LIGATIONAL BEHAVIOUR OF ARYL CHALCOGENOLATES AND DIARYL DICHALCOGENIDES TOWARDS PALLADIUM AND PLATINUM

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TO

LATE MATHURA PRASAD

CERTIFICATE

This is to certify that the thesis entitled, "**Ligational Behaviour of Aryl Chalcogenolates and Diaryl Dichalcogenides Towards Palladium and Platinum**", being submitted by Mr. Sushil Kumar Gupta, 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. Gupta has worked under my guidance and supervision and has fulfilled the requirements for the submission of the thesis, which to my knowledge, has reached the requisite standard.

The results contained in this have not been submitted, in part or in full, to any other University or Institute for the award of any degree or diploma.

26/10/89

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(S.K. Gupta)

ABSTRACT

The thesis entitled "Ligational Behaviour of Aryl Chalcogenolates and Diaryl Dichalcogenides Towards Palladium and Platinum" embodies an account of the synthesis and characterization of the various palladium(II) and platinum(II) complexes with aryl chalcogenolate (ArE^-) and diaryl dichalcogenide (Ar_2E_2) (where E=Se, Te; Ar=Ph, C_6H_4Me-4, C_6H_4OMe-4, C_6H_4OEt-4) ligands. Some hetero binuclear complexes involving Pt and Pd with phenyl chalcogen bridging and the insertion reactions of Pt and Pd into Sn-Te and Sn-C bonds of $Ph_3SnTeAr$ studied in situ are also included in the thesis.

The diaryl dichalcogenide complexes of the types $[PdCl_2(E_2Ar_2)]_2$, $[Pd_2Cl_4(Te_2Ar_2)(PPh_3)_2]$ and $[PtCl_2(Te_2Ar_2)_2]$ have been synthesized from the reactions between Ar_2E_2 and Na_2PdCl_4 (or $Pd(PhCN)_2Cl_2$), $Pd_2Cl_4(PPh_3)_2$ and K_2PtCl_4 under different experimental conditions. The ligand substitution reactions with PPh_3 have been explored.

The monomeric, dimeric and polymeric complexes viz. $[MCl(EAr)(PPh_3)_2]$, $[M(EAr)_2(PPh_3)_2]$, $[MCl(EAr)(PPh_3)]_2$, $[MCl(EAr)]_n$ and $[M(EAr)_2]_n$ (where M = Pd, Pt) have been prepared by reacting different Pd(II) and Pt(II) derivatives with ArE^- generated in situ from the reductive cleavage of Ar_2E_2. The polymeric complexes have been characterized by

carrying out bridge-splitting reactions with mono- and bi-dentate phosphorus ligands.

The chelated chalcogenolates, [M(COD)Cl(TeAr)], [M(COD)$(TeAr)_2$] and [M(DPPE)$(EAr)_2$], have bveen prepared from the reactions between [M(COD)Cl_2] and NaTeAr or $Ph_3SnTeAr$, and between [M(DPPE)Cl_2] and NaEAr. The substitution of diolefin ligand by PPh_3 in the complexes has been studied. Following this methodology, it has been possible to synthesize monomeric [Pd$(TeAr)_2(PPh_3)_2$], which otherwise could not be obtained.

The reactions between [Pt(DPPE)$(EPh)_2$] and Pd$(PhCN)_2Cl_2$ have led to the formation of an interesting class of hetero binuclear complexes [(DPPE)Pt(μ-EPh)$_2$PdCl$_2$].

The reactions of $Ph_3SnTeAr$ with Pt(0) and Pd(0) have been studied in solution by ^1H and ^{31}P NMR. The studies suggest the formation of two cis complexes [M$(PPh_3)_2$(TeAr)$(SnPh_3)$] and [M$(PPh_3)_2$(Ph)$(SnPh_2TeAr)$] in solution.

The molecular weight and conductance measurements and spectral (IR, Far IR, Raman, electronic, ^1H, ^{13}C, ^{31}P, ^{125}Te and ^{195}Pt NMR) data of aryl chalcogenolates and diaryl dichalcogenides of Pd(II) and Pt(II) have led to the

following conclusions:

i) The diaryl dichalcogenide, Ar_2E_2 can ligate with transition metal ions through one or both of the chalcogen atoms.

ii) The aryl chalcogenolate, ArE^-, being highly polarizable, forms interesting monomeric, dimeric and polymeric structures with Pd(II) and Pt(II) derivatives and exhibits terminal as well as bridging mode of linkages.

iii) The order of Lewis acidity towards ArE^- follows the trend $Pd^{II} > Pt^{II}$.

iv) The Te, being larger in size, has higher donor tendency relative to S and Se towards Pd(II) and Pt(II) derivatives.

v) The Pd(II) polymer having aryl tellurol bridges is more resistant to cleavage than that of its platinum analogue.

vi) The Pt and Pd can be inserted into Sn-Te and Sn-C bonds of $Ph_3SnTeAr$ in an oxidative addition reaction.

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