ORGANOMETALLOIDS - SYNTHESIS AND LIGATION REACTIONS

BY

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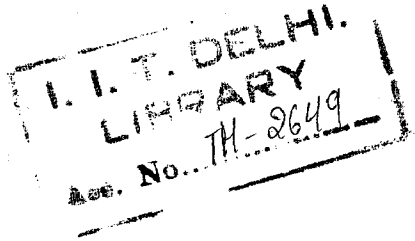

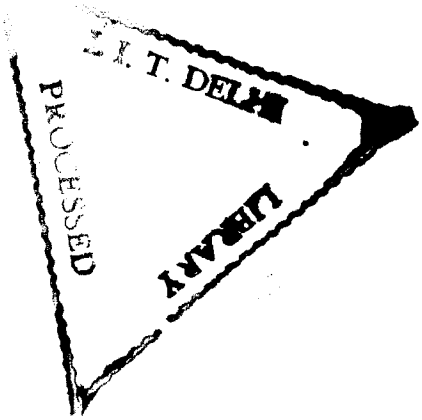

Dedicated

To My Parents

CERTIFICATE

This is to certify that the thesis entitled **"ORGANOMETALLOIDS - SYNTHESIS AND LIGATION REACTIONS"**, being submitted by **Mr. C. Valan Amburose**, 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. C. Valan Amburose has worked under my guidance and supervision and 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.

AK Singh
16.7.99

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ABSTRACT

Synthesis and structural characterization of mixed trihalo-*p*-tolyl antimonates(III) and their bismuth analogue, structural features of tri-*o*-tolyl stibine, μ-oxobridged heterotrinuclear compounds containing Sb(V) and As(III), $Ar_3Sb(OAsPh_2)_2$ and their ligation reactions, synthesis of arsenic and tellurium ligands *viz.*, 2-(2-diphenylarsinoethyl)-1,3-dioxane, 2-(diphenylarsinomethyl)tetrahydrofuran, 2-(4-methoxyphenyltelluro)ethyl ethyl sulfide and bis{2-(4-methoxyphenyl)telluroethyl} ether and their complexation reactions are described in the present thesis.

Mixed trihalo-*p*-tolyl antimonates(III) (**1-7**) of the type $[R_4N][p\text{-tolSbX}_2Y]$ have been prepared from the reaction of R_4NY with $p\text{-tolSbX}_2$ in methanol or ethanol (where R = Et, *n*-Pr, *n*-Bu or *n*-Pe; X = Cl or Br; Y = Br or I and X ≠ Y). These 1:1 electrolytic compounds are dimeric in nature (heavy halogens make the bridges preferentially), as revealed from the crystal structure of $[n\text{-Bu}_4N][p\text{-tolSbCl}_2Br]$ (**4**). The antimony in **4** may be described to possess tetragonal pyramidal geometry or pseudo octahedral geometry, if lone pair is considered. The *p*-tolyl groups in the dimer are in apical positions with respect to $Sb_2Cl_4Br_2$ plane and *trans* to each other. The IR and ^1H, $^{13}C\{^1H\}$ NMR spectra of the compounds **1-7** are characteristic. Bismuth analogue of **4**, $[n\text{-Bu}_4N][PhBiCl_2Br]$ (**8**) also has a dimeric structure with bromo bridges, similar to that of **4**.

Polymorphism is shown by the crystalline $o\text{-tol}_3Sb$. The crystallization of tri-*o*-tolylstibine in hexane yields monoclinic crystals (**9**) whereas in the presence of cobalt chloride in methanol triclinic crystals (**10**) are obtained. The geometry around antimony is distorted tetrahedral in both **9** and **10** with C-Sb-C angles in the range 96.66(2) - 97.4(3)°.

Compounds of the type $Ar_3Sb(OAsPh_2)_2$ (Ar = Ph (**11**) and *p*-tolyl (**12**)) have been synthesized and characterized structurally. They are prepared by the reaction of Ph_2AsLi and Ar_3SbBr_2 under dinitrogen atmosphere with the work up under ambient conditions. The band appearing at 744 cm^{-1} in the IR spectrum of **11** and **12** most probably originates from the asymmetric vibrations of Sb-O-As unit. Molecular ion peak is observed in FAB mass spectrum of **11** but not in that of **12**. The **11** and **12** are characterized structurally. The geometry around antimony in **11** and **12** is regular trigonal bipyramidal and arsenic distorted pyramidal. The distances between arsenic and antimony are within the range 3.330 - 3.418 Å, which is significantly less than the sum of their van der Waals radii (4.210 Å). The reaction of **11** with $RuCl_2(DMSO)_4$ gives $[RuCl_2(DMSO)_2(\mathbf{11})]$ (**13**). The electronic, IR, ^1H and $^{13}C\{^1H\}$ NMR spectral data of **13** suggest octahedral geometry for ruthenium with two Cl atoms *trans* to each other. The reaction of **12** with $(C_6H_5CN)_2PdCl_2$ results in $[PdCl_2(\mathbf{12})]$ (**14**), where **12** appears to coordinate in a bidentate fashion through arsenic.

Hemilabile ligands of (As, O) type 2-(2-diphenylarsinoethyl)-1,3-dioxane (**15**) and 2-(diphenylarsinomethyl)tetrahydrofuran (**16**) are synthesized by the reaction of Ph_2AsLi with the appropriate organic halides. Their complexes having formulae $[PdBr_2(\mathbf{15})_2]$ (**17**), $[PtBr_2(\mathbf{15})_2]$ (**18**), $[PdCl_2(\mathbf{16})]_2$ (**19**) and $[HgBr_2(\mathbf{16})]_2$ (**20**) are synthesized. They all are non-electrolytes in acetonitrile. The signals of groups that are attached to arsenic in ^1H and $^{13}C\{^1H\}$ NMR spectra undergo significant downfield shift when **15** and **16** form complexes **17** - **20**. The oxygen atom(s) of heterocyclic ring do not participate in coordination, as the signals due to $-CH_2-$ groups attached to them remain unaffected on the formation of complexes **17** - **20**. The crystal structures of **17** and **20** are solved. The geometry of palladium in **17** is square planar with two Br atoms *trans* to each other and ligand **15** is linked to palladium in a monodentate fashion

coordinating *via* arsenic. The geometry of mercury in the binuclear complex **20** is distorted tetrahedral whereas that of arsenic is nearly tetrahedral. In **20** also the monodentate **16** coordinates *via* arsenic only.

2-(4-Methoxyphenyltelluro)ethyl ethyl sulfide (**21**) and its complexes, $[PdCl_2(21)]$ (**23**) and $[HgBr_2(21)]_2$ (**24**) are synthesized and characterized by elemental analysis, IR, ^1H and $^{13}C\{^1H\}$ NMR spectra. Structure of **23** has been determined by X-ray diffraction on its single crystals. The geometry around palladium is square planar. Because of the *trans* influence of tellurium in comparison to sulfur, the Pd-Cl(2) bond (2.344(3) Å) is longer than Pd-Cl(1) bond (2.316(4) Å) as the former is *trans* to Te. In **24**, the ligand **21** coordinates in a monodentate fashion, as the signals in its ^1H and $^{13}C\{^1H\}$ NMR spectra due to $-CH_2-$ groups attached to tellurium, are downfield shifted with respect to those of **21** and the signals due to $-CH_2-$ groups that are attached to sulfur are not affected. Thus bromo bridged dimeric structure has been proposed for **24**.

The ligand, bis{2-(4-methoxyphenyl)telluroethyl}ether (**22**) and its complexes of the formulae $[PdCl_2(22)]$ (**25**), $[PtCl_2(22)]$ (**26**) and $[(PPh_3)_2Hg(22)](ClO_4)_2$ (**27**) are synthesized and characterized by elemental analysis, IR, ^1H and $^{13}C\{^1H\}$ NMR spectra. The molecular ion peak (m/z 542) and its fragments in the FAB mass spectrum of **22** authenticate its formation. On the basis of downfield shifts observed in the diagnostic signals of ^1H and $^{13}C\{^1H\}$ NMR spectra, the coordination of **22** in these complexes may be inferred through two tellurium atoms only. The non-participation of oxygen atom in the ligation of **22** in these complexes **25** - **27** is also evidenced by NMR data.

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