$)] (**19**) and $[PdCl_2(\mathbf{L^6})_2]$ (**21**) have been determined and corroborate the inferences made from their NMR spectra in solution. Crystal structure of **11** has also been determined.



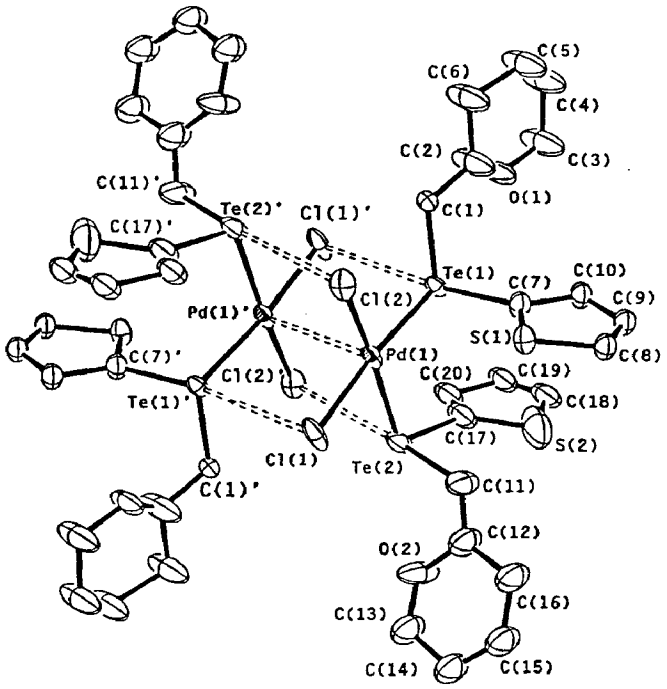
Molecular structure of $[PdCl_2(\mathbf{L^1})_2]_2$ (**2**)



Molecular structure of $[PtCl_2(\mathbf{L^3})]_2$ (**9**)



Molecular structure of 4-$MeOC_6H_4HgBr$ (**11**)



Molecular Structure of $[PdCl_2(L^6)_2]$ (**21**)

Silica gel has been modified using 3-aminopropyltriethoxysilane to synthesize aminopropyl silica gel (APSG), which contains amino functionalities on the surface of silica gel. APSG is reacted with chlorodiphenylphosphine in benzene to synthesize phosphino groups modified silica gel which is further complexed with Pd(II) and subsequently treated with hydrazine hydrate to give PPh_2-Pd(0) complex immobilized silica gel. The immobilized Pd(0) species is used as a catalyst for carbon-carbon coupling reactions between activated alkenes and aryl halides. The catalyst is reusable and only *trans* product is selectively formed by C-C coupling reactions catalyzed by it.

Table of contents

Chapter IV: 1-(4-Methoxyphenyltelluro)-2-[3-(6-methyl-2-pyridyl)propoxy] ethane (L^3), 2-methyl-6-{3-[2-({2-[3-(6-methyl-2-pyridyl)propoxy]ethyl}telluranyl) ethoxy]propyl}pyridine (L^4) and Their Metal Complexes

Chapter V: Tetrahydro-2-furanylmethyl(2-thienyl) telluride (L^5) and tetrahydro-2H-2-pyranylmethyl(2-thienyl) telluride (L^6) and Their Metal Complexes