

Experimental Methodology

2.1 Characterization Techniques

Synthesis and isolation of pure compounds are the most crucial steps of chemical research. Understanding the structural features of organometallic compounds is fundamental to organometallic chemistry. The molecular organometallic complex can be characterized with the help of various techniques qualitatively and quantitatively. Advantageously, some spectroscopic techniques allow the study in the solid phase (Single-crystal XRD, FTIR, elemental analysis etc.) while others in the solution phase (NMR spectroscopy, UV-vis spectroscopy, Mass spectrometry etc.).

2.1.1 Single-Crystal X-Ray Diffraction (SC-XRD)

X-ray suitable crystals were loaded on Bruker AXS Smart Apex CCD diffractometer for single-crystal x-ray diffraction measurements. X-ray generator used monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved using direct methods using SHELXS-97 and refined by full-matrix least-squares on F² using SHELXL-97 [Dolomanov et al., 2009; Sheldrick, 1997a, 1997b]. The hydrogen atoms were included in idealized positions and were refined according to the riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters.

Single-crystal x-ray diffraction is a non-destructive technique used for crystal structure determination. X-ray diffraction pattern results from the constructive interference of monochromatic x-rays and single-crystals. It provides all the crystallographic and structural information such as cell parameters, bond angles, bond distances etc. It works on the principle of Bragg's Law.

$$n\lambda = 2d \sin\theta$$

Where n is the diffraction order, λ is the wavelength of the incident x-ray, d is the interplanar distance or grating constant and θ is the incident angle from the normal.

2.1.2 Nuclear Magnetic Resonance (NMR) Spectroscopy

¹H, ¹³C and ¹¹⁹Sn NMR spectra were recorded in CDCl₃ solution on a Bruker Ascend 500MHz WB NMR spectrometer operating at 500, 125 and 186.5 MHz, respectively. The chemical shifts are referenced with respect to tetramethylsilane (for ¹H & ¹³C) and nBu₂SnCl₂ (for ¹¹⁹Sn). nBu₂SnCl₂ is used as the secondary reference whose ¹¹⁹Sn chemical shift value is δ 130 ppm with respect to tetramethyltin. ¹H and ¹³C NMR spectra were used to detect the various protons/carbons and the ¹¹⁹Sn NMR spectrum provided the information of the chemically distinguishable Sn centers in the complexes.

NMR spectroscopy is an analytical technique used to determine chemically distinguishable nuclei. The principle is based on the local magnetic field around the spinning nucleus. A spinning nucleus generates its local magnetic field in random directions, which gets aligned (either in the same direction or opposite) on applying an external magnetic field. Further, excitation of the electron occurs by radiofrequency pulse followed by emission of electromagnetic waves on relaxation of the electron. The detection of these electromagnetic waves results in the chemical shift (δ) values.

$$\delta = \frac{\nu_{\text{sample}} - \nu_{\text{ref}}}{\nu_{\text{ref}}}$$

Where ν_{sample} is the resonance frequency of the sample and ν_{ref} is the resonance frequency of the reference compound.

2.1.3 UV-Visible spectroscopy

Absorption spectra were recorded on the Varian spectrophotometer Cary 4000 as a reference with a path length of 1 cm. The spectra were recorded in the range of 200-800 nm. With the help of TD-DFT calculations, electronic transitions occurring in the complex were studied, corresponding to the bands observed in the spectrum.

UV-Visible spectroscopy refers to the absorption of UV light or visible light by a sample which results in a distinct spectrum (Absorption vs Wavelength). This spectroscopy follows the Beer-Lambert law, which says the absorption depends directly on the concentration of the sample solution and the intensity of the incident light. This spectroscopy is used to detect the conjugation and presence or absence of chromophores.

$$A = \log_{10} \left(\frac{I_0}{I} \right) = \epsilon cl$$

Where A is the absorbance, I_0 is the intensity of the incident light, I is the intensity of transmitted light, c is the concentration of the sample solution, l is the path length, and ϵ is the molar extinction coefficient.

2.1.4 Fourier Transform Infrared (FTIR) Spectroscopy

FT-IR spectra were recorded on a Bruker vertex 70V Infrared Fourier vacuum spectrometer using the KBr pellet method. Different functional groups and specific bonds present in the complexes were analyzed based on their stretching frequencies.

Fourier Transform Infrared spectroscopy is a technique in which IR radiations are passed through the sample. Some of the radiation gets absorbed, and some get transmitted. It is mainly used to identify the functional groups.

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

Where ν is the stretching frequency of the bond, k is the force constant, and μ is the reduced mass of elements involved in the bond formation.

2.1.5 Electron Spray Ionization Mass Spectrometry (ESI-MS)

ESI-MS spectra were recorded on Bruker-Daltonics, micrOTOF-QII mass spectrometer. Under the electrospray ionization conditions, the dissociation of complexes was observed. The resultant dissociated fragments of the complexes were found in terms of their m/z (mass/atomic number) ratio.

ESI-MS is a destructive technique that ionizes the complex using electrospray by means of high voltage. This technique can dissociate the complex into smaller ionic fragments, which can be analyzed by their m/z value.

2.1.6 Elemental Analysis

Elemental analyses were performed on ThermoFinnigan FLASH EA 1112 elemental analyzer. The bulk purity of the complexes (CHN/CHNS) was analyzed using this technique.

Elemental analysis is a destructive analytical technique that works on the principle of combustion. The combustion of the complexes in the presence of oxygen leads to the form NO_2 , SO_2 , CO_2 , and H_2O gases, which get into a connected GC chamber to give an accurate percentage of elements present.

2.1.7 Thermogravimetric Analysis (TGA)

Thermogravimetric Analyses were performed on TGA-6000 thermal analyzer (Perkin Elmer). The analysis was done from temperatures of 50 to 600°C. The thermal stability of the complexes was analyzed under the nitrogen atmosphere.

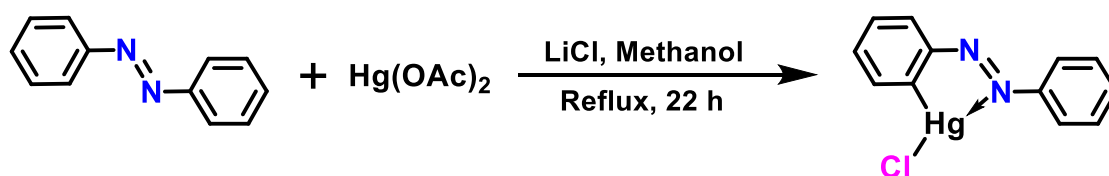
Thermogravimetric Analysis is a powerful technique used for the characterization of solid samples. The principle is based on the simple fact that the sample is weighed continuously as it is being heated to elevated temperatures, and changes in the mass of the sample are studied.

2.2 Synthesis of Starting Precursors

Herein, the synthesis of a few starting precursors is described in detail, which are used in the entire work;

2.2.1 Synthesis of RHgCl (R=2-phenylazophenyl)

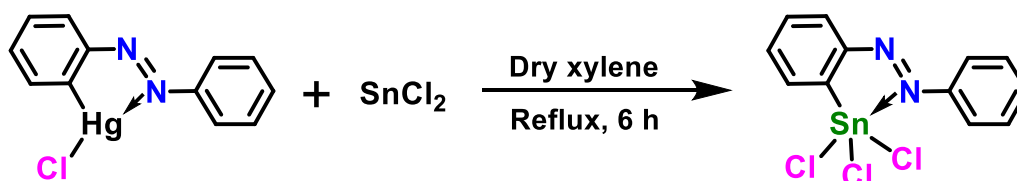
RHgCl is the starting material for synthesizing 2-phenylazophenyl substituted $R\text{SnCl}_3$ and $R_2\text{SnCl}_2$. It was prepared by following the literature procedure (Scheme 2.1) [Roling et al., 1976]. A mixture of azobenzene (6 gm, 33 mmol) and mercuric acetate (10.8 gm, 33 mmol) in 125 ml of methanol was taken in a round bottom flask equipped with a reflux condenser and heated to reflux for 22 h. The reaction mixture was cooled to room temperature and added a solution of LiCl (3 gm, 70 mmol) in warm methanol. The resultant mixture was stirred for 30 min and then poured into 500 ml de-ionized (DI) water. The orange-colored suspension was filtered, and the obtained precipitate was air-dried followed by washing with hexane. Monomercuriated product was extracted from the precipitate by dissolving it in warm toluene. The final product RHgCl was collected and air-dried after evaporation of toluene solution using a rotary evaporator.



Scheme 2.1 Synthesis of RHgCl [Roling et al., 1976].

2.2.2 Synthesis of RSnCl₃ (R=2-phenylazophenyl)

$R\text{SnCl}_3$ was synthesized using the literature procedure (Scheme 2.2) [Vicente et al., 1989]. A mixture of RHgCl (1 gm, 2.4 mmol) and anhydrous SnCl_2 (0.46 gm, 2.4 mmol) in 40ml of dry xylene was heated to reflux for 6 h. The obtained yellow suspension was cooled to room temperature and filtered. The mercurated residue was discarded, and the filtrate was evaporated using a rotary evaporator. Obtained yellow crystalline precipitate was recrystallized in the solvent mixture of DCM:Hexane (1:1). Yellow crystals were obtained after a few days.

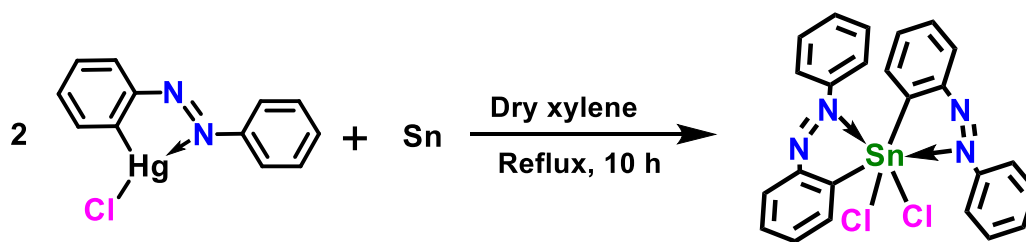


Scheme 2.2 Synthesis of $R\text{SnCl}_3$ [Vicente et al., 1989].

2.2.3 Synthesis of $R_2\text{SnCl}_2$ (R=2-phenylazophenyl)

$R_2\text{SnCl}_2$ was synthesized using the literature procedure (Scheme 2.3) [Briansó et al., 1983]. A mixture of RHgCl (1gm, 2.4 mmol) and metallic tin powder (0.228 gm, 1.2 mol) in 30 ml of dry xylene was heated to reflux for 10 h. The obtained dark yellow suspension was filtered hot. The

mercurated residue was discarded, and the filtrate was evaporated using a rotary evaporator. The obtained yellow solid was washed with methanol and collected as the pure product.



Scheme 2.3 Synthesis of R_2SnCl_2 [Briansó et al., 1983].

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