Chapter 1

Introduction
1.1 Introduction

Design and construction of transition metal mediated, self-assembled molecular entities have experienced extraordinary progress during the past decade, because of their potential for use as sensors, probes, photonic devices and catalysts.\textsuperscript{1-4} Recently, there has been extensive interest in transition-metal complexes containing chalcogen ligands because of their relevance to biological processes and their interesting structural and molecular recognition properties.\textsuperscript{5} The chalcogen atoms have been amongst the most useful and stabilising ligands in numerous metal carbonyl compounds. Transition metal complexes containing the disulfide ligand exhibit a range of interesting reactivity at the sulphur atoms.\textsuperscript{6, 7} Early work in metal-chalcogenide complexes suggested that while sulphur and selenium show similar behavior, the reactivity of tellurium is often unique. During the past decade, compounds containing Re(I) centres have played an important role as molecular components in generating well defined architectures.\textsuperscript{8, 9} Furthermore, the structural and spectroscopic characteristics of Re(I) containing complexes employed in the self-assembly process could permit functional properties such as Lewis acidity, luminescence or redox activity to be introduced into the macrocyclic structure. These properties could be tuned by changing the coordinated ligands.

1.2 Molecular and Supramolecular Chemistry

Molecular chemistry is the chemistry of compounds formed via interactions between atoms. Supramolecular chemistry is the analogous chemistry of assemblies formed via interactions between molecules.\textsuperscript{10} Molecular chemistry usually entails strong particle-particle interactions, such as covalent bond formation, and takes place on an angstrom scale. Supramolecular chemistry involves weaker interactions like hydrogen bonding, dispersion interactions, electron-donor/electron-acceptor interactions and so on and usually takes place on a nanometer scale. Because the organizing forces in supramolecular chemistry are generally weak, advantage is often taken of: (a) favorable symmetry and entropy effects (for example, to achieve macrocycle formation at the expense of linear oligomer formation), (b) preprogramming of synthons toward a particular reaction direction (for example, cis vs trans coordination of a reactive metal centre), (c) molecular or ionic charge, size, and shape complementarity (for example, to template the assembly of a desired higher-order structure), or (d) the reversibility of
supramolecular association (for example, to obtain thermodynamic rather than kinetic products from assembly reactions).

1.3 Self-assembly

Self-assembly is a ubiquitous process and defined as the spontaneous formation of highly ordered, complex, symmetrical molecular or supramolecular structures in pure form, from many starting components (atoms, ions, ligands, etc.), in a single step. Sometimes two or more of the above strategies can be combined to achieve self-assembled products, as a result of a tremendous variety of metal-coordination-based grid, ladder and other semi-infinite structures, as well as discrete molecular structures (triangles, squares, pentagons, hexagons, rectangles, cubes, cylinders, and more complex structures), have been obtained. Recently, self-assembly has been shown to play an important role in the development of molecular materials and in the bottom-up approach to nanofabrication.

1.4 Significance of Re(CO)$_3$ fragment

The one-step production of the Re(CO)$_3$ fragment is of great interest also for the $in situ$ preparation of stable compounds to be used in nuclear medicine ($^{186/188}$Re compounds for radiotherapy), for labelling biological molecules, such as amino-acids and peptides, either by direct binding or through bioconjugation mediated by polyfunctional ligands. Unexpectedly, the cationic fac-[Re(CO)$_3$(CH$_3$CN)$_3$](Y) (Y = PF$_6$, BF$_4$, ClO$_4$) complexes have been scarcely exploited for synthetic purposes. On the other hand, (NEt$_4$)$_2$fac-[ReBr$_3$(CO)$_3$] is a convenient precursor for the preparation of fac-Re(CO)$_3$ compounds to be used in nuclear medicine, as it is water-soluble and can be obtained also by low-pressure carbonylation of radioactive ReO$_4^-$. A similar synthetic pathway also applies to the corresponding (NEt$_4$)$_2$[fac-$^{99m}$TcBr$_3$(CO)$_3$] species.

Mononuclear and dinuclear tricarbonylrhenium(I) complexes of the type [ReBr(CO)$_3$(Ph$_2$PCH$_2$)$_2$NR] (R = Ph, CH$_2$CH$_2$OH, CH$_2$COOCH$_2$Ph, CH$_2$CONHCH$_2$COOCH$_2$Ph, CH$_2$COOH) and [Re$_2$(µ-OR)$_3$(CO)$_6$] have recently been described to efficiently suppress the growth of solid and suspended tumor cell lines. Substitution of the alkoxide or hydroxide ligands and coordination to N7 in purine bases in a fashion similar to cisplatin were anticipated to be a possible mode of action for some
of these complexes. Alberto and coworkers have studied the X-ray structures, kinetic and thermodynamic data of two guanine bound to rhenium and technetium complexes. The interaction data of this complexes with guanine compared to that of [Pt-(NH$_3$)$_2$(H$_2$O)$_2$]$^{2+}$ implies that these complexes were potential cytotoxic agent affecting DNA like cisplatin. The complexes with $^{188}$Re or $^{99m}$Tc could be used as novel radiodiagnostic or therapeutic agents.

1.5 Synthesis of dinuclear metallacycles

For more than a decade, the development of an effective strategy for the preparation of discrete metallacycles in a controlled fashion has attracted a great deal of attention. The coordination chemistry of the dinuclear tetracarboxylate complexes of the transition metals are a focus of interest owing to their wide application in many fields, such as material science, catalysis and as anticancer agents. Dirhodium tetracarboxylate complexes were used as antitumor agents.

Synthesis of sulphur bridged metallacycles

Deeming et al. have reported the reaction of Re$_2$(CO)$_{10}$ with pyridine-2-thione (pySH) in xylene to afford the dinuclear complex [Re$_2$(pyS)$_2$(CO)$_6$] which contains three fused four-membered rings. The novel five-electron donating pyS bridges are easily cleaved by ligand addition and in redistribution reactions with [Re$_2$(MepyS)$_2$(CO)$_6$] complex (Scheme 1.1).

\[
\text{Re}_2(\text{CO})_6 + \xrightarrow{\text{xylene}} \text{N} \text{S} \quad \text{OC} \quad \text{S} \quad \text{OC} \quad \text{CO} \quad \text{CO} \quad \text{OC} \quad \text{CO}
\]

Scheme 1.1 Formation of [Re$_2$(pyS)$_2$(CO)$_6$]

When trinuclear rhenium complex Re$_3$(μ-H)$_3$(CO)$_{11}$(MeCN) was treated with pyridine-2-thiol in toluene at reflux temperature, the sulphur bridged dinuclear rhenium complex was obtained as white crystals (Scheme 1. 2).
Hupp and coworkers reported the stepwise synthesis of rhenium dinuclear metallacycle from Re(CO)$_5$Br. Sulphur bridged dimeric complexes were obtained by treatment of Re(CO)$_5$OTf with alkyl and aromatic thiols at room temperature. The rhenium thiolate dimer was used as a precursor for synthesising molecular rectangles (Scheme 1.3).

Sulphur bridged manganese dinuclear complexes

Treatment of Mn$_2$(CO)$_{10}$ with 3,4-toluenedithiol and 1,2-ethanediithiol in the presence of (CH$_3$)$_3$NO affords manganese based sulphur-bridged complexes [Mn$_2$(CO)$_6$(μ-$η^4$-SC$_6$H$_3$CH$_3$S–SC$_6$H$_3$CH$_3$S)] and [Mn$_2$(CO)$_6$(μ-$η^4$-SCH$_2$CH$_3$S–SCH$_2$CH$_3$S)] (Scheme 1.4).
Scheme 1.4 Formation of [Mn$_2$(CO)$_6$(µ-η$^4$-SC$_6$H$_3$CH$_3$S–SC$_6$H$_3$CH$_3$S)] and [Mn$_2$(CO)$_6$(µ-η$^4$-SCH$_2$CH$_2$S–SCH$_2$CH$_2$S)]

Dinuclear sulphur bridged cobalt complexes

Equimolar amount of Co$_2$(CO)$_8$ and C$_6$F$_5$S–SC$_6$F$_5$ in hexane medium at room temperature yields air stable black colour crystals of dinuclear cobalt complex (Scheme 1.5). The analogous compound was obtained with C$_6$Cl$_5$S–SC$_6$Cl$_5$, as a greenish coloured product.$^{24}$
Scheme 1.5 Formation of $[\text{Co(CO)}_3(\mu-\text{SC}_6\text{F}_5)]_2$

Dinuclear sulphur bridged platinum complexes

When trimethylplatinum(IV)chloride was treated with 1,3-bis(methylthio)propane in benzene, afforded the air stable 1,3-bis(methylthio)propane$\cdot$chlorotrimethylplatinum(IV) (Scheme 1.6).$^{25}$

$$\text{Co}_2(\text{CO})_8 + \text{C}_6\text{F}_5\text{S}-\text{SC}_6\text{F}_5 \xrightarrow{\text{Hexane}} [\text{Co(CO)}_3(\mu-\text{SC}_6\text{F}_5)]_2$$

Scheme 1.6 Formation of $[(\text{PtXMe})_3(\text{MeS(CH}_2)_n\text{SMe})]$ 

Sulphur bridged rhodium complexes

Connelly and Johnson have been reported the synthesis of dinuclear rhodium complexes of the type $[\text{Rh}(\mu-\text{SR})(\eta^5-\text{C}_5\text{H}_5)]_2$ from $[\text{Rh}(\eta^5-\text{C}_5\text{H}_5)(\text{CO})_2]$ and disulphides RSSR ($R = \text{Ph, } p-\text{C}_6\text{H}_4\text{Me, Ph, Bu}^1, \text{CH}_2\text{Ph}$) in toluene or cyclohexane medium (Scheme 1.7).$^{26}$
Scheme 1.7 Formation of \([\text{Rh}(\mu\text{-SR})(\eta^5\text{C}_5\text{H}_5)]_2\)

1.6 Synthesis of Selenium and Tellurium bridged Metallacycles

Selenium bridged ruthenium complex

The reaction of \([\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppm})]\) with PhSeSePh furnished the binuclear compound \([\text{Ru}_2(\text{CO})_4(\mu\text{-SePh})_2(\mu\text{-dppm})]\). The metal core of the compound contains a Se₂Ru₂ butterfly geometry with the wingtips of Se atoms linked with two phenyl groups. The ruthenium-ruthenium backbone is ligated by four terminal carbonyl ligands and bridged by a dppm ligand (Scheme 1.8).\(^{27}\)

Scheme 1.8 Formation of \([\text{Ru}_2(\text{CO})_4(\mu\text{-SePh})_2(\text{dppm})]\)

Selenium bridged palladium complex

Liaw and coworkers have prepared thermally stable dinuclear selenium bridged palladium complexes \([\text{PPN}]\text{Cl}_2\text{Pd}(\mu\text{-SeR})_2\text{PdCl}_2\) from \text{PdCl}_2 and \text{cis-}[\text{Mn}(\text{CO})_4(\text{SeR})_2]. The core geometry of the compound was described as a Pd₂Se₂ distorted square planar complex and each Pd\(^{II}\) atom makes four bonds, two to selenium atoms of bridging phenylselenolates and two with terminal chloride atoms. \text{cis-}[\text{Mn}(\text{CO})_4(\text{SeR})_2]^- serve as
a chelating metalloligand for heterotrinuclear complexes and act as a selenolate ligand-transfer reagent (Equation 1.9).  

\[
2\text{PdCl}_3 + 2\text{EtNH\left[ Mn\left(\text{CO}\right)_{4} \right.} : \text{SeR} \left. \right] \text{PPN} \xrightarrow{\text{CH}_2\text{CN}} \text{[PPN]}_2\text{[Cl:Pd\left(\mu\text{-SeR}\right):PdCl]} + \text{[PPN]}_2\text{[CO]}_2\text{Mn\left(\mu\text{-Cl}\right)\text{Mn\left(\mu\text{-CO}\right)}_3] \quad \text{[Eqn 1.8],}
\]

**Selenium bridged iron complex**

An equimolar amount of \([\eta\text{-C}_5\text{H}_5\text{(CO)}_2\text{Mn=CC}_6\text{H}_5]\text{BBr}_4\) was reacted with \([\text{Et}_3\text{NH}][\text{Fe}_2(\mu\text{-CO})(\mu\text{-SeR})(\text{CO})_6]\) in THF at low temperature to yield selenolate bridged Fe–Fe bonded dinuclear complex \([\text{Fe}_2(\mu\text{-SeR})_2(\text{CO})_6]\) (Scheme 1.10).  

![Scheme 1.10 Formation of \([\text{Fe}_2(\mu\text{-SeR})_2(\text{CO})_6]\)](image)

**Selenium bridged chromium complex**

Goh and coworkers have accounted for the preparation of cyclopentadienyl chromium chalcogenide complex \([\text{CpCr(SePh)}_2]\text{Se}\) from the reaction of \([\text{CpCr(\text{CO})}_3]_2\) with \(\text{Ph}_2\text{Se}_2\). \([\text{CpCr(SePh)}_2]\text{Se}\) readily reacts with \(\text{Cr(\text{CO})}_5\) THF to form the black colour crystals of \([\text{CpCr(SePh)}_2]\text{Se}[\text{Cr(\text{CO})}_3]\) (Scheme 1.11).
Scheme 1.11 Formation of $[\text{CpCr(SePh)}]_2\text{SeCr(CO)}_5$

Selenium bridged platinum complexes

The selenium bridged platinum complexes were synthesised by the reaction of trimethylplatinum(IV)chloride with 1,3-bis(methylthio)propane in benzene, to afford the air stable dinuclear platinum complexes $[1,3\text{-bis(methylthio)propane}]\text{chlorotrimethylplatinum(IV)}$ (Scheme 1.12).$^{31}$

Scheme 1.12  Formation of $[(\text{PtBrMe}_3)_2(\text{MeSe(CH}_2)_n\text{SeMe})]$}

Tellurium bridged osmium complexes

The reaction of Ph$_2$Te$_2$ with unsaturated cluster Os$_3(\mu\text{-H})_2(\text{CO})_{10}$ affords the final product $[\text{OsH(CO)}_3(\text{TePh})]_2$ via a trinuclear osmium complex Os$_3H_2(\text{CO})_{10}(\mu\text{-TePh})_2$.

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The dinuclear compound was characterized by single crystal X-ray crystallographic studies. \([\text{OsH(CO)}_3(\text{TePh})]_2\) compound is centrosymmetric and hence \(\text{Os}_2\text{Te}_2\) ring is constrained to be planar. The two phenyl rings in this product are \(trans\) to each other (Scheme 1.13).

\[
\text{Os}_3(\mu-\text{H})_2(\text{CO})_{10} + \text{Ph}_2\text{Te} \rightarrow \quad \text{Scheme 1.13 Formation of } [\text{OsH(CO)}_3(\mu-\text{TePh})]_2
\]

**Tellurium bridged manganese complexes**

Liaw and coworkers have reported the synthesis of tellurium bridged manganese metallacycles, from \([\text{Mn(CO)}_5]^-\) fragment by the reaction with \((\text{PhTe})_2\) in a three step process (Scheme 1.14).

\[
2[\text{Mn(CO)}_3]^- + (\text{PhTe})_2 \rightarrow 2\text{cis}[\text{Mn(CO)}_4(\text{TePh})_2] \xrightarrow{\text{THF}} [(\text{CO})_3\text{Mn}(\mu-\text{TePh})_2\text{Mn}(\text{CO})_3]^+ \\
\downarrow \quad [\text{Ph}_3\text{C}][\text{BF}_4] \\
(\text{CO})_4\text{Mn}(\mu-\text{TePh})_2\text{Mn}(\text{CO})_4
\]

**Scheme 1.14 Formation of \([(\text{CO})_4\text{Mn}(\mu-\text{TePh})_2\text{Mn}(\text{CO})_4]\)**
1.7 Synthesis of tetranuclear molecular rectangles

Bipyrimidine bridged Re(I) molecular rectangles

Rhenium (I) based molecular rectangles were synthesised from dimetallic edges containing chelating bridge, 2,2'-bipyrimidine (bpym) and Re(CO)$_5$Cl. Bidentate pyridyl ligands were reacted with dinuclear complexes to furnish tetranuclear ionic molecular rectangles (Scheme 1.15).$^{34}$

Scheme 1.15 Formation of $\left[\{\text{Re}_2(\text{CO})_6(\mu\text{-bpym})\}_2(\mu\text{-N-L-N})_2\right]^{4+}$. 

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2,2’-bisbenzimidazolate bridged Re (I) rectangles

Hupp and coworkers have accounted for the synthesis of molecular rectangles featuring rhenium(I) sites organized in pairs by doubly chelating planar ligands such as 2,2’-bisbenzimidazolate (BiBzIm) and then linked by rigid bidentate azine ligands such as 4,4’-bipyridine (bpy) (Scheme 1.16). The pyridyl ligands in the neutral molecular rectangles are stabilized by van der Waals contact of the centres of these ligands. The pyridyl ligands remain relatively planar and in good spatial overlap to facilitate direct electronic interaction. \(^\text{35}\)

![Scheme 1.16 Formation of [Re_2(CO)_6(μ-BiBzIm)]_2(μ-bpy)_2](image_url)

Synthesis of luminescent, pyridyl ligands bridged Re (I) molecular rectangles

Lu and coworkers have achieved neutral rhenium rectangles from Re(CO)_5Br with rigid and bidentate pyridyl ligands as edges. The first step involves synthesis of bimetallic edges obtained from rhenium precursor and a variety of bidentate ligands. Further treatment of bidentate ligands with bimetallic edges with larger bidentate pyridyl ligands produced the tetrametallic rhenium (I) molecular rectangles. These Re (I) molecular rectangles are neutral in nature with larger cavities and exhibited interesting luminescence and molecular recognition properties (Scheme 1.17). \(^\text{9a}\)
Scheme 1.17 Formation of $[\{(\text{CO})_3\text{Re(\mu-L}^1)\text{Br}\}\{\text{Re(\text{CO})}_3(\mu-L}^2)\text{Br}\}]_2$

To increase the cavity dimensions and molecular recognition properties of the metallasupramolecules, novel Re (I) molecular rectangles were synthesised using acetylene, butadiyne and 1,4-bis(ethynyl)-benzene bridges between two pyridine moieties in the azine ligands ($L^2$) on one side and 4,4'-bipyridine ligand was keeping on the other side.\textsuperscript{9b}

**Synthesis of oxamide bridged Ru (II) molecular rectangles**

Jin and coworkers have reported a new series of bi- and tetrannuclear half sandwich ruthenium complexes bearing oxamidato bridges and pyridyl ligands. The binuclear complexes were obtained from oxamide and $[(p\text{-cymene})\text{RuCl}_2]_2$ as starting materials. The binuclear oxamide bridged ruthenium complexes were treated with bipyridyl linkers such as bpy and bpe ligands to furnish Ru (II) molecular rectangles (Scheme 1.18).\textsuperscript{36}
Scheme 1.18 Formation of [(p-cymene)$_4$Ru$_4$(µ-$\eta^4$-oxa-R)$_2$(L)$_2$] (OTf)$_4$

Synthesis of oxalato bridged Ru (II) molecular rectangles

Tetranuclear cationic metallosupramolecules assemblies were generated by Therrien and coworkers from dinuclear ruthenium complex, AgCF$_3$SO$_3$ and 1,2-bis(4-pyridyl)ethylene ligand. The product was isolated and characterized as triflate salt.$^{37}$
1.8 Photophysical properties of Re(I) complexes

A variety of Re(I)-containing complexes have been synthesized because of their photophysical and photochemical properties. The photoluminescent molecules have the advantage of allowing researchers to study the electronic excited-state reactivity and to identify guest inclusion. Several strategies have been developed to improve the luminescence quantum yield, the most prominent being the suitable design of ligands. The photophysical properties of rhenium(I) tricarbonyl complexes of the type $\text{fac-}[\text{Re(CO)}_3(\text{NN})\text{L}]$ (NN = polypyridyl ligand, L nitrogen donor atom) continue to attract much attention due to their interesting excited state properties. The low energy excited state of these rhenium(I) polypyridyl systems is mixed in character involving low lying metal-to-ligand charge transfer (MLCT) states and intraligand (IL) $^3\pi-\pi^*$ excited states. The spin-orbit coupling enhanced the singlet–triplet mixing of the rhenium complex. As a result, rhenium complexes exhibit strong phosphorescent emitters possessing long-lived excited states. Such systems are useful for the design of luminescent sensors and materials for supramolecular devices. Hence, it is necessary to understand their electronic structure and correctly assign their low-lying electronic transitions. The excited states property of the complexes have been explained the potential to act as active catalytic species in the photo and electrocatalytic reduction of $\text{CO}_2$ to $\text{CO}$, and as labeling reagents for biomolecules. The photophysical and
photochemical properties of these systems can be tuned by varying the ligand coordinated to the rhenium(I) tricarbonyl moiety. Complexes that undergo multi-photon process have potential applications as probes in multi-photon microscopy or in tissues.45

1.9 Supramolecular interactions

The non-covalent interaction is the dominant type of weak interaction between macromolecules.46 In general, non-covalent bonding refers to a variety of interactions that are not covalent in nature between molecules or parts of molecules that provide force to hold the molecules, usually in a specific orientation or conformation. These non-covalent interactions include: ionic bonds, hydrophobic interactions, hydrogen bonds, van der Waals forces, and dipole-dipole bonds. The non-covalent interactions or van der Waals forces involved in supramolecular entities may be a combination of several interactions, e.g. ion-pairing, hydrogen bonding, cation–π, π–π interactions etc.47

1.10 π–π Interactions

Non-covalent interactions form the backbone of supramolecular chemistry and include hydrogen bonds (H-bonds), stacking, electrostatic, hydrophobic, and charge-transfer interactions as well as metal ion coordination.48 Extensive efforts have been made to design components that mimic natural systems by undergoing molecular self-organisation through selective non-covalent interactions such as H-bonding, electrostatic, and π–π stacking interactions. Aromatic–aromatic or π–π interactions are important non-covalent intermolecular forces similar to hydrogen bonding. They can contribute to self-assembly or molecular recognition processes when extended structures are formed from building blocks with aromatic moieties.49 As such, π–π interactions range from large biological systems to relatively small molecules.50, 51 Non-covalent interactions between aromatic groups play a role in the binding and conformations all the way from nucleic acids and proteins to benzene.52a–c The understanding and utilization of non-covalent interactions including π–π stacking is of fundamental importance for the further development of supramolecular chemistry and the tuning and prediction of crystal structures.52d–g

“π–π Interaction” is commonly used for stacks of aromatic groups with approximately parallel molecular planes separated by interplanar distances of about 3.3–
3.8 Å. Stacking does not necessarily have to be a perfect face-to-face alignment of the atoms but can also be an offset or slipped packing. The T-shaped conformation is a C–H…π interaction. Both face-to-face and T-shaped conformations are limiting forms in aromatic interactions. Among these, the stacked (facial) arrangements are of particular interest as π–π interactions.

π–π stacking interactions  C-H...π interaction

Enlargement or polarization of the π system changes the picture and conclusions drawn for benzene quite drastically. For example, stacked structures become increasingly favorable with increasing arene size. Larger systems such as pyrene or coronene show an offset π stacking with the hydrogens roughly over ring centres. As such, non-polarized benzene is not necessarily a good model to arrive at an understanding of π–π interactions. Experimental investigations showed that electron withdrawing substituents or hetero atoms lead to the strongest π–π interaction. The face-to-face π stacking of aromatic moieties shows increased stability when both partners are electron-poor, whereas electron donating substituents disfavored a π–π interaction. The π-electron density within the rings is increased and so is the π-electron repulsion.

Pyridine, bipyridine and other aromatic nitrogen heterocycles are known as electron poor ring systems (A) (relatively inert to electrophilic attack, enhanced reaction with nucleophiles). A metal which is co-ordinated to a nitrogen heteroatom will further enhance the electron-withdrawing effect through its positive charge (B). Hence, aromatic nitrogen heterocycles should in principle well suited for π–π interactions because of their low π-electron density. The introduction of heterocyclic N increases the tendency to stack.
Multidentate ligands with pyridine groups or nitrogen heterocycles in general feature prominently as building blocks in the design of metal–ligand networks.\textsuperscript{58} $\pi$–$\pi$ Stacking is an increasingly noted feature in the structural description of metal complexes with these ligands. Furthermore, it is not just a structural phenomenon but also correlates with the solid state luminescence properties of some metal complexes, notably with platinum,\textsuperscript{59} gold\textsuperscript{60} and other metals.\textsuperscript{61} At the same time, few details on the $\pi$ interaction aside from the interplanar distance are usually given. A closer look at the so-called $\pi$–$\pi$ interactions reveals that the term appears to be used for all degrees of slipped stacking. It could even involve a marked degree of deviation from coplanarity, \textit{i.e.} an angular orientation of the ring planes towards a C–H…$\pi$ interaction.\textsuperscript{53a, 62} The $\pi$–$\pi$ Interactions can play an important role in controlling the packing or assembly of compounds. In many structural descriptions of metal–ligand complexes $\pi$–$\pi$ stacking is invoked as a vital role for structural motif. Complexes with aromatic nitrogen heterocycles as ligands reveals that such a $\pi$–$\pi$ stacking is usually an offset or slipped facial arrangement of the rings. The following examples showing $\pi$–$\pi$ and C–H…$\pi$ interaction, (i) 2,2′-bis(benzimidazole) bridged rhenium metallacycle, (ii) 2,5-bis(4-pyridyl)-1,3,5-oxadiazole bridged tetranuclear $[(\text{Cp}^*\text{Ir})_4(\mu\text{-bpo})_2(\mu-\eta^2-\eta^2-\text{C}_2\text{O}_4))(\text{OTf})_4$ complex cation. (iii) macrocycle of salicylidene copper complex.\textsuperscript{63}
1.11 Synthetic strategy for the design and synthesis of metallacycles and metallacyclophanes

When rhenium carbonyl $\text{Re}_2(\text{CO})_{10}$ was treated with diaryl dichalcogenides $\text{REER}$ ($E = \text{S, Se and Te}$) in presence of monodentate pyridine ligands (pyridine, picoline, phenylpyridine), the oxidative addition of aryl disulphides to rhenium carbonyl led to the formation of dinuclear metallacycles. The dinuclear metallacyclic compounds having two rhenium and two chalcogens with substitution of monodentate azine ligands were isolated under facile reaction conditions. Moreover, in case of oxidative addition of bidendate pyridine ligand to $\text{Re}_2(\text{CO})_{10}$ are afforded the tetranuclear metallacyclophanes. The same synthetic strategy was also utilized for the synthesis of selenium-bridged tetranuclear metallacyclophanes using bidentate ligands like $4,4'$-bipyridine, 1,2-bis(pyridylethylene) and 1,4-bis(4-pyridylethynyl)benzene.

**Dinuclear Metallacycles:**

\[
\begin{align*}
\text{RE--ER} & \quad + \quad \text{Re(\text{CO})}_5 \\
& \quad + \quad 2\text{N--L} \quad \rightarrow \\
& \quad \text{Re(\text{CO})}_3(\text{N--L})
\end{align*}
\]

**Tetranuclear Metallacyclophanes:**

\[
\begin{align*}
\text{RE--ER} & \quad + \quad 2\text{Re(\text{CO})}_5 \\
& \quad + \quad 2\text{N--L--N} \quad \rightarrow \\
& \quad \text{Re(\text{CO})}_3 \text{Re--N--L--N--Re(\text{CO})}_3
\end{align*}
\]
1.12 REFERENCES


