

**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

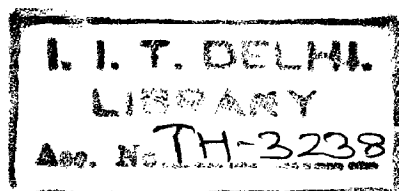
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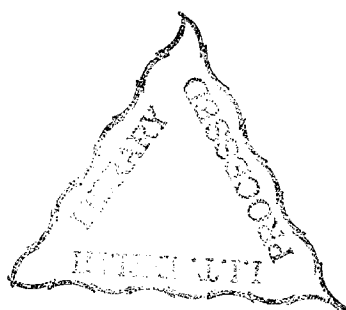
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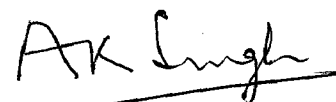


CERTIFICATE

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

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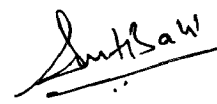
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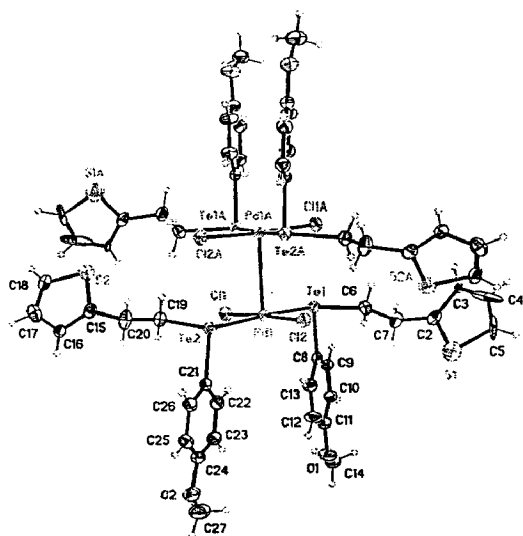
Last but not least I am thankful to the ALMIGHTY.


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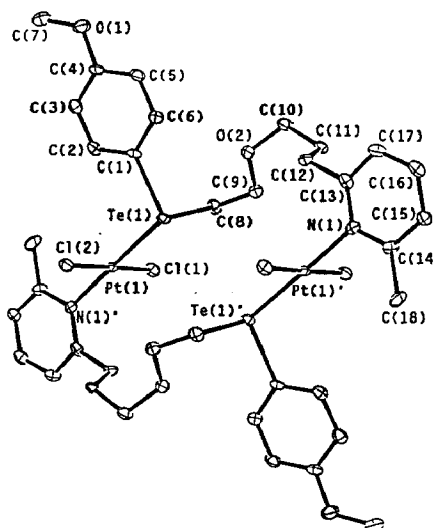
ABSTRACT

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

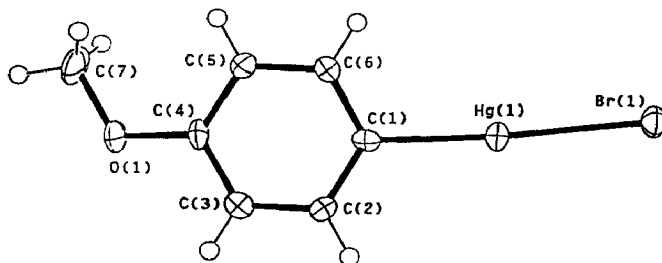
crystallization. Both **11** and **12** have been characterized by spectroscopic methods (IR, ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR along with elemental analyses. The $\text{CH}_2\text{-Te}$ signal in the ^1H (except in case of **1** and **20**) and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of all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



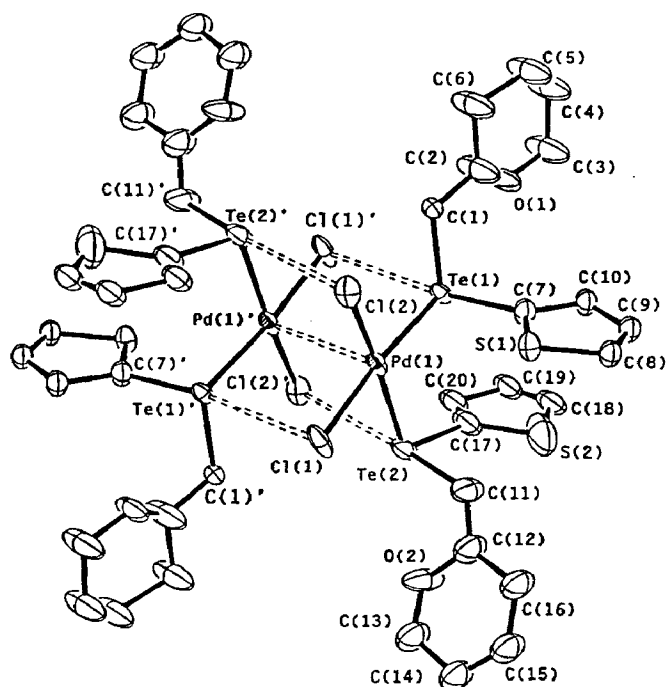
Molecular structure of $[\text{PdCl}_2(\text{L}^1)_2]_2$ (**2**)



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



Molecular structure of 4-MeOC₆H₄HgBr (**11**)



Molecular Structure of $[\text{PdCl}_2(\text{L}^6)_2]$ (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 $\text{PPh}_2\text{-Pd(0)}$ 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.

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