CHAPTER - II
MATERIALS AND METHODS

This chapter deals with the sources from which various starting materials have been obtained and also describes methods for synthesizing those which were not commercially available. Details of the synthetic routes employed for obtaining the optimum yields of starting materials required in the present study are given. In most of the cases, except noted otherwise, the compounds have been prepared by the standard methods reported in the literature. These compounds were purified either by repeated crystallization or fractional distillation till the desired melting/boiling points were obtained. Commercial samples were also purified before use except for AR grade samples.

A brief account of various physico-chemical techniques employed for the identification and structural elucidation of the newly synthesized compounds is also given in this chapter.

2.1 PURIFICATION OF SOLVENTS

2.1.1 Benzene (BDH)

Commercial benzene contains thiophene (b.p. 84°C) which cannot be separated by distillation or by fractional crystallization. Following procedure was used for removing thiophene\(^{(1a)}\).

The benzene was shaken repeatedly with about 15% of its volume of concentrated sulphuric acid in a stoppered separatory funnel, until the acid layer was colourless. After each shaking (lasting a few minutes), the mixture was allowed to settle and the lower layer of acid was drawn off. The benzene was then shaken twice with 10% sodium carbonate solution, again with water, and dried with anhydrous calcium chloride. After filtration, the benzene was distilled through an efficient column and fraction boiling at 80-81°C was collected. It was stored in a stoppered bottle over sodium wire.
2.1.2 **Absolute Ethanol**

Absolute ethanol was prepared by either of the following procedures;
(a) The commercial ethanol was purified by the method described by Vogel\(^{(1b)}\). Commercial sample, refluxed over dry calcium oxide, was treated with magnesium chips and iodine and distilled. The distillate coming out at 78.3°C collected.

(b) Another method\(^{(2a)}\) employed was the use of benzene which forms a ternary azeotrope with ethanol and water, boiling at 64.8°C. 10% benzene and 90% commercial ethanol (v/v) were distilled using glass bead fractionating column. The liquid coming at 64.8°C was rejected and the fraction distilling at 78.3°C was collected for use (Lit. value 78.3°C).

2.1.3 **Methanol** (BDH)

It was first distilled over sodium methoxide, followed by refluxing for about four hours over magnesium methoxide (prepared from magnesium ribbon and distilled methanol in presence of iodine as catalyst) and finally distilled (1c). The distillate coming out at 64°C was collected (Lit. Value 64.9°C).

2.1.4 **Acetonitrile** (E. Merck)

It was purified by Walden and Birrs method\(^{(2b)}\). Impure solvent was repeatedly distilled over fresh amount of phosphorus pentaoxide (Pfizer) till the dehydrating agent (P\(_2\)O\(_5\)) in the flask no longer turns yellow. The solvent was then distilled over anhydrous potassium carbonate to remove traces of phosphorus pentaoxide and finally it was distilled without any drying agent and the fraction distilling at 80-81°C was collected (Lit. Value 82.0°C).

2.1.5 **Chloroform** (E.Merck)

Commercial product contains one percent of ethanol, which is added as stabilizer. Ethanol was removed by shaking it five or six times with about half of its volume of water, then dried over anhydrous calcium chloride for about 24 hours, and distilled (b.p. 61°C, Lit. Value 61.3°C)\(^{(1d)}\).
2.1.6 Acetone (BDH and E.Merck)

Commercial sample of acetone was refluxed with successive small quantities of potassium permanganate until the violet colour persists. It was then dried with anhydrous potassium carbonate, filtered and distilled (b.p., 56.5°C Lit.Value 56.2°C) (1e).

2.1.7 Carbon Tetrachloride (E. Merck)

Commercial sample was distilled before use (b.p.76.5°C, Lit.Value 76.8°C).

2.1.8 Solvent Ether (b.p. 34.5°C), Petroleum Ether (b.p. 40-60°C) and n-Hexane (b.p. 65-70°C)

All the above solvents were dried by storing them over sodium wire, followed by distillation.

2.2 PURIFICATION OF LIGANDS AND REAGENTS

Most of the ligands used during the present investigation were synthesized and the remaining ones were purchased from different commercial sources. All the ligands and reagents were purified by the following procedures.

2.2.1 Acetyl acetone (BDH)

AR grade acetyl acetone was distilled before use (b.p. 138.7°C, Lit.Value 139°C).

2.2.2 Ethyl acetoacetate (BDH) (1f)

The commercial sample contains slight amount of acetic acid and ethyl acetate. To remove these impurities 50 g of ethyl acetoacetate was taken in a separating funnel and shaken with small volume of saturated sodium bicarbonate solution until effervescence ceased. It was then shaken with 10 ml water, dried with 5 g of anhydrous calcium chloride. The solution was decanted through a fluted filter paper into 100 ml round bottomed flask and distilled under diminished pressure (71°C / 12 mm) (b.p. 180°C, Lit. Value 180°C).

2.2.3 8-Hydroxyquinoline (Oxine) (BDH)

The commercial sample was distilled under reduced pressure. Fraction at 100-110 C/5 mm was collected which crystallized on cooling to a white solid (m.p. 74°C, Lit. Value 74-75 °C)(1g).
2.2.4 **Salicylaldehyde** (E. Merck) (1h)

The commercial sample was added to a large excess of luke warm aqueous solution of copper acetate (previously saturated near the boiling point), shaken and kept for several hours in ice. The mixture was filtered and the precipitate was washed thoroughly first with alcohol and then with ether, dried over anhydrous magnesium sulphate and distilled (b.p. 196.1°C, Lit. Value 196.5°C).

2.2.5 **O-Hydroxyacetophenone** (Riedal) (1i)

It was distilled under reduced pressure (105-106°C / 20 mm) (b.p.217.3°C, Lit. Value 218°C).

2.2.6 **2-Hydroxy-1-naphthaldehyde** (BDH, England).

The chemical supplied by BDH, Poole (England) was used as such (m.p. 81.7°C, Lit. Value 82°C).

2.2.7 **Ethylenediamine** (BDH)

Commercial sample was distilled before use (b.p. 116.3°C, Lit. Value 116.5°C).

2.2.8 **O-Phenylendiamine** (BDH, England) (1j)

Commercial sample becomes dark brown on keeping for a long time. It was purified by dissolving the crude product in 100-115 ml hot water containing one gram sodium hyposulphite, and few gram of decolorising carbon. Filtered and cooled in ice-salt mixture. Colourless crystals were separated on a Buchner funnel which were washed with 10 ml of ice water and dried in a vacuum desiccator (m.p. 100.8°C, Lit. Value 100-101°C).

2.2.9 **2-Aminopyridine** (Riedal) (1k)

The commercial sample was distilled under reduced Pressure. The impure sample was taken in round bottomed flask fitted with an air condenser. It was heated in an oil bath at 120-130°C. Fraction coming at 95°C / 10 mm was collected which solidified on cooling to a colourless solid (m.p. 55°C, Lit. Value 55°C).
2.2.10 **Antimony Trichloride** (E. Merck)

It was purified by sublimation technique (3). In this process, a two liter distillation flask was placed on a steam bath, while the upper part of the sphere was cooled with running water. Some SbCl₃ was placed in the flask. When enough fine long crystals were deposited on the cold upper part and no unsublimed SbCl₃ was left in the bottom, the flask was left to cool without being distributed. Then the readily detached crystals were transferred (with tapping) into another dry flask (m.p. 79.4 °C, Lit. Value 79.9 °C)

2.2.11 **Bromine**

E. Merck grade bromine was used as such without further purification.

2.2.12 **Sodium** (IDPL)

Freshly cut sodium in the form of wire was used for drying hydrocarbons and ether solvents. For the preparation of sodium salts of ligands, small pieces of the metal were used.

2.2.13 **Magnesium**

Magnesium (BDH) was employed as such. For Grignard reaction, it was preheated in an electric oven at 150-170 °C for 2 hours and then cooled in a desiccator.

2.2.14 **Bromobenzene** (BDH)

It was used as such (b.p. 155.1 °C, Lit. Value 155-156 °C).

2.3 **PREPARATION OF PARENT ORGANOANTIMONY COMPOUNDS**

Owing to the extremely hydrolysable nature of the halides and alkoxides of antimony as well as the products, special precautions were taken to exclude moisture during the course of the present reactions. All glass apparatus fitted with interchangeable standard ground glass joints were used. Prior to each experiment, the required glass apparatus were well washed with chromic acid, followed by water. These were rinsed with distilled water and then dried in an oven at 140-160°C for about 3-4 hours. Finally these were cooled in a desiccator and assembled while hot, protecting them from atmospheric moisture by anhydrous calcium
chloride guard tubes. All the reactions were carried out under the atmosphere of dry nitrogen.

Special weighing tubes and transfer tubes fabricated with standard joints were used for handling the reactants as well as the products.

2.3.1 Preparation of Triphenylstibines

The synthesis was carried out according to the reported method\(^{(4)}\) as given below.

In a two liter round bottomed, three necked flask fitted with a mercury-sealed mechanical stirrer, a reflux condenser, and a separating funnel, was placed 40 g (1.65 mol) of magnesium turnings. This was covered with 200 ml of dry ether, and there was then added 100 ml of a mixture of 260 g (1.65 mol) of dry bromobenzene and 800 ml of dry ether. As soon as the reaction started, 200 ml more of dry ether was added and the remainder of the bromobenzene solution at such a rate as to cause gentle boiling (about two hours), with external cooling.

When all the bromobenzene was added, there was added slowly through the separatory funnel a solution of 114 g (0.5 mol) of freshly distilled antimony trichloride in 300 ml of dry ether. When all the SbCl\(_3\) was added (about two hours), the mixture was heated on the steam bath for one hour to ensure completion of the reaction.

When cooled, the reaction mixture was poured slowly with stirring into one liter ice and water. Most of the triphenylstibine came in ether layer. The hydrolysis mixture was filtered through a Buchner funnel and the residue extracted three times with 100 ml portions of ether. The aqueous layer was separated and extracted twice with 200 ml portions of ether. The combined ether portions were evaporated slowly on a steam bath to remove the ether and there remained a yellow semi-solid which crystallized to a whitish yellow solid on cooling. It was purified from a small amount of biphenyl which was present in the crude products. The crude triphenylstibine was dissolved in 200 ml petroleum ether (40-60 °C) by
warming on a steam bath. The filtrate on cooling in freezing mixture gave small prisms of triphenylstibines.

Yield 105 g, 60 %

m.p. 50 °C (Lit. Value 49 °C)

**Analysis**

<table>
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<tr>
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<th>%H</th>
<th>%Sb</th>
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2.3.2 **Preparation of triphenylantimonydibromide**

Triphenylantimonydibromide was prepared by bromination of triphenylantimony in petroleum ether (40-60). To a stirring solution of triphenylantimony (15.0 g) in petroleum ether (40-60 C) (100ml) bromine (7.7 g 2.5 ml) solution in the same solvent was added dropwise till a light brown colour of bromine persisted. The reactants were refluxed for 1 hour. The white product, obtained during the course of the reaction was separated by decanting the supernatant liquid. The white product, Ph₃SbBr₂, was further purified by recrystallization from chloroform or benzene-hexane mixture.

Yield 18.0 g (83%)

m.p. 213 °C, Lit. Value 212-214°C

**Analysis**

<table>
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2.3.3 **Preparation of triphenylantimonydichloride**

Triphenylantimonydichloride was prepared by passing chlorine slowly through a solution of triphenylantimony (15g) in petroleum ether (40-60 C). Filtration and crystallization from the same solvent or dry ethanol yielded the title compound.
Yield 16.5g (92%)
m.p. 145°C, Lit. value 1435 C(6)

Analysis

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2.3.4 Preparation of Triphenylantimonydimethoxide(8)

To an ice cold solution of 0.1 mol of sodium methoxide (prepared by the reaction of sodium with methanol) in 100 ml of dry methanol was added, a solution of triphenylantimonydibromide (25.6 g, 0.05 mol) in 100 ml of benzene slowly with constant stirring. The reaction mixture was stirred for 1 h at room temperature and then filtered. The filtrate on concentration in vacuo afforded triphenylantimonydimethoxide. Recrystallization from benzene yielded the desired product.

Yield 17.0g, 80%
m.p. 101.5 (Lit. Value 102°C)

Analysis

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2.3.5 Preparation of Triphenylantimonydibromide(9,10)

For the preparation of triphenylantimonydibromide, trimethylantimony was prepared by the reaction of freshly distilled antimony trichloride (10.3 g) in ether and methyl magnesium iodide (prepared from 48.5 g methyl iodide and 3.4 g magnesium in dry ether) under nitrogen atmosphere at -5°C. As the reaction progressed, the mixture in the flask turned grey. Towards the end of the reaction, two phases were formed, the upper yellow layer and a brownish black layer (lower). The reaction flask was cooled to -20°C. The above ethereal layer was
decanted and the residue was extracted twice with portions of 50 ml of ether. The combined filtrate was concentrated in vacuo. The receiver containing ethereal solution of trimethylantimony was kept in ice and to this, a solution of bromine (3.2 g 1.1 ml) in carbon tetrachloride, was added dropwise in slight excess and the reaction mixture was gently stirred at room temperature for 2-3 hours. Subsequent filtration and recrystallization from 95% ethanol yielded white crystalline product, trimethylantimonydibromide.

Yield 13.2 g, 90%

m.p. 171.2°C (Lit. Value 172°C)

Analysis

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<td>51.87</td>
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2.3.6 Preparation of Trimethylantimonydimethoxide

Trimethylantimonydimethoxide was prepared by the reaction of trimethylantimonydibromide (4.3 g) and sodium methoxide (prepared from 0.6 g sodium) in methanol. Reactants were refluxed for two hours. Methanol was evaporated under vacuum giving a pasty mass. This was dissolved in benzene and sodium bromide was filtered off, the filtrate was concentrated under reduced pressure, giving a colourless liquid. The product was purified by distillation under reduced pressure.

Yield 2.0 g, 66.4 %

m.p. 46°C/0.4 mm

Analysis

<table>
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2.4 PHYSICO-CHEMICAL STUDIES

The details of physico-chemical studies employed for the characterization and structural elucidation of the newly synthesized compounds are described below.

2.4.1 Melting Point (m.p)

The m.p. of the compounds were determined on an electrically operated melting point apparatus and the values reported are uncorrected.

2.4.2 Analysis

All the compounds were analysed for their carbon, hydrogen, nitrogen, halogen and antimony contents.

(i) Analysis for Carbon, Hydrogen and Nitrogen

Analysis for carbon and hydrogen and nitrogen contents of compounds was carried out by the microanalytic laboratories of regional sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow (U.P).

(ii) Analysis for Halogen

The compound was first fused with anhydrous sodium carbonate in the presence of small amount of sodium hydroxide to convert the halogen content into ionic halide. The solution was then prepared in distilled water, made up to a known volume and subjected to halogen estimation, volumetrically\(^{(12a, 12b)}\).

(iii) Analysis of Antimony

The antimony content of the compounds was determined by the procedure as reported by Ouchi et al.\(^{(13)}\). About 100 mg of exactly measured sample in 250 ml glass beaker was digested with 0.2 g of potassium persulphate and 3 ml concentrated sulphuric acid for 2 hours. It was heated on a sand bath, and then ammonium persulphate was added (10 times, 0.2 g each portion and added at 5 min intervals). Just after the addition of last portion of the persulphate, the sample was heated about 5 min more and then cooled. About 8 ml of concentrated hydrochloric acid, 100 ml of water and 2 g of potassium iodide were added to it, sequentially. The antimony content was then estimated iodimetrically\(^{(12c)}\).
2.4.3 Molecular Weight Determination

The molecular weight, of the compound soluble in benzene were determined cryoscopically using purified benzene as the solvent. A Beckmanns freezing point apparatus of accuracy ± .01C was used. A known quantity of the compound was added to a fixed volume of benzene after adjusting the thermometer, and the depression in freezing point was noted.

The following formula was used or the determination of molecular weight;

\[
M = \frac{1000 W_2 \times K_f}{W_1 \times T}
\]

Where

- \(M\) = Molecular weight of the compound
- \(W_1\) = Weight of the solvent
- \(W_2\) = Weight of the solute
- \(K_f\) = Freezeing point constant for the solvent
- \(T\) = Depression in freezing point

2.4.4 IR Spectra

IR Spectra study serves as a powerful tool in understanding the molecular structure and bonding of chemical compounds in solid state. For organometallic compounds it can roughly be divided into the regions – the high frequency (4000-650 cm\(^{-1}\)) or NaCl region and the low frequency (650-50 cm\(^{-1}\)) or far infrared region. The bands due to the organic moiety appear mainly in the former region, and those due to the skeleton consisting of the metal-carbon bonds appear in the latter region. Thus, the former is ligand sensitive and is important in characterizing the organic moiety, where as the latter is metal sensitive and is useful in characterizing the metal involved.

The interpretation of spectra data in the case of complex compounds is achieved by employing either the empirical method or the theoretical method based on normal coordinate analysis. For simple molecules theoretical method is not
normally difficult, but for large molecules (particularly when these have low symmetry), it is frequently difficult to definitely assign all frequencies.

When a ligand is changed in a complex, two contributions in frequency must be considered. An increase in point mass and equilibrium separation may be expected to decrease the corresponding frequencies. However, if the ligand replacement involves a change in bond type, this will have a more pronounced effect leading to an increase in frequency as the bond order increases. Similar behaviour may be expected as the central metal atom is replaced. The change in frequency again reflects the change in mass and bonding capacity of the central atom\(^{14}\).

In organometallic Chemistry empirical method of analysis is very commonly employed. There are two states in the utilization of spectral data by the empirical method. The observed frequencies (mostly ligand sensitive) are first assigned to group frequencies taking into account the local site symmetry of the ligand. Following the assignment of frequencies, empirical correlation are attempted, using one of the characteristics bands in assigning the nature of bonding with the change of ligand around the central atom.

Complications arise in the empirical assignments of bands in the far IR region. The bands in this region are mostly due to metal-ligand vibrations. The molecular geometry around the metal atom may be arrived at by looking into the possible point group symmetry around the metal, observed spectra and the correlation table for the given symmetry.

IR spectra in the range 4000-400 cm\(^{-1}\) were recorded in KBr pellets on a SP-1200 spectrometer. The instrument was calibrated using polystyrene film. Far IR spectra of some of the complexes were recorded in 600-100 cm\(^{-1}\) range on a Fourier spectrophotometer polytech FIR 30. The following abbreviation have been used to denote the intensities of various absorptions. v = very; s = strong; m = medium; w = weak; sh = shoulder and br = broad.

The wave-numbers reported are accurate to the extent of ±5 cm. The data collected have been tabulated in various chapters.
2.4.5 NMR Study

High resolution NMR spectroscopy can be used to study a wide variety of chemical problems, the solution of which is extremely tedious to obtain by other methods. $^1$H and $^{13}$C NMR spectroscopy have been utilised to study a wide variety of tedious chemical problems, which include molecular structures, stereochemistry, hindered rotation, dissociation phenomena exchange and hydrogen bonding processes.

Because of the greater importance of NMR technique, a large volume of literature in the form of research papers, books, monographs, complications of NMR spectra, and review articles is constantly being published.

In organometallic chemistry this technique has been extensively employed to characterize and solve spectral problems concerning the structure and conformation of molecules in solution. The most frequently used tool is $^1$H NMR spectroscopy. The significance of NMR spectroscopy in chemistry is due to its ability to distinguish a particular nucleus with respect to its environment in the molecule i.e., resonance frequency of an individual nucleus is influenced by the distribution of electrons in the chemical bonds of the molecule.

In proton NMR there will be different signals for protons of different nucleus in a compound. This effect produced by the different chemical environment of the proton in the molecule, is known as chemical shift. For practical purposes this chemical shift is defined as follows;

$$\delta = \frac{\nu_{\text{substance}} - \nu_{\text{reference}}}{\nu_o}$$

Here $\nu_o$ is the operating frequency of the spectrometer employed (for example, 100 MHz in the present case). Unit of scale is part per million (ppm). Tetramethylsilane is generally used as reference compound in PMR spectra.

Now a days $^{13}$C NMR spectroscopy has developed into a standard technique available in the chemical laboratory for determination of the structure of compounds. The spectra are obtained with $^{13}$C NMR signal of tetra methyl silane as internal reference and a heteronuclear lock system usually employing the $^2$H
resonance of the solvent CDCl$_3$. Chemical shifts of resonance in organic molecules span a region of about 250 ppm.

The assignment of $^{13}$C NMR resonance can be difficult. In order to maximize sensitivity, it is usual to measure $^{13}$C NMR spectra with complete proton decoupling. The proton coupling may be retained with some increase in sensitivity by the use of “off centre” double resonance$^{(15)}$. From the multiplicity of the pattern observed it is possible to determine the number of protons attached to each carbon atom. Thus a carbon atom with one proton attached appears as a doublet.

During recent years, with the introduction of complete $^1$H decoupling, tetramethylsilane has been commonly accepted as the internal $^{13}$C NMR reference, and the direction of increasing frequency$^{(16-19)}$ (decreasing magnetic field ) is taken as being positive . Literature results, quoted with respect to other reference compounds, have been re-referenced to TMS using Eq.(1-3).

$$\delta(\text{TMS}) = \delta(\text{CS}_2\text{ internal}) + 192.8 \quad (\text{Eq. 1})$$
$$\delta(\text{TMS}) = \delta(\text{C}_6\text{H}_6) + 128.5 \quad (\text{Eq. 2})$$
$$\delta(\text{TMS}) = \delta(\text{CDCl}_3) + 77 \quad (\text{Eq. 3})$$

$^1$H NMR spectra of the complexes prepared during this work were recorded in CDCl$_3$ solution on a Jeol JNM FX 100 NMR spectrometer, using TMS as an internal standard. $^{13}$C NMR spectra of some of the complexes were also recorded as complete proton decoupled resonance in CDCl$_3$ at room temperature using TMS as internal standard. The positive chemical shifts are downfield from the references$^{(20-24)}$. 

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REFERENCES

1. A.I. Vogel, ‘Practical Organic Chemistry’, 2\textsuperscript{nd} Ed., Longmans, London 1967, (a) p.172; (b) p.167 ; (c) p.169; (d) p. 176 ; (e) p.171; (f) p. 478; (g) p. 830 ; (h) p. 704 (i) p 676; (j).p. 640 ; (k) p. 1008.


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