Chiral complexes: from fundamental chirality to helicene chemistry
For My Dear Mother “Latifa”

For My Kind Father “Mahmoud”

For My Friendly Brother “Bilal”

And Sisters “Nihal, Manal, and Batoul”

“Knowledge is the revival of hearts from ignorance, sights from blindness, and physical strength from weakness”

IMAM ALI (A.S.)
For My Lovely Wife Malak

And My Adorable Baby Haidar

“Ask always for Knowledge and don’t demand something instead because all people are dead, but scholars are immortal”

IMAM ALI (A.S.)
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Abbreviations

Å: Angstrom
BuLi: Butyl Lithium
Bpy: 2,2’-bipyridine
CO : Carbonyl
CPL: Circularly Polarized Luminescence
CD: Circular Dichroism
CE: Cotton Effects
DFT: Density Functional Theory
DMSO: Dimethylsulfoxide
DMF: Dimethyformamide
de: diastereomeric excess
DSC: Differential Scanning Calorimetry
ee: enantiomeric excess
ECD: Electronic circular dichroism
FTIR: Fourier Transform Infrared
FLUOR: Fluorescence
fac: Facial
ge_{em}: Emission dissymmetry factor
g_{ab}^{an}: Absorption Anisotropy factor
GC-MS: Gas Chromatography-Mass Spectrometry
HF: Hartee Fock
HPLC: High-Performance Liquid Chromatography
HOMO: Highest occupied molecular orbital
IL: Intraligand
IR: Infrared
KSCN: Potassium thiocyanate
KSeCN: Potassium selenocyanate
LC: Ligand centered
LCP: Left circularly polarized light
LF: Ligand field
LLCT: Ligand-to-ligand charge transfer
LiAlH₄ (LAH): Lithium Aluminum Hydride
LPL: Laboratoire de Physique des Lasers
LUMO: Lowest unoccupied molecular
mer: meridional
MLCT: Metal-to-ligand charge transfer
MTO: Methyl trioxo Rhenium
NH₄SCN: Ammonium thiocyanate
NMR: Nuclear Magnetic Resonance
OC: Octahedral
OFET: Organic Field Effect Transistor
OR: Optical Rotataion
PHOS: Phosphorescence
PLD: Pulsed Laser Deposition
PV: Parity Violation
PNC: Parity non-conservation
PVED: Parity Violation Energy Difference
Py: pyridine
rac: racemic
R.T.: Room temperature
RCP: Right circularly polarized light
R-NC: Isocyanides
THF: Tetrahydrofuran
TGA: Thermo Gravimetric Analysis
Tmhd: 2,2,6,6-tetramethyl heptadione
UV: Ultra-Violet
VCD: Vibrational Circular Dichroism
Vis: visible
Z: Atomic Number
ε: Molar absorption coefficient
τ: Lifetime
Φ: Quantum yield
[α]_{D}^{23}: Specific optical rotation
[θ]_{D}^{23}: Molar optical rotation
Table of Contents

Acknowledgements ............................................................................................................3
Abbreviations ......................................................................................................................5
General Introduction ............................................................................................................11

Chapter I: Parity Violation effects in chiral molecules

A. Parity violation in chiral molecules: definitions and former studies .........................13
I.1 Introduction and context of our work ..........................................................................13
I.2 Chirality and fundamental symmetry operators .........................................................14
I.3 First observation of parity violation (PV) at the nuclear level ....................................15
I.4 Parity violation observation in atoms .......................................................................17
I.5 Parity violation in molecules .....................................................................................18
   I.5.1 CHFCIBr 1: synthesis, resolution and PV tests. ...................................................19
   I.5.2 New experimental setup ....................................................................................20
   I.5.3 Basic theoretical PV considerations ................................................................21
   I.5.4 CHFClI: synthesis and resolution .....................................................................22
   I.5.5 Spectroscopic studies of CHFClI .....................................................................23
I.6 PV in heavy metal-containing molecules ....................................................................24
   I.6.1 Chiral oxorhenium complexes: interesting candidates for PV differences calculations ...26
      I.6.1.1 Chiral oxorhenium complexes bearing a Tp ligand .........................................26
      I.6.1.2 “3+1” oxorhenium complexes ....................................................................28

B. Synthesis and characterization of new potential candidates for PV observation ......30
I.1 New approach toward chiral oxorhenium derivatives starting from methyltrioxorhenium (MTO) .............................................................................................................30
I.2 Synthesis and characterization of oxorhenium(VII) complex {28} .........................31
   I.2.1 Synthesis of enantiopure 1-mercapto-propan-2-ol ligand ...................................31
   I.2.2 Synthesis of enantiopure oxorhenium(VII) complex 28 ....................................33
   I.2.3 IR and VCD spectroscopic studies ....................................................................34
   I.2.4 Theoretical PV differences and supersonic molecular beam attempts ...............36
I.3 Synthesis and Characterization of OxoRhenium (VII) complex \{33\} .................................. 38

I.3.1 Synthesis of enantiopure 2-mercaptocyclohexan-1-ol ............................................ 39

I.3.2 Synthesis of enantiopure oxorhenium(VII) complex 33 ........................................... 40

I.3.3 TGA/DSC analysis ................................................................................................. 41

I.3.4 IR and VCD spectroscopic studies .......................................................................... 42

I.3.5 Theoretical PV energy differences and supersonic molecular beam attempts .......... 44

I.4 Synthesis and characterization of selenirane \{38\} ......................................................... 44

I.4.1 2-Methyl selenirane: preparation and mechanism .................................................... 44

I.4.2 IR and VCD spectroscopic studies .......................................................................... 45

I.4.3 Reactivity of 2-methyl selenirane 38 ............................................................ 46

I.5 Asymmetric carbons with C-F stretching band coordinated to heavy Pt metal ............ 47

I.5.1 Introduction ........................................................................................................... 47

I.5.2 Synthesis of asymmetric carbon coordinated to heavy Pt(IV) metal ......................... 49

I.5.3 TGA/DSC analysis ................................................................................................. 52

I.6 Ru(tmhd) \{3\} .............................................................................................................. 53

I.7 Conclusion and prospects ......................................................................................... 54

References: .................................................................................................................. 56

Experimental Part ........................................................................................................ 62

Chapter II: Helicenes bearing 2,2'-bipyridine functionality

II.1 Introduction ........................................................................................................... 77

II.2 Properties of azahelicenes ...................................................................................... 78

II.3 Synthesis of azahelicenes ........................................................................................ 81

II.3.1 Photocyclization .................................................................................................. 81

II.3.2 Metal induced synthesis ....................................................................................... 84

\(\text{a- Stille-Kelly coupling} \) .................................................................................... 84

\(\text{b- Metal-catalyzed cycloisomerization} \) ................................................................. 85

\(\text{c- Ortho-metalation (metallahelicenes synthesis)} \) .................................................. 86

II.4 Towards Helicenes bearing bipyridine functionality ............................................... 87

II.5 Results and discussion .......................................................................................... 89
II.5.1 3-(2-Pyridyl)-4-aza[4]helicene (62) ................................................................. 89
   a)- Synthesis ........................................................................................................... 89
   b)- $^1$H NMR spectroscopic studies .................................................................... 90
   c)- X-Ray diffraction studies ................................................................................. 91
II.5.2 3-(2-Pyridyl)-4-aza[6]helicene (63) ................................................................. 91
   a)- Synthesis ........................................................................................................... 91
   b)- $^1$H NMR spectroscopic studies .................................................................... 92
II.5.3 3,14-Di-(2-pyridyl)-4,13-diaza[6]helicene (64) ................................................. 92
   a)- Synthesis ........................................................................................................... 92
   b)- $^1$H NMR spectroscopic studies .................................................................... 93
   c)- X-Ray diffraction studies ................................................................................. 93
II.6.1 Absorption studies .......................................................................................... 94
II.6.2 Emission Studies ............................................................................................ 95
II.7 Chiroptical Properties ....................................................................................... 97
   II.7.1 Optical rotation (OR) ................................................................................... 98
   II.7.2 Circular Dichroism (CD) .............................................................................. 98
II.8 3-Pyridinium-4-azonia[6]helicene 75. ................................................................ 100
II.9 Circularly Polarized Luminescence (CPL) Spectroscopy .................................. 105
II.10 Conclusion ......................................................................................................... 107
References .................................................................................................................. 109
Experimental Part ...................................................................................................... 114

Chapter III: Chiral Rhenium tricarbonyl complexes coordinated to helicenes

III.1 Introduction ........................................................................................................ 125
III.2 Re(CO)$_3$(N$^\equiv$N$')$Cl complexes ................................................................ 125
   III.2.1 Synthesis of neutral Re(CO)$_3$(N$^\equiv$N$'$)Cl complexes .......................... 125
   III.2.2 Photophysical Properties .......................................................................... 127
      III.2.2.1 UV/vis absorption spectroscopy .......................................................... 127
      III.2.2.2 Emission spectroscopy ................................................................. 128
Chapter IV: "Roll-Over" Cyclometalated Pt complexes

IV.1 Introduction “Roll-Over” Cyclometalation ................................................. 171
IV.2 Reactions of “roll-over” cyclometalated complexes ...................................... 177
IV.3 Synthetic Applications .................................................................................. 178
IV.4 Results and Discussion ........................................................................................................... 181
  VI.4.1 Synthesis and NMR characterization of “Roll-over” cyclometalated species ................. 181
    a)- (H$_4$-bpy)PtDMSOMe ........................................................................................................ 181
    b)- (H$_6$-bpy)PtDMSOMe ........................................................................................................ 182
IV.4.2 Reactivity of “Roll-over” cyclometalated species with acids ........................................... 184
    a)- Reaction with HCl: non-protonated species ........................................................................ 184
    b)- Reaction with [18-crown-6.HBF$_4$.H$_2$O]: protonated species ....................................... 186
IV.4.3 Photophysical Properties .................................................................................................... 187
IV.4.4 Synthesis and Characterization of enantiopure “Roll-Over” cyclometalated complexes
.................................................................................................................................................. 189
    a)- Optical Rotation .................................................................................................................. 190
    b)- CD and acid-base chiroptical switching ............................................................................. 190
    c)- CPL ..................................................................................................................................... 192
IV.5 Conclusion ............................................................................................................................... 194
References ....................................................................................................................................... 195
Experimental Part .......................................................................................................................... 198
Appendices .................................................................................................................................... 204
Résumé ............................................................................................................................................ 213
General Introduction

Heavy metal complexes such as rhenium or platinum complexes display large spin-orbit coupling and consequently show large parity violation (PV) effects at the molecular level and rich photophysical properties.

Parity violation is a fundamental symmetry breaking that is known to be responsible for a tiny energy difference between the two left-handed and right-handed enantiomers of a chiral molecule. This parity violation energy difference (PVED) has not yet been measured at the molecular level, although several attempts have been reported in the literature. The experimental attempts done in 2000 by J. Crassous, C. Chardonnet, and coworkers on CHFCIBr using a CO\textsubscript{2} laser-based ultra-high resolution IR spectroscopy were not successful but gave an upper limit of 10 Hz for this effect. In our aim to measure PVED between two enantiomers in collaboration with theoreticians, physicists, and spectroscopists, the synthesis of chiral oxorhenium, platinum, and ruthenium complexes is being developed in our team. Chapter I, part IA, describes the definition with some bibliographic aspects of parity violation, how it was discovered and verified experimentally at the nuclear level, and the developments toward measuring it at the molecular level, starting from CHFCIBr to CHFClI, and ending with some chiral oxorhenium complexes that were synthesized in the past for this purpose. A new experimental set-up based on highly accurate IR spectroscopy on a molecular beam developed by physicists is also described. Part IB presents the synthesis of chiral oxorhenium complexes derived from methyl trioxorhenium (MTO) and enantiopure mercapto-alcohol ligands. Vibrational circular dichroism (VCD) spectroscopy has revealed an important tool for studying the stereochemistry of these chiral complexes. Furthermore, these complexes exhibit the necessary parameters for performing spectroscopy on a molecular beam and PV tests since i) they are able to sublime, ii) they possess Re=O stretching band that lies in the same IR region as CO\textsubscript{2} laser which is used during experimental attempts to measure $\Delta E_{PV}$, and iii) theoretical calculations showed that they possess high PVED values between the two enantiomers. However these complexes may display some stability problems during the production of the molecular beam. Chiral fluorinated molecules bearing an asymmetric carbon coordinated to a Pt center were prepared. These chiral heavy metal complexes display an IR C-F stretching band compatible with the CO\textsubscript{2} laser, they show very good thermal stability but they don’t sublime. On the other hand, Ru(tmhd)\textsubscript{3} (tmhd: 2,2,6,6-tetramethyl-3,5-heptanedionate) shows a very efficient sublimation property, however it doesn’t possess a stretching band compatible with the CO\textsubscript{2} laser and the enantiomeric resolution using chiral HPLC has failed up to now. Some progress is still necessary to find out the better candidate for experimental PV observation on a chiral molecule.

Chapter II deals with another field of chirality. It describes the synthesis of [4] and [6]helicenes bearing either one or two 2,2’-bipyridine functionalities. These helicene-bpy ligands were characterized by multinuclear NMR and X-ray diffraction studies. Their photophysical and chiroptical properties were investigated. They were found to absorb between 230 and 430 nm,
and displayed efficient blue fluorescence at room temperature accompanied by long-lived green phosphorescence at low temperature. In order to study their chiroptical properties, enantiomers were separated using HPLC over chiral stationary phases. Enantiopure helicene-bipyridines display high specific and molar optical rotations, strong electronic circular dichroism (ECD) and circularly polarized luminescence (CPL). We investigated the ECD and CPL activity of \([6]\)helicene-bpy in comparison with its protonated version. Upon protonation, a significant decrease in the ECD-active bands and a bathochromic shift in the CPL bands were observed.

The coordination ability of helicenes bearing one or two 2,2'-bipyridine moieties is described in Chapter III and Chapter IV. Chapter III describes the \(N^N\)' chelating behavior with rhenium(I) tricarbonyl systems. Re(I)tricarbonyl(X) complexes with diimine coordinating ligands such as bipyridine show a rich photophysics. Getting benefit from i) the \(\pi\)-conjugated system, ii) the helical chirality, and iii) the coordinating behavior of helicene-bpy, we studied the effect of the metal (Re) on the chiroptical properties of helicenes as well as their photophysical properties. Different chiral rhenium complexes (mono and bimetallic) were synthesized and characterized by multinuclear NMR and X-ray diffraction studies. We then investigated the influence of rhenium coordination on the photophysical and chiroptical properties. In the UV-vis absorption spectra, a new band appears due to the incorporation of Re metal and is ascribed to metal-to-ligand charge transfer (MLCT) that is also observed in the ECD spectra of enantiopure complexes. These complexes exhibit phosphorescence derived from \(^3\)MLCT at room temperature and \(^3\)IL at low temperature, but display low quantum yields. Replacing the Cl ligand by pyridine or isocyanides in \([4]\)helicene-bipyridine-Re(CO)\(_3\)Cl complexes can lead to a significant increase of the quantum yield from 0.1% to 8% and 16% respectively.

In Chapter IV, the \(N^C\)' chelating behavior of \([4]\) and \([6]\)helicene-bpy ligands was studied. Using an electron-rich Pt precursor, C-H activation was achieved to prepare "roll-over" cyclometalated Pt(II) complexes. These complexes were characterized by multinuclear NMR and X-ray diffraction studies. No significant effect was observed on the UV-vis absorption spectra of "roll-over" cyclometalated complexes as compared to the starting ligands. However, upon protonation of the uncoordinated N atom, a significant decrease in the molar absorption coefficient was observed in the UV-vis absorption spectra together with the appearance of a new band at low energy. This new band also appeared in the ECD spectra of the enantiopure "roll-over" cycloplatinated complexes, and a significant decrease in the specific and molar optical rotations was observed. Moreover, the CPL activity of protonated and non-protonated species was studied. Interestingly, the reversibility of the protonation/deprotonation is very fast and efficient and enabled us to obtain a metallohelicene based acid-base chiroptical switch.
A. Parity violation in chiral molecules: definitions and former studies

I.1 Introduction and context of our work

Chirality is important in chemistry, biology and physics. For chemists, chirality is a challenge, notably in the development and synthesis of molecules for pharmaceuticals, agrochemicals, flavors, and more recently, in supramolecular chemistry and nanotechnology. The development of catalysts for stereoselective synthesis is one of the most important tasks of modern chemistry. In biology, homochirality is a hallmark of life in that nature shows, with very few exceptions, a distinct preference for L-amino acids and D-sugars over their mirror images. However, the origin of biohomochirality remains unknown.

As soon as the term chirality is mentioned, other terms such as symmetry, asymmetry, dissymmetry, mirror-image ... directly come to mind! Taking a look through the lake below, one sees the geometric mirror-image of the real world, but sometimes it appears as qualitatively different.

If one look at the mirror-image of a written text, he will realize that the written language in the mirror world is unknown to him! As questioned by G. H. Wagnière: “suppose ‘enantiomorphous’ human beings existed, would their languages necessarily be different from those of the inhabitants of Earth? So then, why would we be living in the world as it is, and not in the mirror world? Or why they don’t both coexist, and why the nature prefers one over the other?”
A priori the four fundamental forces (gravitational, electromagnetic, strong and weak) that rule out the world should predict that any experiment should give exactly the same results as its mirror-image experiment and consequently should show the same probability of occurring. This has been the belief of physicists as well as the chemists until 1956 since when it was discovered by Lee and Yang, Chinese theoreticians, that this was not true in experiments involving the weak force, a force occurring between elementary particles. They actually discovered that elementary particles (electrons, protons ...) are intrinsically chiral and that the all matter was dissymmetric!

Then, if we consider the two enantiomers of one chiral molecule, they are not anymore enantiomers and there is a slight energy difference between them due to the weak force in atoms and elementary particles that breaks the right and left-handed symmetry! This breakdown of mirror-image symmetry is called Parity Violation (PV) or Parity Non Conservation (PNC) (Figure 1.1) and has never been unambiguously experimentally observed in chiral molecules up to now. As will be explained in the following paragraphs, we are aiming at measuring such PV effects in chiral molecules, in close collaboration with physicists, spectroscopists and theoreticians.

I.2 Chirality and fundamental symmetry operators

In 1848, Louis Pasteur discovered the property of optical isomerism. Pasteur discovered that there were two forms of crystals of sodium ammonium tartrate where some were hemihedral to the right and others to the left i.e. they were mirror-images. These two forms, when dissolved in alcohol and submitted to the 'polarimètre de Biot', were found to rotate the plane of a linearly polarized light in two different directions --- one to the left, the other to the right. When mixed in equal quantities, these two forms did not show optical rotatory power anymore. With this experiment, Pasteur demonstrated for the first time that the two forms of the same chemical compound, sodium ammonium tartrate, may have different spatial arrangements. The stereoisomerism was born. Later on in 1874 Le Bel and van't Hoff discovered independently the asymmetric carbon.⁸

Figure 1.1 The broken mirror: enantiomers are not really enantiomers.
The general definition of the term "chirality" was first formulated in 1884 by Lord Kelvin⁹: “I call any geometrical figure, or group of points, chiral, and say that it has chirality, if its image in a plane mirror, ideally realized, cannot be brought to coincide with itself”.

The term chirality is derived from the Greek word χειρ (kheir), which means hand, and the term enantiomers defines the two mirror-images comes from “enantios” which means opposite. In terms of symmetry, a molecule is chiral if it lacks rotation-reflection axes $S_n$, or belongs to the point-group $C_n$, or $D_n$ (or else $O$, $T$, $I$).⁸

In Physics, objects of opposite chirality are connected by the parity operation ($P$) which converts $(x,y,z)$ into $(-x,-y,-z)$ (Figure 1.2), combined with charge conjugation ($C$) which converts charge $q$ into $-q$, and time reversal ($T$) which converts $t$ into $-t$ in the CPT theorem: a mirror universe where all particle positions are reflected about some plane (parity inversion), all particles are replaced by their antiparticles (charge conjugation), and all momenta are reversed (time reversal) will evolve according to the same physical laws as the present universe.¹⁰

![Figure 1.2 Fundamental symmetries $P$ and combinations ($CP$) are not conserved.](image)

In other words, the exact symmetry that is conserved in all universe laws is $CPT$, which means that the exact enantiomer should be found in the “antiworld”!

**I.3 First observation of parity violation (PV) at the nuclear level**

As mentioned before, physicists were convinced that parity was conserved in all experiments, that is any experiment with its mirror image should give exactly the same results until 1956 where parity violation or non-conservation of parity was first predicted by the theoretical physicists Lee and Yang¹¹ for weak interactions.
The weak forces are mediated by the neutral weak $Z^0$ bosons (weak neutral current) resulted from the interaction between electrons and constituents of the nuclei (Figure 1.3), a mechanism precisely described by the standard electroweak theory\textsuperscript{15} that combines the weak and electromagnetic interactions.

![Figure 1.3 Neutral weak boson $Z^0$](image)

Lee and Yang stated in their paper\textsuperscript{11}: "To decide unequivocally whether parity is conserved in weak interactions, one must perform an experiment to determine whether weak interactions differentiate the right from the left." And they proposed several experiments. In 1957, the Nobel Prize in Physics was given to Lee and Yang for their important prediction.

One of the simplest experiments to observe PV involved $\beta$-decay that is indeed mediated by the weak force. It is a type of radioactive decay in which a beta particle (an electron or a positron) is emitted from an atomic nucleus.\textsuperscript{12} There are two types of beta decays: $\beta^{-}$ and $\beta^{+}$. In the case of beta decay that produces an electron emission, it is referred to as beta minus ($\beta^{-}$), while in the case of a positron emission as beta plus ($\beta^{+}$).

A relatively simple possibility is to measure the angular distribution of the electrons coming from $\beta$ decays of oriented nuclei. If $\theta$ is the angle between the orientation of the parent nucleus and the momentum of the electron, an asymmetry of distribution between $\theta$ and $180^\circ - \theta$ constitutes an unequivocal proof that parity is not conserved in $\beta$ decay.

This asymmetry effect has been observed in the case of oriented Co$^{60}$ by Wu et al. in December 1956\textsuperscript{13}. It has been known for some time that Co$^{60}$ nuclei can be polarized by the Rose-Gorter method in cerium magnesium (cobalt) nitrate, and the degree of polarization detected by measuring the anisotropy of the succeeding gamma rays.

Cobalt-60 is an unstable isotope of Cobalt that $\beta$ decays to the stable isotope nickel-60, an electron and an electron antineutrino. The stable nickel nucleus is activated by the reaction and emits two gamma rays, hence the overall nuclear equation of the reaction is:

$$^{60}\text{Co} \rightarrow ^{60}\text{Ni}^* + \bar{\nu}_e + e^- + 2\gamma$$

The principle of Wu’s experiment is described in Figure 1.4a where using liquid Helium, Cobalt-60 nuclei were cooled to a temperature of about 0.01 K to reduce atomic vibrations to effectively
zero. A uniform magnetic field across the sample of Cobalt-60 was needed to magnetically align the atomic nuclei so that their spin axes point in a preferred direction (namely, parallel to the magnetic field in the z-direction). The beta and gamma counting is then started. Equal number of electrons should be emitted parallel and anti-parallel to the magnetic field if the parity is conserved as depicted in Figure 1.4c, but a large beta asymmetry was observed. The emission of β particles is more favored in the direction opposite to that of nuclear spin i.e. more electrons are emitted in the direction opposite to the magnetic field, thus verifying experimentally that parity is violated at the level of weak interactions (Figure 1.4b).

I.4 Parity violation observation in atoms

After the parity non-conservation in weak interactions had been discovered at the nuclear level, Zel’dovich raised the question if parity violation, also named parity non conservation, could also be observed at the atomic level?\textsuperscript{14}

The development of electro-weak interaction theory by Weinberg\textsuperscript{15} enabled to understand that the effects in the atoms depend mainly on the weak neutral currents, and the parity violation is caused by the exchange of neutral $Z^0$ bosons (Figure 1.3) between atomic electrons and quarks in the nucleus with no destroy or creation of charges. It also led to the conclusion that the effects should grow as the third power of the atomic number $Z$.\textsuperscript{17a,c}

This $Z^3$-law offered successful experiments in heavy atoms, where parity violation was observed by measuring a small optical rotation in Bismuth vapor,\textsuperscript{16} or by observing highly forbidden transitions in Cesium.\textsuperscript{17}
1.5 Parity violation in molecules

The weak neutral currents that are responsible for the parity violation in atoms are, of course, also operative in molecules. PV effects manifest themselves in a chiral molecule by a small energy difference ($\Delta E_{PV}$) between the two enantiomers, and therefore they could possibly be observed by absorption spectroscopy techniques capable of measuring such small energy differences. V. S. Letokhov pointed out in 1975\textsuperscript{18} on the difference of energy levels of left and right molecules due to weak interactions and charged currents that may lead to observable effects or a small energy shift in molecular spectra, trying to indicate a possible connection between weak interactions and biological isomerism. He mentioned in his paper that the odd (Parity-odd) part of potential of the electron-proton (ep)-interaction makes a small odd addition to the energy of Coulomb interaction between electrons and nuclei. In other words, the $P$-odd disturbance caused by ep-interaction removes the degeneration of energy levels of left and right molecules, so that the energy levels become different, thus the vibrational and rovibrational levels of energies $E_{vib}$ and $E_{rot}$ differ respectively with relative values ($\Delta \nu / \nu$) about $10^{-16} - 10^{-17}$ (Figure 1.5).

![Fig.1.5](image)

Parity violation effects in chiral molecules have never been clearly observed experimentally. Interestingly, infra-red (IR) spectroscopy has been the focus of several groups, following the original idea of Letokhov.\textsuperscript{18} In 1977, Glorieux \textit{et al.} tried to measure differences in absorption energies of camphor enantiomers.\textsuperscript{19} The resolution reached (300 kHz) was too low to evidence PV effects.

In this time period, Letokhov and his group subsequently searched for $\Delta \nu$ splittings by laser sub-Doppler absorption spectroscopy in the spectrum of racemic CHFCIBr,\textsuperscript{20} where he proposed the experimental protocol envisaged in Figure 1.6.
I.5.1 CHFClBr 1: synthesis, resolution and PV tests.

Bromochlorofluoromethane (CHFClBr) 1, one of the simplest chiral molecules, was synthesized in 1893 by the Belgian chemist Frédéric Swarts21 by direct decarboxylation of bromochlorofluoroacetic acid (FClBrCO\textsubscript{2}H) 2 under basic conditions (Scheme 1.1).

The resolution of (±)-1 was the serious challenge due to the presence, at the same tetrahedral carbon atom, bromine and chlorine which have similar atomic properties. In 1989, Doyle and Vogl22 isolated samples of (+) and (-)-2 having 66% and 42% enantiomeric excess (ee), respectively, after a series of recrystallizations of {((±)-2,(-)-strychnine} salts ((-)-strychnine is a chiral natural alkaloid). Then by heating at 100-120° C in diethylene glycol (DEG), the partially resolved strychnine salts of (+) and (-)-2 undergo a clean decarboxylation into (+) and (-)-1 respectively, with retention of the optical activity (Scheme 1.1).23 Moreover, the S-(+) and R-(−) absolute configuration was solved in 1997 for the first time by Collet, Crassous, and co-workers.24,25

![Scheme 1.1 Synthesis of (+)- and (-)-1 by decarboxylation from partially resolved (-)-strychnine salts of (+)- and (-)-2.](image)

Due to its simplicity, 1 has long been considered as the molecule of choice for the search of parity violation effects at the molecular level. Indeed, the group of Christian Chardonnet, Benoît Darquié and coll. at the Laboratoire de Physique des Lasers in Villetaneuse, are physicists specialists of metrology that have developed a CO\textsubscript{2} laser-based ultra-high resolution IR spectroscopy since 1997.26 In order to look for PV effects, they probed the hyperfine structure of the strong \nu\textsubscript{4} C-F stretching band of CHFClBr (Figure 1.6)27 on samples prepared by Crassous and coworkers and tried to measure a difference between the left and right-handed enantiomers.
They recorded simultaneously the spectra of the two enantiomers $S$-$(+)$-$1$ with $56\%$ ee and $R$-$(−)$-$1$ with $22\%$ ee placed respectively in twin 3 m long Fabry-Perot cavities (Figure 1.6). A final mean value of 3.7 Hz was obtained for the frequency difference, with a standard deviation of 47.2 Hz. Statistical and systematic errors were estimated to be respectively $\pm 2$ and $\pm 5$ Hz. Taking into account the enantiomeric excesses of the samples, the first energy difference measurement over 10 days measurements finally gave

$$\Delta \nu_{PV} = \nu(R-(-)\text{-}1) - \nu(S-(+)\text{-}1) = 9.4 \pm 5.1 \pm 12.7 \text{ Hz}$$

This result is therefore negative, but it gives an upper bound of $\Delta \nu / \nu \leq 3.9 \times 10^{-13}$ for the PV effect. Later on, it was repeated in 2002 with samples of higher ee’s and the experimental sensitivity obtained over 7 days measurements was $5 \times 10^{-14}$. In contrast, theoretical studies predicted that PV differences for the C-F stretch of CHFClBr is in the order of $-2.4$ MHz corresponding to $\Delta \nu / \nu \approx -8 \times 10^{-17}$. This reveals therefore the existence of a big error due to uncontrollable residual gases present in the absorption cells that induce collisions between molecules and consequently collisional shifts of the transition frequencies. As a conclusion, no evidence for PV effects at the molecular level, but an industrious effort has been carried out to improve and upgrade the experimental set-up of the apparatus used to measure the PV shifts.

### I.5.2 New experimental setup

The major problem in measuring experimentally PV differences by Darquié, Chardonnet and coworkers was intermolecular collisions which are responsible for both a frequency shift and a broadening of the molecular line, and consequently spoil the precision of the measurements. To circumvent this problem, the LPL decided to develop an experimental setup adapted to the spectroscopy of chiral molecules for a new PV experiment based on supersonic molecular beam spectroscopy using the powerful ultra-high resolution technique of Doppler free two-photon Ramsey fringes, as recently developed in Chardonnet’s team on SF$_6$ for molecular frequency metrology (Figure 1.7). Supersonic molecular beam spectroscopy was introduced by Klemperer and presents the major advantage of eliminating intermolecular collisions. A
A supersonic beam is much more interesting than a regular thermal beam since, due to the many collisions occurring at the very beginning of the supersonic expansion, the rotational temperature drops down to a few K (thermal and internal energy are converted into a large common translational kinetic energy) thereby assuring a high degree of cancelation of errors. Another consequence is that lower energy levels are strongly populated which will amplify the spectroscopic signal of the probed levels.

Consequently, the principle is similar to the previous experiment on CHFClBr: comparing the frequency of the same rovibrational line for two enantiomers of a chosen chiral molecule. The spectra of both enantiomers will then be recorded in identical experimental conditions with the same setup. Any frequency difference will be interpreted as a PV effect which can only be due to the weak interaction. The LPL group benefits from his know-how in laser frequency control. The reference laser is actually connected to the primary frequency standard located at the laboratory LNE-SYRTE (Laboratoire National d’Essais-Systèmes de Référence Temps Espace) at Paris Observatory. In addition, the LPL CO$_2$ laser frequency control is limited by laser frequency noise to about 0.1 Hz after a few minutes and shows an accuracy and stability over a day of $10^{-16}$ (~10 mHz), limited by that of the LNE-SYRTE reference frequency.$^{35}$

Figure 1.7 Principle of the Ramsey fringes experiment considered for the observation of PV in molecules. A frequency-controlled CO$_2$ laser interrogates an alternate beam of right- and left-handed molecules.

I.5.3 Basic theoretical PV considerations

Theory plays a very important role in this field as it can provide predictions of PV effects and thus helps in guiding experimental research. The parity-violating energy can be written as a sum of atomic contributions:$^{36}$

$$E_{PV} = \sum_A E_{PV}^A$$
in which the weak charge $Q_{\nu:A} = -N_A + Z_A(1 - 4 \sin^2 \theta_W)$ appears, where $Z_A$ and $N_A$ are the number of protons and neutrons, respectively, of nucleus $A$. $\theta_W$ is the Weinberg mixing angle,\(^{37}\) and $G_f$ is the Fermi weak coupling constant.

At the atomic level\(^{17}\), it was indicated that the parity-violating effect is proportional to $G_f \alpha Z^3$. However, at the molecular level, spin-orbit effects grow roughly thus that $\Delta E_{PV}$ becomes proportional to $G_f \alpha^2 Z^5 \eta$,\(^{38}\) where $\alpha$ is the fine structure constant, and $\eta$ is a so-called symmetry factor depending on the molecular connectivity and geometry. As a conclusion, the $Z^5$-dependence suggests that the effect will be strongly favored in molecules containing heavy elements close to the chiral center.\(^{39}\)

### 1.5.4 CHFCII: synthesis and resolution

The synthesis and resolution of CHFCIBr (1) assisted in the examination of analogous molecules of CHXYZ type that may contain heavier atoms than in 1. P. Schwerdtfeger and coworkers performed accurate \textit{ab initio} calculations on fluorohalogenomethanes\(^{31,40,41}\) 3, 4 and 5. The theoretically PV energy differences obtained for the C-F fundamental transitions between $R$ and $S$ enantiomers are shown in Table 1.1.

<table>
<thead>
<tr>
<th>CHFCI (1)</th>
<th>CHFCH (3)</th>
<th>CHFBrI (4)</th>
<th>CFCIBrI (5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2.4 mHz</td>
<td>-23.7 mHz</td>
<td>-50.8 mHz</td>
<td>+11.6 mHz</td>
</tr>
</tbody>
</table>

CHFBri (4) seemed to be the most promising molecule, and CHFCII (3) has been considered for a while as a potential candidate due its interesting features such as the calculated PV difference, and the high vapor pressure that allows investigation by supersonic molecular beam spectroscopy.\(^{42,43}\) The synthesis of racemic 3 was achieved by Haszeldine \textit{et al.} in 1952\(^{44}\) then by Novak \textit{et al.}\(^{45}\) Later on, Crassous \textit{et al.} succeeded to prepare (+)- and (-)-3 enantiomers with 63% and 20% ee's respectively by the highly enantioselective decarboxylation of the partially resolved (-)-strychnine salts of chlorofluorooiodoacetic acid (ClFICO$_2$H)\(^{46,47}\) with different moderate diastereomeric excesses (de's) (Scheme 1.2). The $S$- (+)- and $R$- (-) absolute configuration for compound 3 was ascertained by vibrational circular dichroism (VCD) in the gas phase.\(^{46}\)
An advantage of CHFClI (3) is that its high vapor pressure allows for the production of a supersonic molecular beam and its study by Rovibrational Fourier Transform InfraRed (FTIR) spectroscopy. FTIR is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. FTIR spectroscopy of the fundamental $\nu_4$ C-F stretching band of CHFClI has been performed by the group of Pierre Asselin and Pascale Soulard at the LADIR (UPMC) in a supersonic jet and in a static cell at room temperature. Figure 1.8 displays a characteristic PQR rovibrational structure of the $\nu_4$ band of CHFClI recorded at the same resolution (0.008 cm$^{-1}$) in the cell (a) and in a supersonic expansion (b). The stick spectrum (Figure 1.8(c)) displays possible coincidences with P($J$) and R($J$) lines of the 9.4 $\mu$m band of the CO$_2$ laser. Because of the too small quantity of (3) available, the quality and the resolution of the infrared jet spectrum were not high enough to perform a precise rovibrational analysis of the $\nu_4$ band. The microwave spectroscopy of CHFClI on a supersonic molecular beam has also been examined by the group of Thérèse Huet in Lille.

Scheme 1.2 Resolution of salts and synthesis of $S$-(-)- and $R$-(-)-3 by decarboxylation of partially resolved salts in triethylene glycol (TEG).

I.5.5 Spectroscopic studies of CHFClI

An advantage of CHFClI (3) is that its high vapor pressure allows for the production of a supersonic molecular beam and its study by Rovibrational Fourier Transform InfraRed (FTIR) spectroscopy. FTIR is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. FTIR spectroscopy of the fundamental $\nu_4$ C-F stretching band of CHFClI has been performed by the group of Pierre Asselin and Pascale Soulard at the LADIR (UPMC) in a supersonic jet and in a static cell at room temperature. Figure 1.8 displays a characteristic PQR rovibrational structure of the $\nu_4$ band of CHFClI recorded at the same resolution (0.008 cm$^{-1}$) in the cell (a) and in a supersonic expansion (b). The stick spectrum (Figure 1.8(c)) displays possible coincidences with P($J$) and R($J$) lines of the 9.4 $\mu$m band of the CO$_2$ laser. Because of the too small quantity of (3) available, the quality and the resolution of the infrared jet spectrum were not high enough to perform a precise rovibrational analysis of the $\nu_4$ band. The microwave spectroscopy of CHFClI on a supersonic molecular beam has also been examined by the group of Thérèse Huet in Lille.
This experiment demonstrated the feasibility of high resolution supersonic beam spectroscopy in molecules. However, this molecule is not stable enough and to date, synthesis in enantiopure form and gram-scale quantities can hardly be achieved.

I.6 PV in heavy metal-containing molecules

P-odd effects scale approximately like $Z^n$ ($n \approx 5$; $Z =$ atomic number)$^{38}$, thus it limits the choice to heavy-element-containing compounds (either as ligands or chiral centers). Depending on this hypothesis, Peter Schwerdtfeger proposed in 2003 different molecules that are known in the literature where each one contains a heavy-element center.$^{49}$ The full optimization of these molecules using density functional theory (DFT)$^{50}$ followed by four-component all-electron Dirac-Fock calculations, lead to large P-odd effects (Table 1.2). The reported calculations on heavy metals opened a new door for new candidates, especially those of 6th row, for high resolution spectroscopy to measure the PV difference.$^{49}$ Another advantage in using heavy-element-containing compounds may also be the feasibility in producing such molecules in large quantities and with an ee of 100%.

**Figure 1.8** FTIR spectra of the $\nu_4$ band of CHFCII recorded at 0.008 cm$^{-1}$ resolution (a) in a room temperature static cell; (b) in a supersonic expansion respectively; (c) stick spectrum of $P(J_{K_aK_c})$ and $R(J_{K_aK_c})$ lines of the 9.4 μm band of the CO$_2$ laser.
Consequently, some challenges are to be faced to succeed in measuring PV effects in molecules by high-resolution FTIR spectroscopy: first one needs to have thermodynamically stable molecules with a heavy metal at the chiral center, and second to be accessible to high resolution optical spectroscopy experiments carried out in the CO₂ laser frequency range between 878 and 1108 cm⁻¹, i.e. finding a heavy element system with stretching or bending frequencies in this particular frequency range. To reach this range, the M-L stretching force constant should be reasonably large to counterbalance the large reduced mass between M and L. Therefore, thermodynamically stable chiral species are required with a light ligand and heavy metal double bond. Moreover, such complexes are usually non volatile solids which constitute a big difficulty for producing a molecular beam for high resolution gas phase spectroscopy.

Table 1.2: Total PVED (\(\Delta E_{PV} = 2E_{PV}\)) in Hz for selected complexes. A negative sign indicates that the enantiomer is the P-odd-stabilized form.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\Delta E_{PV}) [Hz]</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>0.162</td>
</tr>
<tr>
<td>8</td>
<td>58.4</td>
</tr>
<tr>
<td>9</td>
<td>-1.74</td>
</tr>
<tr>
<td>10</td>
<td>115</td>
</tr>
<tr>
<td>11</td>
<td>316</td>
</tr>
<tr>
<td>12</td>
<td>-232</td>
</tr>
<tr>
<td>13</td>
<td>264</td>
</tr>
<tr>
<td>14</td>
<td>26.8</td>
</tr>
</tbody>
</table>
After an extensive investigation by Peter Schwerdtfeger and Radovan Bast, it appeared that the two most promising candidates in the literature are Os(η⁵-C₅H₅)(=CHPh)Cl(PPr₃) (15) involving a Os=C double bond, and Re(η⁵-Cp*)(=O)(CR₃)Cl (Cp* = C₅(CH₃)₅) (16) involving Re=O double bonds (Figure 1.9) with respective IR transitions 901 cm⁻¹ and 989 cm⁻¹, that fit the CO₂ laser frequency range. Moreover, Schwerdtfeger obtained from four-component relativistic Hartree Fock (HF) calculations large PV effects, around 1 Hz, between the corresponding enantiomers (Figure 1.9).

Figure 1.9 Comparison of PV effects |Δνₚᵥ| for halogenomethanes (1, 3) and transition metal complexes (15, 16)

I.6.1 Chiral oxorhenium complexes: interesting candidates for PV differences calculations

The transition metal complexes 15 and 16, compared to fluorohalogenomethanes, had shown that organometallic complexes containing heavier atoms may display higher PV effect. However, complexes 15 and 16 have limited utility for the proposed PV experiment as they are expected to easily racemize due to the presence of the pentamethylcyclopentadienyl ligand (Cp*), but they gave some ideas about the synthesis of new classes of transition metal complexes as done by Jeanne Crassous, Laure Guy, and coworkers who synthesized two families of chiral oxorhenium complexes based on either hydrotris(1-pyrazolyl)borate (Tp) or sulfur ligands.

The oxorhenium samples studied first were the two enantiomers reported in the literature (Scheme 1.3).

I.6.1.1 Chiral oxorhenium complexes bearing a Tp ligand

The use of chiral ephedrine ligand enables the transfer of chirality towards the stereogenic rhenium center since only one diastereomer was obtained among the two possible ones as depicted in Scheme 1.3. Their absolute configuration were determined by X-ray crystallography and then confirmed by VCD spectroscopy studies.

The abbreviation "VCD" derives from "Vibrational Circular Dichroism". In contrast to classical IR spectroscopy in which absorptions spectra are recorded due to vibrational excitation with
nonpolarized IR radiation, VCD spectroscopy detects the difference in absorption from right- and left-handed circularly polarized IR radiation ($\Delta A = A_L - A_R$) of optically active compounds and provides three-dimensional structural information.

The interaction of chiral molecules and light shows different absorption for both enantiomers depending on the circular polarization of light. The absorption of right-handed circularly polarized light $A_R$ and left-handed circularly polarized light $A_L$ for optically active compounds is of different intensity. The difference $\Delta A = A_L - A_R$ is unequal to zero and many transitions of the IR spectrum are CD-active for chiral molecules. This phenomenon is known as circular dichroism.

The VCD spectrum of complex 17 enantiomers is shown in Scheme 1.4; the strong infrared band at 930 cm$^{-1}$ corresponding to Re=O stretching mode is VCD active.

**Scheme 1.3** Synthesis of Tp-based chiral oxorhenium enantiomeric complexes 17.
Despite the easy preparation of enantiopure oxorhenium complex 17, and the chirality at the Rhenium center, the bulkiness and high molecular weight complicates the spectroscopic analysis of a molecular beam due to problems of recondensation on the inner walls of vacuum chambers, and also precludes any accurate PV calculations.

I.6.1.2 “3+1” Oxorhenium complexes

In contrast to the bulk oxorhenium complexes bearing Tp ligands, where bulkiness is a major problem that affects the accuracy as well as the ability in PV differences measurements, the interest was to simplify the chemical structure of the candidates. Crassous, Guy et al. focused on the synthesis of new oxorhenium complexes belonging to the “3+1” mixed family bearing a simple structured tridentate ligand 19 (1,1-dimethyl-1,5-dithiol-3-thiapentane) and one monodentate ligand, inspired from the oxorhenium complex 18.\(^5\)

\[
\begin{align*}
\text{Scheme 1.4 IR and VCD and infrared spectra of Tp-based chiral oxorhenium enantiomeric complexes 17.}
\end{align*}
\]

The synthesis of a dissymmetric version of 18 was based on the use of oxorhenium precursor ReO(Cl)\(_3\)(PPh\(_3\))\(_2\) with the tridentate ligand 19 and one monodentate ligand in refluxing THF and presence of sodium acetate.\(^5\)\(^6\)\(^7\) Upon complexation, a stereogenic Rhenium center is introduced due to the dissymmetry originated from the presence of gem-dimethyl in 19 (Scheme 1.5).
This method allows the synthesis of a large panel of oxorhenium complexes by modifying the monodentate ligand. The different complexes synthesized are summarized in Scheme 1.6. Moreover, the enantiopure complexes were resolved through HPLC separation over chiral stationary phases, and the enantiomerically pure complex 20 can be used in forward reactions, with MeI for example, to obtain enantiomerically enriched samples of iodo complex 25 (Scheme 1.6) with retention of configuration at the Re center, thus allowing direct access to a variety of enantioenriched mixed “3+1” oxorhenium complexes either with iodo complexes or with replacing the iodine with other nucleophiles such as 4-bromobenzenethiol to obtain complex 26. The chiral environment of the stereogenic Re center is also verified by VCD spectroscopy studies where active bands around 1000 cm\(^{-1}\) and 500 cm\(^{-1}\) corresponding to Re=O and Re=S stretching bands respectively are observed. Thus, it became obvious that VCD spectroscopy is an indispensable tool to inspect the chiral environment around Re and its influence on the fundamental Re=O stretching mode.

Substantially, Tp as well as sulfur ligand-based complexes present the advantages of having active VCD intense band around 1000 cm\(^{-1}\), and being synthesizable in several grams scale in enantioenriched forms. However in contrast to bulkiness problem in Tp, simple chiral sulfur
ligand-based complexes are sufficiently compact to enable the theoretical determination of their PV effect. Table 1.3 summarizes the theoretically calculated PV vibrational frequency differences by density functional theory (DFT) and Hartree-Fock (HF) calculations conducted by Trond Saue, Radovan Bast and coworkers (UPS, Toulouse) for various chiral oxorhenium complexes 20 and 25 in comparison with 15 and 16. The results indicated PV shifts in the order of 100 mHz or higher for 20 and 25, which are about one order of magnitude smaller than the corresponding shifts in 15 and 16. This evidences the strong effect of the chiral environment around the stereogenic center on the calculated PV shifts.

**Table 1.3:** Calculated PV vibrational shifts between the two enantiomers (A-C or R-S) of chiral rhenium and osmium complexes discussed previously. HF: Hartee-Fock; DFT: Density Functional Theory (B3LYP).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Transition</th>
<th>Transition frequency (cm⁻¹)</th>
<th>PV Shifts (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>HF</td>
</tr>
<tr>
<td>15</td>
<td>0 → 1</td>
<td>884</td>
<td>-3.085</td>
</tr>
<tr>
<td>16</td>
<td>0 → 1</td>
<td>1019</td>
<td>-2.077</td>
</tr>
<tr>
<td>20</td>
<td>0 → 1</td>
<td>1012</td>
<td>-1.585</td>
</tr>
<tr>
<td>25</td>
<td>0 → 1</td>
<td>1027</td>
<td>+0.157</td>
</tr>
</tbody>
</table>

Unfortunately, the sublimation properties of these chiral oxorhenium complexes were not so efficient to prepare them in the gas phase seeded supersonic molecular beam. Tp ligand-based oxorhenium complex 17 showed difficulties in sublimation, it sublimes at 160 °C, but the molecular flux is too weak for supersonic beam spectroscopy, while sulfur-based oxorhenium complexes have evidenced slow decomposition between 150 °C and 190 °C.

**B. Synthesis and characterization of new potential candidates for PV observation**

**I.1 New approach toward chiral oxorhenium derivatives starting from methyltrioxorhenium (MTO)**

In parallel to the development of experimental setup performed by physicists, we are trying to synthesize other chiral oxorhenium complexes characterized by strong stability upon heating and low sublimation temperatures in order to avoid the problems of decomposition or recondensation on the inner walls of vacuum chambers, as well as candidates with more pronounced dissymmetry around the stereogenic rhenium center, in contrast to sulfurated ligand-based complexes, as evidenced by theoretical calculations showing that PV is very sensitive to the chiral environment around the stereogenic center. In particular, commercially available achiral oxorhenium complex methyltrioxorhenium (MTO), a molecule employed in catalysis, and chiral derivatives of MTO have already been described in the literature. The most interesting point in using MTO for preparing chiral oxorhenium derivatives is its sublimation...
property (40°C under 0.01 mbar),\textsuperscript{63} that can facilitate our purpose for generating molecular beam.

Interestingly, our coworkers in spectroscopy recently reported the first high resolution CO\textsubscript{2} laser absorption spectra of MTO both in a cell and in a molecular jet\textsuperscript{64} \textit{i.e.} MTO has the ability to form the supersonic molecular beam which constitutes a major step towards the targeted objective. We thus decided to explore the chemistry of MTO and focus on the development of synthesis of simple chiral derivatives that fulfill the parameters needed for the experimental setup to measure PV shifts between two enantiomers.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{mto.png}
\caption{Methyltrioxorhenium (MTO)}
\end{figure}

I.2 Synthesis and characterization of oxorhenium(VII) complex \{28\}

The design of a good metal complex candidate for PV observation necessitates a suitable ligand or in advance an enantiopure ligand design, which can coordinate to the metal sphere and form a stable enantiopure complex. Different ligands derived from epoxides have been synthesized. The choice is based on their versatile chemistry to synthesize different bi- or tridentate ligands as well as their assistance in the subliming properties of the final transition metal complexes.\textsuperscript{65,66}

Inspired by the complex 27 prepared by Espenson and coworkers,\textsuperscript{65} that sublimes at 140°C under vacuum line, we were interested in preparing the simple enantiopure oxorhenium(VII) complex 28, that was already reported by Espenson in racemic form and showed reasonable stability.\textsuperscript{65}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{complexes.png}
\caption{Oxorhenium(VII) complexes 27 and 28}
\end{figure}

I.2.1 Synthesis of enantiopure 1-mercapto-propan-2-ol ligand

Chiral ligands are of great importance since they can control or transfer the chirality to the Re metal center as already shown.\textsuperscript{61,62} Consequently, enantiopure 1-mercapto-propan-2-ol can be readily prepared from enantiopure propylene oxide.
An epoxide is cyclic ether with three ring atoms defining approximately an equilateral triangle which makes it highly strained. The strain ring makes epoxides more reactive than other ethers especially towards nucleophilic addition type reactions. Consequently, the ease of opening the 3-membered cycle by different nucleophiles widens the scope towards the synthesis of different simple ligands. Fortunately, the commercial availability of some epoxides in their enantiopure forms facilitates the synthesis of simple enantiopure ligands (Scheme 1.7). It’s important to mention that nucleophilic addition under basic conditions is regioselective i.e. the nucleophile attacks the least substituted carbon in accordance with the standard $S_{N}2$ nucleophilic addition reaction process. Moreover, in the presence of only one stereogenic carbon center, the nucleophilic substitution proceeds via retention of configuration as described in Scheme 1.8.

![Scheme 1.7 Enantiopure commercial available propylene oxide](image)

**Scheme 1.7** Enantiopure commercial available propylene oxide

![Scheme 1.8 Nucleophilic attack under basic conditions of propylene oxide with retention of configuration](image)

**Scheme 1.8** Nucleophilic attack under basic conditions of propylene oxide with retention of configuration

Based on these information, the enantiomers of the 1-mercapto-propan-2-ol ($R$(-) and $S$-(+)) ligands can be synthesized using enantiomerically pure propylene oxide as described in Scheme 1.9. The regioselective opening of $R$-(+)- and $S$-(-)-propylene oxide with trityl thiol, respectively, gave the alcohols $R$-(+)- and $S$-(-)-29 with 90% yield. The subsequent deprotection followed by *in situ* oxidation with iodine yielded quantitatively disulfide $R,R$-(-)- and $S,S$-(-)-30, which were finally reduced by LiAlH$_4$ to $R$-(+) and $S$-(+)-31 with 84% yield. Their optical rotation showed mirror-imaged relationship and higher than the published data (Table 1.4), while all spectroscopic characteristics are in agreement with already published results.68
I.2.2 Synthesis of enantiopure oxorhenium(VII) complex 28

The strategy of preparing simple chiral easily sublimable MTO derivatives seems an appealing route to find a suitable candidate molecule for the experimental PV test. Our target molecule was therefore the enantiopure oxorhenium complexes (+)- and (-)-28 which are chiral derivatives of MTO, synthesized by reacting MTO with the enantiopure mercaptopropan-2-ol (-)- and (+)-31 ligands respectively in anhydrous DCM at room temperature for 3-5 hours to isolate the desired complex as yellow precipitate in quantitative yield as depicted in Scheme 1.10

The formation of 28 is characterized by the deshielding of the protons resonances corresponding to 31 after complexation (see exp. part). This complex starts to sublime after heating at 40 °C.

Table 1.4 $[\alpha_{D}^{23}]$ data in comparison with published results

<table>
<thead>
<tr>
<th></th>
<th>$S$(-)-29</th>
<th>$R$(-)-29</th>
<th>$S$, $S$(-)-30</th>
<th>$R$, $R$(-)-30</th>
<th>$S$(-)-31</th>
<th>$R$(-)-31</th>
<th>$S$(-)-28</th>
<th>$R$(-)-28</th>
</tr>
</thead>
<tbody>
<tr>
<td>Published data⁵⁸</td>
<td>-27.5</td>
<td>+199.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Our Results</td>
<td>-54.4</td>
<td>-54.4</td>
<td>+232</td>
<td>-236</td>
<td>-166</td>
<td>+172</td>
<td>+17</td>
<td>-17</td>
</tr>
</tbody>
</table>

Scheme 1.9 Synthesis of the enantioenriched ligand 1-mercapto-propan-2-ol [(R)(+)-31 and (S)(-)-31] from (R)(+)- and (S)(-)-propylene oxide respectively.

Scheme 1.10 Synthesis of the enantioenriched oxorhenium complexes $R$(-)- and $S$(-)-28 from MTO and enantioenriched $R$(-)- and $S$(-)-31 respectively.
under vacuum line, and this character assisted the formation of single crystals obtained in a Schlenk tube after sublimation under vacuum. Due to significant disorder of the methyl group coming from the two possible configurations of the stereogenic carbon center, the X-ray structure of complex 28 was solved in the non-centrosymmetric \( P2_1 \) space-group. A final Flack parameter of 0.46 was obtained, indicating the presence of a racemic mixture. As depicted in Figure 1.10, the rhenium center is pentacoordinated, the C1 atom is trans to the O3 oxygen, and the Re, O3, S, C1 lie in the same plane, while the two oxo groups are symmetrically placed on each side of this plane (for example, angles O3–Re–O1: 100.661° and O3–Re–O2: 105.031° for one of the four independent molecules of the unit cell). Consequently the oxygen atoms O1 and O2 only differ in their chemical environment due to the proximity of the asymmetric carbon C2. The Re–O bond lengths in the two oxo groups are classic (1.675 to 1.687 Å). Since oxorhenium complexes most often crystallize in a square pyramidal geometry, with an oxygen atom of the Re=O bond being placed in the apical position, the geometry around the rhenium atom is rather uncommon. Finally, in the solid state the methyl group C3 is placed in the equatorial position, and the dihedral angle O3-C2-C4-S within the five-membered ring is about -51°. The conformational analysis of complex 28 has been further explored using density functional theory (DFT) calculations, as discussed in the next section.

![Figure 1.10 X-ray crystallographic structure of the complex R-(+)-28 (only one enantiomer shown)](image)

I.2.3 IR and VCD spectroscopic studies

The experimental VCD spectra of 28 are depicted in Figure 1.11. The VCD shows a mirror-image relationship. It exhibits a strong VCD active absorption band at 1060 cm\(^{-1}\) (dissymmetry factor \( \Delta \varepsilon / \varepsilon = 1.5\times10^{-4} \)) which corresponds to the oxorhenium symmetric Re=O stretching bond (the antisymmetric stretch, although not accessible to our VCD spectrometer, is also visible on the experimental IR spectrum of Figure 1.13a at ~ 980 cm\(^{-1}\)). The presence of such bands indicates the chiral environment around the rhenium atom, although the rhenium is not a stereogenic center in itself.

VCD spectroscopy, which has been under-explored in chiral complexes, can be a very powerful tool to study the dissymmetric environment around the metal center. In order to get more insight into the latter, the IR and VCD spectra of complex 28 were calculated and compared to experiment.
The IR and VCD spectra were calculated by Radovan Bast (UPS, Toulouse). Using the R enantiomer and starting from the X-ray structure in which the S–Re bond is placed in the cis position to the Re–Me one, a potential energy scan along the O3–C2–C4–S dihedral angle at the DFT level using the B3LYP functional (def2-TZVPP basis) was carried out and two stable conformers (Figure 1.12), 28-c1 and 28-c2 at the O3–C2–C4–S dihedral angles −39.8° and +37.5° were identified for a subsequent calculation of IR and VCD spectra.

**Figure 1.11** IR and VCD spectra of (-)-31 (blue) and (+)-31 (red).

**Figure 1.12** B3LYP (def2-TZVPP basis) equilibrium structures of the theoretically studied conformers.
In order to verify the findings obtained using the relative energies and to obtain more insight into the chiral environment around the metal center, the simulated IR and VCD spectra of complex 28 were compared to the experimentally recorded spectra (Figure 1.13 a and b). We note that the match is not perfect, but the agreement between experimental and simulated spectra seems to be better for the Stuttgart ECP/6-31Gd basis, already employed in ref. 55 and 56, than for the def2-TZVPP basis set. This can probably be attributed to error cancellation effects. Overall, the VCD spectrum calculated for the R-stereochirality using the Stuttgart ECP/6-31Gd basis set reproduces the experimental spectrum for the (+) enantiomer well, except for the peak at 1160 cm$^{-1}$. The discrepancy may be due to the flexibility of the five-membered rhenacycle in solution that induces additional conformations. In conclusion, this conformational analysis and IR/VCD studies show that although the Re atom is not strictly speaking a stereogenic center, the Re–O stretching bond at 1012 cm$^{-1}$ has a strong well-defined chiroptical signature that is a testimony of the chiral environment around the metal center. This makes the enantiopure chiral oxorhenium(VII) complex 28 a good candidate for a PV measurement. For this reason, the PV vibrational shifts associated with the Re–O stretching modes were predicted using relativistic DFT calculations, as described in the following.

![Figure 1.13a](image1.png) Overlay of the simulated Boltzmann-averaged IR spectra for complex 28 (black solid lines, B3LYP, scaled), and the experimental spectrum (blue dashed line, 90 mg in 1 mL of CD$_2$Cl$_2$, 100 μm cell, 4 cm$^{-1}$ resolution, 3000 scans).

![Figure 1.13b](image2.png) Overlay of the simulated Boltzmann-averaged VCD spectra for complex R-28 (black solid lines, B3LYP, scaled), and the experimental spectra (red and blue dashed lines correspond, respectively, to (+)-28 and (-)-28, 90 mg in 1 mL of CD$_2$Cl$_2$, 100 μm cell, 4 cm$^{-1}$ resolution, 3000 scans).

I.2.4 Theoretical PV differences and supersonic molecular beam attempts

The theoretical calculations were carried out by Radovan Bast and Trond Saue (UPS, Toulouse). Table 1 summarizes the results of our computational study of the selected two conformers 28-c1 and 28-c2 (Figure 1.12), where we have studied the symmetric and anti-
symmetric Re=O stretching mode frequencies using HF and two density functional approximations, the hybrid B3LYP and the non-hybrid PBE exchange–correlation functionals. Comparing the 4-component DC Hamiltonian PV fundamental transition frequency differences Δν0→1 (Table 1.5), one can first note that our calculations predict PV vibrational frequency differences in the sub-Hz range, above the anticipated experimental uncertainty in the frequency difference measurement. This is an encouraging result for our collaboration. However, from the theoretical point of view, the significant variation of the calculated PV transition frequency differences is troubling, showing high sensitivity to both the method applied (HF or density functional approximations) and to structural changes. Comparing HF with B3LYP and PBE we see that the order of magnitude can change as well as the sign. In principle one should rather trust the DFT calculations, since they incorporate electron correlation, but the performance of DFT functional with respect to PV shifts for these heavy element compounds needs further study. If we single out one method then a slight modification of the structural periphery seems to have a major effect on the chiral environment around the heavy atom (as exemplified by the sign change between the PV shifts for 28-c1 and 28-c2 in Table 1.5).

Table 1.5 Calculated reduced masses (in amu), vibrational transition frequencies (in cm⁻¹) of the anti-symmetric and symmetric Re=O stretches for the conformers 28-c1 and 28-c2, with corresponding 4-component DC Hamiltonian PV fundamental transition frequency differences Δν0→1 (in Hz).

<table>
<thead>
<tr>
<th>Conformer</th>
<th>Mode</th>
<th>Method</th>
<th>Red. Mass</th>
<th>Harmonic</th>
<th>Fundamental</th>
<th>PV shifts</th>
</tr>
</thead>
<tbody>
<tr>
<td>28-c1</td>
<td>asym</td>
<td>HF</td>
<td>14.2074</td>
<td>1106</td>
<td>1102</td>
<td>-0.211</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B3LYP</td>
<td>15.7268</td>
<td>986</td>
<td>982</td>
<td>0.078</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PBE</td>
<td>15.8522</td>
<td>951</td>
<td>944</td>
<td>0.195</td>
</tr>
<tr>
<td></td>
<td>sym</td>
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<td>8.7326</td>
<td>1174</td>
<td>1165</td>
<td>0.344</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B3LYP</td>
<td>12.8095</td>
<td>1022</td>
<td>1010</td>
<td>0.150</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PBE</td>
<td>14.8015</td>
<td>980</td>
<td>968</td>
<td>0.036</td>
</tr>
<tr>
<td>28-c2</td>
<td>asym</td>
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<td>15.2424</td>
<td>1106</td>
<td>1102</td>
<td>0.219</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B3LYP</td>
<td>15.7515</td>
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<td>981</td>
<td>-0.119</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PBE</td>
<td>15.8566</td>
<td>950</td>
<td>944</td>
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</tr>
<tr>
<td></td>
<td>sym</td>
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<td>1175</td>
<td>1165</td>
<td>-0.056</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B3LYP</td>
<td>7.2491</td>
<td>1021</td>
<td>1010</td>
<td>-0.170</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PBE</td>
<td>13.1114</td>
<td>979</td>
<td>966</td>
<td>-0.084</td>
</tr>
</tbody>
</table>
This makes parity violation \textit{chemically} interesting, as detailed analysis of the underlying mechanism may provide a deeper understanding of the electronic structure of chiral molecules. It should be emphasized that conformational averaging, as carried out in the simulation of IR and VCD spectra in Section 4, is not an issue in the ultra-high resolution experiment since it will resolve individual lines of each conformer.

Considering the success in synthesis of enantiopure oxorhenium(VII) complex 28, verification of the chiral environment by optical rotation and VCD, and theoretical estimation that PV differences are adequate to perform the experiment, it was encouraging to test its ability to form supersonic molecular beam.

Unfortunately, 28 was not thermally stable, although at low temperature it showed several months stability. Based on $^1$H NMR, X-ray, and published results on such oxorhenium complex, 28 decomposes back to MTO with the sulfide intermediate 30, and Re(VI) dimer 32 bridged by O group (Scheme 1.11) as evidenced by X-ray diffraction studies (Figure 1.14) of single crystals obtained from slow diffusion of DCM / pentane.

![Scheme 1.11 Decomposition of 31](image)

![Figure 1.14 X-ray structure of Re(VI) dimer 32](image)

\section*{1.3 Synthesis and Characterization of OxoRhenium (VII) complex \{33\}}

The diversity of epoxides expands the design of different mercapto-alcoholate ligands. Thus, we thought about preparing ligands with higher boiling points than mercapto-1-propan-2-ol that may increase the thermal stability of the corresponding oxorhenium complex. Relying on the previous results, our target complex was the oxorhenium(VII) 33 complex bearing 2-mercaptocyclohexan-1-ol.
I.3.1 Synthesis of enantiopure 2-mercaptopcyclohexan-1-ol

Racemic 2-mercaptopcyclohexan-1-ol \(36\) can be readily prepared from cyclohexene epoxide using the same strategy used for 1-mercaptopropan-2-ol (Scheme 1.12).

Unlike enantioselective synthesis of \(31\), the separation of the two enantiomers in these steps is needed. Chiral HPLC over a chiral stationary phase was used to separate the disulfide intermediate \(35\), where we were able to isolate the two enantiomers \(RRRR\) and \(SSSS\), from the meso compound \(RRSS\) (Scheme 1.13). Then, the reduction of enantiopure sulfide intermediate by LAH goes on in a stereoselective manner. The specific rotation values \([\alpha]_D^{23}\) (Table 1.6) support also the mirror-imaged relationship.

The separation was conducted by the group of Christian Roussel and Nicolas Vanthuyne, (Marseille University). The separation of \((-)\)-35 from meso-35 and \((+)\)-35 is achieved on a chiral column, Chiralpak IC (250 x 10 mm), thermostated at 30 °C with hexane/ethanol 90/10 as mobile phase of flow-rate = 5 ml/min, and UV detection at 254 nm. \((-)\)-36 is collected between 9 and 10.5 minutes with \(ee = 98\%\), and \((+)\)-35 and meso-35 are collected together between 10.5 and 14 minutes. Then, Chiralpak IA (250 x 10 mm), thermostated at 30 °C with hexane/ethanol 50/50 as mobile phase of flow-rate = 5 ml/min and UV detection at 254 nm, was used to separate \((+)\)-35 (collected between 8 and 12 minutes with \(ee > 99.5\%\)) from meso-35 (collected between 12 and 22 minutes).

Table 1.6 \([\alpha]_D^{23}\) data for 35, 36 (C = 3.8 x 10^{-3} M), and 33 (C = 2.75 x 10^{-3} M) in DCM.

<table>
<thead>
<tr>
<th>(1S,1'S,2S,2'S)- (+)-35</th>
<th>(1R,1'R,2R,2'R)- (-)-35</th>
<th>1S,2S- (+)-36</th>
<th>1R,2R- (-)- 36</th>
<th>1S,2S- (-)- 33</th>
<th>1R,2R- (+)-33</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\alpha]_D^{23})</td>
<td>+333</td>
<td>-335</td>
<td>+102</td>
<td>-98</td>
<td>-84</td>
</tr>
</tbody>
</table>
I.3.2 Synthesis of enantiopure oxorhenium(VII) complex 33

The enantiopure ligand has proven to control or provide the Re complex with chiral environment, even if Re is not a stereogenic center itself as we previously observed in complex 28. Consequently, enantiopure oxorhenium complex 33 was prepared from MTO and enantiopure 2-mercaptocyclohexanol 36 in anhydrous DCM at room temperature for 3 hours (Scheme 1.14). After vacuum pumping of DCM, easily handled red powder was observed corresponding to 33 as verified by $^1$H NMR that showed deshielding effect of the protons resonances of 36 after complexation. Moreover, it showed a good stability in the solid state but not as solution (several weeks at room temperature) under vacuum/argon pressure as evidenced by $^1$H NMR spectroscopy that was studied relative to time (Figure 1.15). In addition, this complex possesses the ability to sublime under vacuum line at 40-60 °C.

Scheme 1.13 Separation of the enantiopure sulfide precursors 35 by chiral HPLC to prepare the enantiopure 36

Scheme 1.14 Synthesis of the enantioenriched oxorhenium complexes $^{1S,2S}$-(-)33 from MTO and enantioenriched $^{1S,2S}$-(-)36.
We see that at room temperature under argon/vacuum, the complex showed a good stability, while after 24 hours it starts to decompose in CDCl₃ (MTO starts to appear; singlet) and under atmospheric oxygen.

I.3.3 TGA/DSC analysis

In order to study the thermal stability of complex 33, thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) were carried out using TGA/DSC 1 STAR® System instrument in flowing dry nitrogen at the heating rate of 5°C/min on approximately 6 mg sample. In general, thermal analysis, as defined by ICTAC (International Confederation for Thermal Analysis and Calorimetry), is a name given to a group of techniques in which a property of the sample is monitored against time or temperature while the temperature of the sample is programmed and the sample is kept in a specified atmosphere. **TGA** measures the weight and hence mass of a sample as a function of temperature where it allows us to i) detect changes in sample mass (gain or loss), ii) determine stepwise changes in mass, iii) determine temperatures that characterize a step in the mass loss or mass gain curve, thus is very suitable technique to study the temperature stability of oxorhenium(VII) complex 33.

In **DSC**, the heat flow in and out of a sample and a reference material is measured as a function of temperature as the sample is heated, cooled or held isothermally at constant temperature. **DSC** allows us to i) detect endothermic and exothermic effects, ii) determine peak areas (transition and reaction enthalpies), iii) determine temperatures that characterize a peak or other effects, such as melting, vaporization, sublimation points, etc… iv) measure specific heat capacity.

Figure 1.15 ¹H NMR studies of 33 in solid state under argon/vacuum, atmospheric oxygen, and in solution.
The result of TGA and DSC measurements of 33 are shown in Figure 1.16. The thermogram indicates that the complex is thermally stable up to nearly 136 °C. The DSC curve shows an endothermic peak at 44 °C, but without mass loss in the TG curve. It indicates that this temperature is the melting point of the complex. At 136 °C an endothermic peak is observed in the DSC curve, corresponding to a weight loss in the TG curve, it shows that the complex undergoes thermal decomposition with the formation of volatile reaction products.

I.3.4 IR and VCD spectroscopic studies

The IR spectra of the two enantiomers coincides properly and the experimental VCD spectra of 33 (Figure 1.17) shows also a mirror-image relationship. They exhibit a strong VCD active absorption band corresponding to Re=O symmetric bond stretching at ~1025 cm\(^{-1}\) with \(\Delta v/e = 6.9 \times 10^{-5}\). Indeed, the presence of enantiopure ligand provides a chiral environment around the rhenium atom, although the rhenium is not a stereogenic center in itself.
In our attempts to determine the absolute configuration of 33 as well as the free ligand, the experimental measurement of their VCD spectra compared to the calculated spectrum, that fit properly with each others, were used to determine the absolute configuration \((1S, 2S)^{(-)}\) and \((1R, 2R)^{(+)\text{-}33}\) for oxorhenium complex 33 (see Figure 1.18) and those for the free ligand 36 and the corresponding disulfide as summarized in Schemes 1.13 and 1.14.

**Figure 1.17** Top: IR spectra of complex \((-)\text{-}33\) and \((+)-33\); bottom: VCD spectra of \((-)-33\) (blue) and \((+)-33\) (red). * Solvent

**Figure 1.18** Plain black line: calculated structure of complex with \((1R, 2R)\) stereochemistry; Dotted lines: experimental VCD spectra of enantiomers \((1R, 2R)^{(+)\text{-}33}\) (red dotted line) and \((1S, 2S)^{(-)-33}\) (blue dotted line) recorded in CD$_2$Cl$_2$. 
I.3.5 Theoretical PV energy differences and supersonic molecular beam attempts

The theoretically calculated PV shifts (B3LYP) of 33 indicated difference higher than 100 mHz. In addition, the intrinsic features of this complex concerning its reasonable stability, ability to sublime under vacuum line at 40-60 ºC, and the existence of Re=O bond stretching compatible with CO$_2$ laser in the IR region, opened a glimmer of hope towards hitting the main target which is making supersonic molecular beam. Indeed, it is still under investigation.

I.4 Synthesis and characterization of selenirane {38}

The versatile chemistry of propylene oxide is not confined only with nucleophilic substitution reactions, moreover, thiranes (cycle with S) can be synthesized in one step reaction from epoxides by using KSCN$^{73}$ or NH$_4$SCN$^{74}$ in the presence of catalytic amount of cyanuric chloride (2,4,6-trichloro-1,3,5-triazine). Scheme 1.15 describes the synthesis of 2-methylthiirane 37 from propylene epoxide.

Selenirane, or cycles-containing selenium atoms, are still very rare in the literature$^{75}$ and in our intention to prepare oxorhenium complexes with selenium-containing coordinating ligands, selenirane was prepared from propylene oxide and KSeCN using the same synthetic procedure as thiranes.

\[
\text{O} \xrightarrow{\text{NH}_4\text{SCN or KSCN}} \text{Cl} \xrightarrow{\text{N}} \text{N} \xrightarrow{\text{N}} \text{Cl} \quad \text{2-methylthiirane 37}
\]

2,4,6-trichloro-1,3,5-triazine

Scheme 1.15 The synthesis of 2-methylthiirane from propylene epoxide

I.4.1 2-Methyl selenirane: preparation and mechanism

Biphasic reaction (water/ethyl acetate) of propylene oxide and KSeCN with cyanuric chloride (Scheme 1.16) afforded 2-methylselenirane (38) after column chromatography as yellow oil with ~80% yield as identified by $^1$H NMR (Figure 1.19) and GC-MS with major peak appeared at 121 m/z indicating its exact molecular weight. Cyanuric chloride had the indispensable role, where 0.3 eq is needed for the reaction to take place effectively. The corresponding mechanism for preparation of 2-methylselenirane 38 could be the same as that explained for thiiranes$^{74}$ as described in Scheme 1.16. It enables to propose the $R$-(+) and $S$-(-) absolute configuration for 38.
I.4.2 IR and VCD spectroscopic studies

Enantiopure 2-methyl selenirane (R and S) were prepared from enantiopure S and R propylene epoxide, respectively. The reaction goes on through inversion of configuration as depicted in the mechanism (Scheme 1.16). An important advantage of VCD spectroscopy is the ability to analyze chiral molecules having no chromophore. For example, the IR and VCD spectra of the two (+) and (-) enantiomers of 2-methyl selenirane 38 were recorded (Figure 1.20) where the chiral environment of the selenirane cycle is translated into mirror image VCD spectra related to the two enantiomers. This mirror-imaged relationship has also been revealed by optical rotation {S-38: \( [\alpha]_D^{23} = -82; \) R-38: \( [\alpha]_D^{23} = +82 \)}. In order to confirm the R-(+) and (S)-(−) absolute
configuration and therefore the stereochemical course of the reaction, the calculation of the VCD spectrum is under progress in the group of Jochen Autschbach in Buffalo University.

I.4.3 Reactivity of 2-methyl selenirane 38

After the synthesis of 38, we examined its reactivity towards nucleophilic reaction with trityl-thiol deprotonated by $n$-BuLi in THF. After treatment, compound 39 was obtained with good yield (Scheme 1.17), however the attempts to deprotect sulfur by trifluoracetic acid or oxidize towards disulfide bridge failed and resulted in unidentified products.

![Figure 1.20 Top: IR spectra of complex (R) and (S)-38; bottom: VCD spectra of (R)- 38 (red) and (S)- 38 (blue).](image)

**Scheme 1.17** Reactivity of methyl selenirane towards nucleophile.
Besides nucleophilic addition, we thought about oxidizing 38 to prepare 2-methyl selenirane 1-oxide as a possible candidate for PV measurements since the Se=O stretching band lies in the same region as CO\textsubscript{2} laser band (Scheme 1.18). Theoretical calculations done by Radovan Bast showed \( \Delta E_{\text{PV}} \sim 2.4 \) mHz, but unfortunately we were not able to form the desired product probably due to the elimination of seleninic acid and formation of alkenes during oxidation of selenides as previously documented.\textsuperscript{77}

\[ \begin{array}{c}
\text{Se} \\
2\text{-methylseleniran}e \\
\text{38}
\end{array} \xrightarrow{[O]} \begin{array}{c}
\text{Se} \\
2\text{-methylseleniran}e \text{ 1-oxide}
\end{array} \]

Scheme 1.18

I.5 Asymmetric carbons with C-F stretching band coordinated to heavy Pt metal

Introduction and context of our work

I.5.1 Introduction

Organic compounds containing C-F bond stretching are very interesting for PV differences measurements, but unfortunately they are expected, by the aid of theoretical calculations, to show very small PV difference between the two enantiomers since, as we mentioned previously, PV is directly proportional to \( \sim Z^5 \). To go beyond this problem, the strategy was to prepare fluorinated chiral methanes coordinated to a heavy transition metal i.e. asymmetric carbon with C-F bond stretching and a heavy atom. This strategy could be achieved by two means: i) either functionalization of the halogenated C by the Grignard Reagent pathway then by transmetallation with M-X to produce the F-C-M target molecule (where M is a transition metal, and X is a halogen for example).

\[ X-M^{(n)} + F_{R^2}C_{R^1}M' \xrightarrow{\text{transmetallation}} F_{R^2}C-M^{(n)} + M'X \]

\[ M' = \text{Li, MgX, ZnX} \]

However, preparing these type of fluorinated Grignard reagents is very difficult, if it is impossible; ii) or by using oxidative addition of the halogenated methane to a transition metal as summarized below.

\[ M^{(n)} + X-Y \xrightarrow{\text{oxidative addition}} M_{(n+2)}X \]

\[ M_{(n+2)}Y \]
The oxidative addition reaction represents one of the most fundamental processes in transition metal chemistry, and it plays an invaluable role in many synthetic and catalytic reactions, particularly in organic synthesis. In particular, organoplatinum chemistry has been of major interest to chemists because platinum forms a wide range of complexes that are stable enough to allow their solution chemistry to be studied in great details. Furthermore, two electron oxidation and reduction reactions between three oxidation states (0, +2, and +4) are an integral part of the chemistry of platinum, with the oxidative addition process dominating the reactions of the metal in its lower oxidation states.

Ever since the report of the oxidative addition of MeI to $\text{cis-}[\text{Pt}(\text{o-tolyl})_2(\text{py})_2]$ by Doyle et al.\textsuperscript{79} in 1963, the versatility of nitrogen-donor ligands, especially diimines, had showed great effect in stabilizing the platinum(IV) products. This is most probably due to the favorable electronic (strong σ-donor/weak π-acceptor) and steric properties of the nitrogen-donors. Furthermore, the “hard” nature of nitrogen enhances the nucleophilicity of the platinum(II) center,\textsuperscript{78} an important feature in $S_{N_2}$-type reactions where electron-rich metal centers (i.e., those possessing high-energy HOMOs with substantial nonbonding character) are required to activate the substrate. The oxidative addition of a wide variety of A–B reagents, including reagents with C–X (X = halogen), Sn–X, or C–O bonds, to the electron rich platinum(II) center of [PtMe$_2$(N$^\text{N'}$)], in which N$^\text{N'}$ are various diimine ligands such as bpy (2,2'-bipyridyl) and phen (1,10-phenanthroline), has been extensively investigated by Puddephatt and coworkers\textsuperscript{78,80} who were able to predict a mechanism pathway for the oxidative addition by performing mechanistic studies of the reaction of MeI with [Pt(Ph)$_2$(bpy)]\textsuperscript{81} (Scheme 1.20).

The kinetic data were consistent with a $S_{N_2}$-type mechanism, whereby the metal center acts as a nucleophile and attacks the carbon atom of the substrate to afford the transient cationic intermediate [PtMe(Ph)$_2$(bpy)]I that subsequently rearranges to give the final product [PtIMe(Ph)$_2$(bpy)] (Scheme 1.19).

\begin{center}
\textbf{Scheme 1.19} Bimolecular ($S_{N_2}$-type) oxidative addition proposed pathway between MeI and [Pt(Ph)$_2$(bpy)].
\end{center}
This mechanism was directly evidenced by the observation of the cationic species at low temperature by using $^1$H-NMR spectroscopy in the reaction of MeI with [PtMe$_2$(bpy)] in polar solvents such as CD$_3$CN and acetone-$d_6$ (Scheme 1.20). The authors concluded that the oxidative addition step occurs simultaneously with solvent coordination and that the entry of the anion into the coordination sphere to displace the solvent proceeds very rapidly due to the large trans effect of the methyl ligand and the superior Lewis basicity of the anion over the solvent.

![Scheme 1.20 Bimolecular (S$_n$2-type) oxidative addition proposed pathway between MeI and [Pt(Me)$_2$(bpy)].](image)

**I.5.2 Synthesis of asymmetric carbon coordinated to heavy Pt(IV) metal**

Based on these interesting results, we investigated the reaction of [PtMe$_2$(bpy)] with asymmetric halogenated alkanes such as halothane (CF$_3$CHBrCl), CF$_3$CHFI, and CHFClI. Pt(IV) complex 40 was prepared by mixing [PtMe$_2$(bpy)] with big excess of halothane in anhydrous acetone at room temperature for 24 hours (Scheme 1.21), where after vacuum evaporation of the solvent a white precipitate was observed.

![Scheme 1.21 Oxidative addition of halothane to [Pt(Me)$_2$(bpy)] in acetone at room temperature for 24 hours.](image)
Similar to other Pt(IV) complexes, 40 has an octahedral geometry formed by trans oxidative addition of halothane. Table 1.7 summarizes the different bond lengths around the Pt(IV) metal center.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-40</td>
<td>Pt-41</td>
</tr>
<tr>
<td>Pt-N1</td>
<td>2.151</td>
</tr>
<tr>
<td>Pt-N2</td>
<td>2.155</td>
</tr>
<tr>
<td>Pt-C1</td>
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<tr>
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<td>2.057</td>
</tr>
<tr>
<td>Pt-C3</td>
<td>2.062</td>
</tr>
<tr>
<td>Pt-Br</td>
<td>2.535</td>
</tr>
<tr>
<td>Pt-I</td>
<td></td>
</tr>
</tbody>
</table>

In the same manner, Pt(IV) complex 41 (Scheme 1.22) was synthesized as evidenced by $^1$H (Figure 1.23) and $^{19}$F-NMR spectroscopy and X-ray diffraction (Figure 1.24). The major interest of this compound is the asymmetric carbon coordinated to heavy metal and containing C-F stretching band that is compatible with CO$_2$ laser used during PV differences investigation.
**Figure 1.23** $^1$H NMR spectrum of 41 in CD$_2$Cl$_2$ (400 MHz)

Similar to Pt(IV) complex 40, 41 has an octahedral geometry formed by trans oxidative addition of CF$_3$CFHI (Figure 1.24) where (+)-41 crystallized in a centrosymmetric space group $P2_1$ during slow evaporation of Heptane/2-PrOH (1:1) solution mixtures. The different bond lengths around the Pt(IV) metal center are summarized in Table 1.7.

**Scheme 1.22** Oxidative addition of CF$_3$CHFI to [Pt(Me)$_2$(bpy)] in acetone at room temperature for 24 hours.

In order to resolve 40 and 41 to their corresponding enantiomers, HPLC separations were performed in the group of C. Roussel and N. Vanthuyne (Chirosciences, Marseille) and were carried out using chiral stationary phase Lux-Cellulose-2 (250 x 10 mm) to afford (+)/(-)-40 and
(+)/(-)-41 with ee 94-98.5%. Table 1.8 summarizes the specific rotation values \([\alpha_d]^{23}\) for each enantiomer in CH\(_2\)Cl\(_2\) at room temperature and concentration equal to 1g/L.

<table>
<thead>
<tr>
<th></th>
<th>(-)-40</th>
<th>(+)-40</th>
<th>(-)-41</th>
<th>(+)-41</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\alpha_d]^{23})</td>
<td>-82</td>
<td>+84</td>
<td>-17</td>
<td>+15</td>
</tr>
</tbody>
</table>

1.5.3 TGA/DSC analysis

These compounds are air stable and show a good thermal stability as revealed for example by TGA/DSC analysis of 40 (Figure 1.25). Under N\(_2\) atmosphere and rate 10 \(^\circ\)C/min, an endothermic peak appeared at \(\sim 195 \, ^\circ\)C within DSC curve, accompanied with no mass loss and refers probably to the melting point of 40. The thermogram indicates the thermal stability up to 220 \(^\circ\)C where 25% of the initial mass was lost, in accordance with the DSC curve that shows an exothermic peak. Later on, at 335 \(^\circ\)C another exothermic peak is observed in the DSC curve, corresponding to 60% weight loss in the TG curve. The TG curves shows that decomposition of the complex is probably due to some carbon combustion and the exothermic peaks appeared within DSC curve are probably due to some crystallization processes.

![Figure 1.25 TGA – DSC analysis of Pt(IV) complex 40.](image)

Pt(IV) complex 40 is thermally stable up to 220 \(^\circ\)C, but unfortunately 40 and 41 don’t sublime, thus we were not able to study them within the supersonic molecular beam. However, in the
future, we are interested in studying Pulsed Laser Deposition (PLD) of these complexes instead of heating the sample to produce the molecular beam and to study their spectroscopy.

**I.6 Ru(tmhd)$_3$**

Ru(tmhd)$_3$ [$\text{tmhd} = 2,2,6,6$-tetramethylheptane$-3,5$-dione] is a neutral $D_3$-symmetric complex with a Ru$^{3+}$ and three acetyl-acetonate derivatives as ligands (Figure 1.26). Ru is a stereogenic center where the chirality is that of OC-6 complexes (octahedral) possessing three bis(chelate) substituents. The configuration of such complexes is determined by the principle of “skew line convention” which arises from the geometry of a helix.

The determination of the configuration can be easily accomplished by locating three metal-ligand bonds in front of the plane of the paper and three behind. If one turns to the right when going from the front to the rear the complex is ($\Delta$), while in the opposite case it is ($\Lambda$) (Figure 1.23).

Ru(tmhd)$_3$ can supposedly be easily synthesized from hydrated Ruthenium trichloride and tmhd = 2,2,6,6-tetramethylheptane$-3,5$-dione. The intrinsic feature of this complex is that it evaporates at 250 $^\circ$C without any dissociation, thus it shows an excellent thermal stability. Moreover, this complex can be purified by sublimation with 100% yield efficiency between 120-140 $^\circ$C. A sample was furnished to us by Jacques Bonvoisin (CEMES, Toulouse).

To study the compatibility of this complex with the experimental setup used for measuring PV difference, IR spectrum was recorded. Different sharp and broad peaks were observed between 1610 and 1130 cm$^{-1}$ that don’t coincide with the CO$_2$ laser band around 1000 cm$^{-1}$. However, the future use of Quantum Cascade Lasers (QCLs) may enable us to examine different wavelength domains. In parallel, we will try to modulate the system to obtain a more suitable molecule.
The enantiomeric resolution of the two enantiomers was of special interest for performing supersonic molecular beam experiments due to its efficient sublimation. Unfortunately, resolving the two enantiomers by chiral HPLC over different chiral transition phases failed up to now. This is due to the low polarity of the compound. We envision in the near future preparing derivatives that should be more polar and therefore easier to resolve into their enantiomers. In addition, the spectroscopy on a molecular beam will be tried.

I.7 Conclusion and prospects

In this chapter, we have described the combined efforts during recent years of physicists and chemists, experimentalists and theoreticians, toward the first observation of PV in molecular systems. This collaboration started 15 years ago when in 1999 the synthesis and separation of the enantiomers of CHFClBr by Collet and Crassous enabled a first test of PV by the LPL group, using saturation spectroscopy in absorption cells. This experiment having shown its limits, a new setup based on molecular beam spectroscopy using the two-photon Ramsey fringes technique is currently being developed. Transition metal complexes such as oxorhenium complexes display more pronounced PV effects, but it has been up to now impossible to prepare a molecular beam with such molecules. Therefore, our efforts have relied on synthesizing analogs of MTO such as 28 and 33, where the latter showed some interesting sublimable properties toward preparing a molecular beam. Moreover, we were able to prepare Pt(IV) complexes coordinated to asymmetric carbon with C-F stretching band, but these complexes didn’t sublime. Consequently, and along the same lines, we would like to investigate the oxidative addition of asymmetric halogenated hydrocarbons toward other metals such as iridium and gold in the near future.

[AuMe(L)] complexes (L = PMe₃, PPh₃, PMe₂Ph …) have reasonable stability and ability to sublime efficiently at temperatures lower than 100 °C. Puddephatt and coworkers⁸⁵ reported under certain conditions (ligand and solvent) the oxidative addition of CF₃X, mainly CF₃I, to [AuMe(L)] complexes that yields [AuMe₂(CF₃)(L)] when L = PMe₃ or PMe₂Ph (Scheme 1.23). Moreover, Sanner and coworkers⁸⁶ also reported the synthesis of air- and moisture-stable

\[
\nu/\text{cm}^{-1}
\]

Figure 1.26 IR spectra of Ru(tmhd)₃ in CD₂Cl₂

The enantiomeric resolution of the two enantiomers was of special interest for performing supersonic molecular beam experiments due to its efficient sublimation. Unfortunately, resolving the two enantiomers by chiral HPLC over different chiral transition phases failed up to now. This is due to the low polarity of the compound. We envision in the near future preparing derivatives that should be more polar and therefore easier to resolve into their enantiomers. In addition, the spectroscopy on a molecular beam will be tried.

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[Au(CF₃)₂X(PR₃)] by the oxidative addition of CF₃X (X = I, Br) to [Au(CF₃)(PR₃)] (R = Me, Et).

\[
\begin{align*}
H_3C—Au—L & \xrightarrow{CF_3I} [AuMe(CF_3)I(L)] & H_3C—Au—L & \xrightarrow{H_3C—Au—L} \text{Me_3P—Au—CH₃} + I—Au—L
\end{align*}
\]

**Scheme 1.23** Oxidative addition CF₃I to gold(I) derivatives

On the other hand, Hughes and coworkers reported the oxidative addition of different R₇I (R₇ = CF₃, CF₂CF₃, CF(CF₃)(CF₂CF₃)) to Ir(I) complexes, such as [Cp*Ir(CO)₂] and [acacIr(CO)₂], to obtain the corresponding Ir(III) complexes [Cp*(R₇)IrI(CO)] and [acac(R₇)IrI(CO)₂], respectively. The most interesting point about these complexes, either Ir(III) or Au(III), is the presence of CF₃ group that enhances the volatility, and the C-F bond stretching that can be observed using the ultra-stable CO₂ laser from the physicists.

Inspired by these complexes, we would like to study the oxidative addition of asymmetric halogenated hydrocarbons such as halothanes, CF₃CHFI, or CFHClI to Au(I) or Ir(I) derivatives to prepare different Au(III) and Ir(III) complexes as possible candidates for PV difference calculations (Scheme 1.24).

**Scheme 1.24**
References:


9. L. Kelvin (W. Thomson; 1884), *The Baltimore Lectures* (revised edn. 1904); see e.g., http://chirality.ouvaton.org/research.htm.


82 (a) R. J. Puddephatt, J. D. Scott, *Organometallics* 1985, 4, 1221; (b) M. Crespo, R. J. Puddephatt, *Organometallics* 1987, 6, 2548.


Experimental Part

Most experiments were performed using standard Schlenk techniques. Solvents were freshly distilled under argon from sodium/benzophenone (THF) or from phosphorus pentoxide (CH$_2$Cl$_2$). Starting materials were purchased from ACBR (MTO, CF$_3$CFHI) or from Aldrich. Column chromatography purifications were performed in air over silica gel (Merck Geduran 60, 0.063–0.200 mm). $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AM300 and 400. Chemical shifts were reported in parts per million (ppm) relative to Si(CH$_3$)$_4$ as external standard and compared to the literature. IR and VCD spectra were recorded on a Jasco FSV-6000 spectrometer. Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) were carried out using TGA/DSC 1 STAR$^e$ System (METTLER TOLEDO) instrument in flowing dry nitrogen. Specific rotations (in deg cm$^{-2}$ g$^{-1}$) were measured in a 10 cm thermostated quartz cell on a Jasco P1010 polarimeter. Elemental analyses were performed by the group CRMPO, University of Rennes 1.

$^{S}$-(-)-1-(tritylthio)propan-2-ol $[S$-(-)-29]$^1$

\[
\text{HO-a} \quad \text{b,c} \quad \text{SCPh$_3$} \quad \text{d}
\]

$n$-BuLi (4.78 mmol, 2.5 M, 1.91 mL) was added dropwise to a triphenylmethanethiol solution (4.67 mmol, 1.29 g) in 15 mL of distilled THF cooled at 0 $^\circ$C, where a red-rose color persisted. S-(-)-propylene oxide (4.28 mmol, 0.3 mL) was then added dropwise at 0 $^\circ$C with a change in color to pale yellow. The reaction mixture was stirred overnight, quenched with 20% AcOH in 20 mL methanol, diluted with water, and then extracted with ethyl acetate. Purification over silica gel column chromatography (pentane–ethyl acetate, 9:1) provided 1.29 g of $S$-(-)-29 as white precipitate with 90% yield.

$[\alpha]_{D}^{23} = -54.4$ (C = 10$^{-3}$ M, CH$_2$Cl$_2$).

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.40–7.50 (6H, m, H$_{\text{ar}}$), 7.19–7.37 (9H, m, H$_{\text{ar}}$), 3.43 (1H, sxt, J = 6.2 Hz, H$_b$), 2.40 (1H, d, J = 1.1 Hz, H$_c$), 2.38 (1H, s, OH), 1.07 (3H, d, J = 6.1Hz, H$_d$). (Identical to literature$^1$).

The same procedure was used for the preparation of the $R$-(+)-29 enantiomer $[\alpha]_{D}^{23} = +54.4$ (C = 10$^{-3}$ M, CH$_2$Cl$_2$).

2S,2'S-(+)-1,1'-disulfanediylbis(propan-2-ol) [S,S-(+)-30]²

![Chemical Structure](image)

S-(+)-29 (300 mg, 0.897 mmol) dissolved in 50 ml DCM/Methanol (9:1) solution was added in portions (30 min) over Iodine solution, 1.1 g in 500 ml DCM/Methanol (9:1). The reaction mixture was stirred at room temperature for 30 min, quenched with 10% aqueous Sodium thiosulfate and washed with brine. The organic layer was separated and the aqueous layer was extracted with ethyl acetate twice, dried over MgSO₄, and concentrated in vacuum to provide a dark brown precipitate which was purified by silica gel chromatography (ethanol (5%)/chloroform) to provide S,S-(+)-30 as a yellow-brown oil (81mg, 99%).

\[ [\alpha]_D^{23} = +232 \text{ (C = 2.7x10}^{-3} \text{ M, CH}_2\text{Cl}_2) \]

\(^1\)H NMR (300 MHz, CDCl₃) \( \delta \)
3.93 - 4.25 (1 H, m, \( H^a \)), 2.90 (1 H, dd, \( J=13.6, 3.4 \text{ Hz, H}^b \)), 2.69 (1 H, dd, \( J=13.7, 8.5 \text{ Hz, H}^c \)), 2.41 (1 H, br. s, \( \text{O}H \)), 1.31 (3 H, d, \( J=6.0 \text{ Hz, H}^d \))

\(^13\)C NMR (75 MHz, CDCl₃) \( \delta \)
65.93 (CH), 47.55 (CH₂), 22.02 (CH₃).

The same procedure was used for the preparation of the other enantiomer \([R,R-(+)-30]\) \[ [\alpha]_D^{23} = -236 \text{ (C = 2.7x10}^{-3} \text{ M, CH}_2\text{Cl}_2) \].

S-(+)-1-mercaptopropan-2-ol [S-(+)-31]²

![Chemical Structure](image)

100 mg of S,S-(+)-30 in THF was added dropwise of a stirring solution of LAH (3 eq.) in THF at 0°C, then stirred for 24 hrs at 50°C. The reaction was quenched with diluted HCl and then extracted with ether, dried over MgSO₄, and concentrated under vacuum to obtain S-(+)-31 (84.4 mg, 83.6%) as pale-yellow oil.

\[ [\alpha]_D^{13} = -166 \text{ (C = 5x10}^{-2} \text{ M, CH}_2\text{Cl}_2) \].

\(^1\)H NMR (300 MHz, CDCl₃) \( \delta \)
3.77 - 3.86 (m, 1 H, \( H^a \)), 2.74 (dd, 1 H, \( J=14.1, 3.6 \text{ Hz, H}^b \)), 2.5 (dd, 1 H, \( J=13.8 \text{ Hz, H}^c \)), 1.27 (d, 3 H, \( J=6.0 \text{ Hz, H}^d \)).

\(^13\)C NMR (75 MHz, CDCl₃) \( \delta \)
68.3 (CH), 33.3 (CH₂), 21.7 (CH₃).

The same procedure was used for the preparation of the other enantiomer \([R-(+)-31]: \left[ \alpha \right]_{D}^{23} = +172 \text{ (C = 5\times10^{-2} M, CH}_2\text{Cl}_2)\]

\(\text{S}-(\text{-})\text{- oxorhenium complex 28}\)

\[
\begin{align*}
\text{MTO (110 mg, 0.44 mmol) was dissolved in 10 ml distilled DCM, S}-(\text{+})\text{-31 (0.44 mmol) was then added, and the reaction mixture was stirred overnight under argon. Solvent was removed under reduced pressure to obtain 142 mg of S}-(\text{-})\text{-28 as a yellow-orange precipitate in quantitative yield.} \\
\left[ \alpha \right]_{D}^{23} = -17 \text{ (C = 3.1\times10^{-3} M, CH}_2\text{Cl}_2).}
\end{align*}
\]

\(^1\text{H NMR (300 MHz, CDCl}_3\text{)} \delta 5.30 (1 \text{ H, sxt, } J=6.1 \text{ Hz, H}^a), 3.84 (1 \text{ H, dd, } J=11.3, 5.3 \text{ Hz, H}^b), 3.46 (1 \text{ H, dd, } J=11.7, 7.2 \text{ Hz, H}^c), 2.50 (3 \text{ H, s, H}^e), 1.51 (3 \text{ H, d, } J=6.0 \text{ Hz, H}^d).

\(^{13}\text{C NMR (75 MHz, CDCl}_3\text{)} \delta 90.63 (\text{CH}^a), 46.16 (\text{CH}_2^b), 29.75 (\text{CH}_3^c), 20.82 (\text{CH}_3^d).

The same procedure was used for the preparation of the other enantiomer \(R-(+)-28: \left[ \alpha \right]_{D}^{23} = +17 \text{ (C = 3.1\times10^{-3} M, CH}_2\text{Cl}_2).\)

\(\text{2-(tritylthio)cyclohexanol [34]}\)

\[
\begin{align*}
\text{BuLi (10.5 mmol, 2.5 M, 4.2 ml) was added dropwise to triphenylmethanethiol solution (9.9 mmol; 2.73 gr) in 20 ml distilled THF cooled at 0°C, where a red-rose color persisted. Cyclohexene Oxide (9.9 mmol, 1 ml) was then added dropwise at 0°C with change in color to pale yellow. The reaction mixture was stirred for 24 hrs, quenched with 20% AcOH in 20 ml methanol, diluted with water, and then extracted with ethyl acetate. Purification over silica gel column chromatography (pentane/ethyl acetate; 9:1) provided the product 34 as a white precipitate (3.337 g, 90% yield).} \\
\text{1H NMR (400 MHz, CDCl}_3\text{)} \delta 7.48 - 7.68 (6 \text{ H, m, H}^\text{ar}), 7.11 - 7.39 (9 \text{ H, m, H}^\text{ar}), 3.29 (1 \text{ H, td, } J=9.1, 3.9 \text{ Hz, H}^a), 2.07 - 2.21 (1 \text{ H, m, H}^b), 1.94 - 2.07 (1 \text{ H, m, H}^c), 1.58 (1 \text{ H, dd, } J=9.2, 3.64 \text{ Hz, H}^d), 1.40 - 1.52 (2 \text{ H, m, H}^e), 0.83 - 1.36 (4 \text{ H, m, H}^f).
\end{align*}
\]
2,2'-disulfanediyldicyclohexanol [35]

2-(tritylthio)cyclohexanol 34 (1 gr, 2.67 mmol) dissolved in 100 ml DCM/Methanol (9:1) solution was added in portions (30 min) over Iodine solution, 1.7 g in 150 ml DCM/Methanol (9:1). The reaction mixture was stirred at room temperature for 1 hr, quenched with 10% aqueous Sodium thiosulfate and washed with brine. The organic layer was separated and the aqueous layer was extracted with ethyl acetate twice, dried over MgSO₄, and concentrated under vacuum to provide a dark brown precipitate which was purified by silica gel chromatography (ethanol (5%)/chloroform) to provide 35 as yellow-brown oil (350 mg, 99%).

\[
\begin{align*}
\text{1H NMR (400 MHz, CDCl}_3\text{) } & \delta \text{ ppm 3.53 (1 H, td, } J=9.6, 4.6 \text{ Hz, H}_a, 2.86 (1 H, br. s, O}H, 2.52 - 2.67 (1 H, m, H}_b, 2.03 - 2.21 (2 H, m, H}_c, 1.71 - 1.86 (2 H, m, H}_d, 1.21 - 1.60 (4 H, m, H}_e,f). \\
\text{13C NMR (101 MHz, CDCl}_3\text{) } & \delta \text{ ppm 72.8 (C}_a, 58.5 (C}_b, 34.2 (C}_2, 31.6 (C}_4, 26.1 (C}_5, 24.3 (C}_6). 
\end{align*}
\]

The HPLC resolution over chiral stationary phase enabled the separation of the two enantiomers RRRR-(+-)-35 and SSSS-(++)-35 that showed specific rotations \([\alpha]_{D}^{23} = +333 / -335\), respectively (C = 3.8 x 10⁻³ M, CH₂Cl₂).

1S,2S-(+-)2-mercaptocyclohexanol [1S,2S-(++)-36]

(340 mg, 1.29 mmol) of (1S,1'S,2S,2'S)-(++)-35 in THF was added dropwise to a stirring solution of LAH (3 eq.) in THF at 0°C, then stirred for 24 hrs at 50°C. The reaction was quenched with diluted HCl and then extracted with ether, dried over MgSO₄, and concentrated under vacuum to obtain (1S,2S)-(++)-36 (280 mg, 82%).

\[
\begin{align*}
[\alpha]_{D}^{23} = +102 \text{ (C = 3.8 x 10}^{-3} \text{ M, CH}_2\text{Cl}_2). \\
\text{1H NMR (400 MHz, CDCl}_3\text{) } & \delta \text{ ppm 3.13 (1 H, td, } J=9.85, 4.14 \text{ Hz, H}_a, 2.63 (1 H, br. s, O}H, 2.37 - 2.52 (1 H, m, H}_b, 1.95 - 2.15 (2 H, m, H}_c, 1.72 (1 H, dd, } J=9.3, 2.8 \text{ Hz, H}_d, 1.59 - 1.68 (1 H, m, H}_e, 1.15 - 1.39 (5 H, m, S}H, H}_e,f). 
\end{align*}
\]
$^{13}$C NMR (101 MHz, CDCl$_3$) δ 76.65 (CH$^a$), 47.68 (CH$^b$), 36.50 (CH$_2$$^c$), 34.03 (CH$_2$$^d$), 26.54 (CH$_2$$^e$), 24.72 (CH$_2$$^f$).

(1R,2R)-(−)-36 was prepared using the same procedure but starting with (1R,1'R,2R,2'R)-(−)-35: $[\alpha]_D^{23} = -98$ (C = 3.8 x 10$^{-3}$ M, CH$_2$Cl$_2$).

(1S, 2S)-(−)-oxorhenium complex 33

MTO (94 mg, 0.37 mmol) was dissolved in 7 ml distilled DCM, (1S,2S)-(+)–2-mercaptocyclohexanol 36 (50 mg, 0.37 mmol) in 3 ml DCM was then added, and the reaction mixture was stirred for 3 hrs under argon. Solvent was removed under reduced pressure to obtain 134 mg of (1S, 2S)-(−)-33 as an orange-red precipitate in quantitative yield.

$[\alpha]_D^{23} = +86$ (C = 2.75 x 10$^{-3}$ M, CH$_2$Cl$_2$).

$^1$H NMR (400 MHz, CDCl$_3$) δ 3.90 (1 H, td, $J$=10.73, 3.89 Hz, H$^a$), 3.19 - 3.32 (1 H, m, H$^b$), 2.40 (3 H, s, H$^g$), 2.05 - 2.19 (2 H, m, H$^c$), 1.65 - 1.78 (2 H, m, H$^d$), 1.31 - 1.50 (2 H, m, H$^e$), 1.08 - 1.26 (2 H, m, H$^f$).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 90.46 (CH$^a$), 57.75 (CH$^b$), 33.67 (CH$_2$$^c$), 32.62 (CH$_2$$^d$), 30.16 (CH$_3$$^g$), 24.54 (CH$_2$$^e$), 22.69 (CH$_2$$^f$).

The same procedure was used for the preparation of the other enantiomer $R$-(+)-33: $[\alpha]_D^{23} = -84$ (C = 2.75 x 10$^{-3}$ M, CH$_2$Cl$_2$).

2-methylselenirane (38)

Propylene oxide (1.429 mmol, 0.1 ml) was added to a stirring mixture of potassium selenocyanate (1.429 mmol, 206 mg) and cyanuric chloride (0.3 eq, 80 mg) and stirred for 10 min at room temperature. Then it was diluted with water, stirred overnight at room temperature, extracted with ethyl acetate, dried, and purified over silica gel chromatography to obtain the desired product 38 (138 mg, 80%) as yellow oil.
$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.07 – 4.24 (1 H, m, H$_a$), 3.31 (1 H, dd, $J$ = 12.1 Hz, 4.1 Hz, H$_b$), 3.1 (1 H, dd, 12.1 Hz, 7.5 Hz, H$_c$), 1.39 (3 H, d, $J$ = 6.4 Hz, H$_d$).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 66.7 (C), 38.29 (C$_2$H), 22.75 (C$_3$H$_3$).

The enantiopure (-)-38 and (+)-38 compounds were prepared from enantiopure R(+) - and S(-)-propylene oxide, respectively; (-)-38: $\left[\alpha\right]_{D}^{23}$ = -82; (+)-38: $\left[\alpha\right]_{D}^{23}$ = +82 (C = 2 x 10$^{-3}$ M, CH$_2$Cl$_2$).

Pt(IV) complex 40

BpyPt(II)Me$_2$ (88 mg, 0.23 mmol) prepared according to literature$^3$ was dissolved in 7 ml anhydrous acetone. Large excess of halothane was added (~40-50 eq.) and the reaction mixture was stirred in darkness under argon for 24 hours where the color was changed to pale-yellow. Evaporating the solvent by vacuum pumping resulted in the formation of the desired product 40 as white precipitate (130 mg) in quantitative yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.81 - 8.86 (1 H, m, $^2$J$_{Pt-H}$ = 18Hz, H$_6$), 8.76 – 8.80 (1 H, m, $^2$J$_{Pt-H}$ = 18Hz, H$_6$), 8.16 (2 H, m, H$_{3,3'}$), 7.98 - 8.08 (2 H, m, H$_{4,4'}$), 7.55 - 7.66 (2 H, m, H$_{5,5'}$), 4.03 - 4.30 (1 H, m, H$_a$), 1.64 (3 H, s, $^2$J$_{Pt-H}$ = 67.0 Hz, H$_b$), 1.52 (3 H, s, $^2$J$_{Pt-H}$ = 67.9 Hz, H$_c$).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -66.74 (m).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 153.87 (C), 153.45 (C), 147.05 (CH, $J_{Pt-C}$ = 8.0 Hz), 146.59 (CH, $J_{Pt-C}$ = 14.2 Hz), 137.81 (CH, $J_{Pt-C}$ = 3.7 Hz), 137.75 (CH, $J_{Pt-C}$ = 3.1 Hz), 125.03 (CH, $J_{Pt-C}$ = 12.3 Hz), 124.98 (CH, $J_{Pt-C}$ = 13.5 Hz), 124.73 CF$_3$, q, $J_{C-F}$ = 278.8 Hz), 121.67 (CH, $J_{Pt-C}$ = 8.6 Hz), 121.44 (CH, $J_{Pt-C}$ = 9.2 Hz), 35.90 (CH, q, $J_{C-F}$ = 32.6 Hz), 0 (CH$_3$, $J_{Pt-C}$ = 611 Hz), -4.06 (CH$_3$, $J_{Pt-C}$ = 611Hz).

$^3$ G. Minghetti, S. Stoccoro, M. A. Cinellu, B. Soro, A. Zucca, Organometallics 2003, 22, 4770.
Pt(IV) complex 41

\[
\text{bpyPt(II)Me}_2 (88 \text{ mg, 0.23 mmol}) \text{ was dissolved in 7 ml anhydrous acetone. Large excess of CF}_3\text{-CHFI was added (~40-50 eq.) and the reaction mixture was stirred in darkness under argon for 24 hours where the color was changed to pale-yellow. Evaporating the solvent by vacuum pumping resulted in the formation of the desired product 41 as white precipitate (140 mg) in quantitative yield.}
\]

\[
\begin{align*}
1^1\text{H NMR (400 MHz, CDCl}_3) & \delta 8.68 - 8.83 (2 \text{ H, m, H}^{6,6'}, 8.19 - 8.21 (2 \text{ H, m, H}^{3,3'}), 8.04 - 8.08 (2 \text{ H, m, H}^{5,5'}), 7.52 - 7.67 (2 \text{ H, m, H}^6), 4.85 - 5.09 (1 \text{ H, m, H}^a), 1.71 (3 \text{ H, s, }^2J_{\text{Pt-H}} = 68.5 \text{ Hz, H}^b), 1.49 (3 \text{ H, s, }^2J_{\text{Pt-H}} = 69.0 \text{ Hz, H}^c) \\
19^1\text{F NMR (376 MHz, CD}_2\text{Cl}_2) & \delta -73.9 (m) \\
13^1\text{C NMR (101 MHz, CD}_2\text{Cl}_2) & \delta 156.06 (C), 155.71 (C), 148.3 - 148.6 (m, 2CH), 139.74 - 139.78 (m, 2CH), 126.7 - 127 (m, 2CH), 123.6 - 123.8 (m, 2CH), 77.9 - 80.8 (m, CH), -3.8 (CH\text{, }^3J_{\text{Pt-C}} = 614 \text{ Hz, CH}), -6.0 (CH\text{, }^3J_{\text{Pt-C}} = 614\text{Hz}), \text{one C missing.}
\end{align*}
\]

Analytical chiral HPLC separation for compound 35

The sample is dissolved in ethanol, injected on the chiral columns, and detected with an UV detector at 254 nm and a polarimeter. The flow-rate is 1 ml/min.

Major products are meso-35, (-)-35 and (+)-35, sign given by the on-line polarimeter in the mobile phase used.

<table>
<thead>
<tr>
<th>Column</th>
<th>Mobile Phase</th>
<th>t meso</th>
<th>t (-)</th>
<th>t (+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chiralpak IA</td>
<td>Hexane/ethanol (50/50)</td>
<td>8.42</td>
<td>9.40</td>
<td>14.17</td>
</tr>
<tr>
<td>Chiralpak IA</td>
<td>Hexane/2-PrOH (50/50)</td>
<td>4.82</td>
<td>5.30</td>
<td>5.94</td>
</tr>
<tr>
<td>Chiralpak IC</td>
<td>Hexane/ethanol (90/10)</td>
<td>11.01</td>
<td>9.39</td>
<td>11.01</td>
</tr>
<tr>
<td>Chiralpak ID</td>
<td>Hexane/ethanol (70/30)</td>
<td>9.87</td>
<td>11.47</td>
<td>17.71</td>
</tr>
</tbody>
</table>
Two minor enantiomers can be seen on Chiralpak IC, eluted at 6.77 and 7.61 minutes.

**Semi-preparative separation for compound 35:**

Injections on two different chiral columns are needed to separate the different compounds

1 – First step on Chiralpak IC.

- Sample preparation: About 930 mg of compound 35 are dissolved in 52 ml of ethanol.
- Chromatographic conditions: Chiralpak IC (250 x 10 mm), thermostated at 30 °C, hexane/ethanol 90/10 as mobile phase, flow-rate = 5 ml/min, UV detection at 254 nm.
- Injections: 130 times 400 µL, every 14 minutes.
- Collection: both minor enantiomers (35-imp) are collected between 7 and 9 minutes, (-)-35 is collected between 9 and 10.5 minutes and (+)-35 and meso-35 are collected together between 10.5 and 14 minutes.
- First fraction: 16 mg of 35-imp
- Second fraction: 236 mg of (-)-35 with ee = 98%

2 – Second step on Chiralpak IA.

- Sample preparation: About 600 mg of (+)-35 and meso-35 are dissolved in 32 ml of ethanol.
- Chromatographic conditions: Chiralpak IA (250 x 10 mm), thermostated at 30 °C, hexane/ethanol 50/50 as mobile phase, flow-rate = 5 ml/min, UV detection at 254 nm.
- Injections: 40 times 800 µL, every 25 minutes.
- Collection: meso-35 is collected between 8 and 12 minutes and (+)-35 between 12 and 22 minutes.
- First fraction: 337 mg of meso-35
- Second fraction: 215 mg of (+)-35 with ee > 99.5%
Chromatograms of the collected fractions:

**meso-35**

Analytical chiral HPLC separation for compound 40

- The sample is dissolved in ethanol, injected on the chiral columns, and detected with an UV detector at 254 nm and CD 254nm. The flow-rate is 1 mL/min.
Semi-preparative separation for compound 40

- Sample preparation: About 98 mg of compound 40 are dissolved in 30 mL of ethanol.

- Chromatographic conditions: Lux-Cellulose-2 (250 x 10 mm), hexane / ethanol (7/3) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.

- Injections: 200 times 150 μL, every 2.5 minutes.

- Collection: the first eluted enantiomer is collected between 11.1 and 11.7 minutes and the second one between 12.3 and 12.9 minutes.

- First fraction: 43 mg of the first eluted ((-, CD 254 nm)-enantiomer) with ee > 98.5%

- Second fraction: 40 mg of the second eluted ((+, CD 254 nm)-enantiomer) with ee > 97.5%

- Chromatograms of the collected enantiomers:
Lux-Cellulose-2
Heptane / ethanol (7/3)

UV Results

<table>
<thead>
<tr>
<th>Retention Time</th>
<th>Area</th>
<th>Area %s</th>
<th>Capacity factor</th>
<th>Relative RT</th>
<th>Resolution (USP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.78</td>
<td>59744</td>
<td>1.08</td>
<td>2.93</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>12.73</td>
<td>5462815</td>
<td>98.92</td>
<td>3.24</td>
<td>0.00</td>
<td>1.93</td>
</tr>
</tbody>
</table>

Lux-Cellulose-2
Heptane / ethanol (7/3)

UV Results

<table>
<thead>
<tr>
<th>Retention Time</th>
<th>Area</th>
<th>Area %s</th>
<th>Capacity factor</th>
<th>Relative RT</th>
<th>Resolution (USP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.84</td>
<td>6946246</td>
<td>99.36</td>
<td>2.95</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>12.81</td>
<td>44490</td>
<td>0.64</td>
<td>3.27</td>
<td>0.00</td>
<td>2.09</td>
</tr>
</tbody>
</table>
Analytical chiral HPLC separation for compound 41

- The sample is dissolved in ethanol, injected on the chiral columns, and detected with an UV detector at 254 nm and CD 254nm. The flow-rate is 1 mL/min.

Semi-preparative separation for compound 41

- Sample preparation: About 170 mg of compound 41 are dissolved in 170 mL of ethanol.

- Chromatographic conditions: Lux-Cellulose-2 (250 x 10 mm), hexane / 2-PrOH (1/1) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.

- Injections: 180 times 950 μL, every 8 minutes.

- Collection: the first eluted enantiomer is collected between 8.7 and 9.6 minutes and the second one between 10.3 and 11.6 minutes.

- First fraction: 63 mg of the first eluted ((+, CD 254 nm)-enantiomer) with ee = 96%

- Second fraction: 71 mg of the second eluted ((-, CD 254 nm)-enantiomer) with ee = 94.5%

- Chromatograms of the collected enantiomers:
Lux-Cellulose-2
Heptane / 2-PrOH (1/1)

<table>
<thead>
<tr>
<th>UV Results</th>
<th>Retention Time</th>
<th>Area</th>
<th>Area %</th>
<th>Capacity factor</th>
<th>Relative RT</th>
<th>Resolution (USP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.94</td>
<td>8239288</td>
<td>98.00</td>
<td></td>
<td>2.31</td>
<td>1.00</td>
<td>0.00</td>
</tr>
<tr>
<td>12.02</td>
<td>168493</td>
<td>2.00</td>
<td></td>
<td>3.01</td>
<td>1.30</td>
<td>3.63</td>
</tr>
</tbody>
</table>
VCD measurements

Samples of (+)- / (-)-28, ~9 mg per 200 μL CD₂Cl₂, and (+)- / (-)-33, 10 mg in 0.5 mL CD₂Cl₂, and (+)- / (-)-38, ~90 mg per 1 mL CD₂Cl₂ were placed in a 200 μm, 500 μm, and 500 μm path length cells with BaF2 windows, respectively. IR and VCD spectra were recorded on a Jasco FVS-6000 VCD spectrometer with 3000 scans acquired and averaged at 4 cm⁻¹ resolution. An overlay of the observed spectra for the two enantiomers, combined with the simulated Boltzmann-averaged VCD spectrum for complex R-28 in two different basis sets, is presented in Fig. 1.13. The average VCD spectrum of the two enantiomers was used as the VCD baseline.
II.1 Introduction

[n]-Helicenes are molecules with ortho-fused aromatic and/or heteroaromatic rings (n = number of fused rings) that adopt a helical shape as a consequence of the steric hindrance between the terminal rings. They are characterized by intriguing features such as extended π-conjugation, chirality, huge optical rotation values, ability to self-assemble, etc ... From n ≥ 5, the steric repulsion between terminal rings makes the helicenes configurationally stable and therefore renders them chiral even though they have no asymmetric carbon (inherent chirality). They can wind in opposite directions, left-handed and right-handed. On the basis of the helicity rule proposed by Cahn, Ingold, and Prelog in 1966, a left-handed helix is designated “minus” and denoted by $M$ whereas a right handed one is designated “plus” and denoted by $P$. (Figure 2.1).

![Figure 2.1 Schematic representation of two mirror images carbo[6]helicene with M and P helicity](image)

After the first synthesis of helicenes 42 and 43 by Meisenheimer and Witte in 1903 (Scheme 2.1), then the synthesis and resolution of carbo[6]helicene (also named hexahelicene) by Newman in 1950s, a great deal of work has been carried out on helicenes with a backbone composed either of carbon atoms only or containing heteroatoms. In the latter case, particular interest has been paid to thiahelicenes, a class of molecules with alternating thiophene and benzene rings.

![Scheme 2.1](image)

Currently, azahelicenes are gaining increasing interest due to the presence of nitrogen atom that has the possibility to exhibit fascinating coordination chemistry, as well as shows good reactivity towards the change in the pH environment, alkylation, and oxidation reagents. The
involvement of the nitrogen lone pair in any of these reactions, either coordination, protonation/deprotonation, or methylation can induce a peculiar impact on the chiroptical properties of the helicene molecule.

II.2 Properties of azahelicenes

In 2003, Venkataraman and co-workers reported the first triarylamine-based helicenes 44 and 45 capable of emitting circularly polarized luminescence\(^{8a}\) (CPL; for more details see section II.7.1) as shown in Figure 2.2, where the preferential absorption / emission of left- and right-handed circularly polarized light, expressed in circular dichroism (CD) and CPL spectra, are identical in magnitude and opposite in sign for the two enantiomeric species.

![Figure 2.2](image)

Figure 2.2 (A) and (C) CD spectra 44 and 45 in CHCl\(_3\); (B) and (D) CPL spectra of 44 and 45 in CHCl\(_3\), respectively.

Caronna and coworkers investigated the fluorescence properties of aza-helicenium derivatives for cell imaging.\(^{9a}\) Hude fibroblast cells were incubated in the presence of 46 for different times. Interestingly, the images recorded at the end of the uptake process (60 min - Figure 2.3) display dual color fluorescence observable in different cell regions.
The green color emitted might suggest that 46 is localized in the nuclear region of the cells due to the high affinity of helicenium salts toward DNA$^{9b}$. The more external parts of the cells appeared as red colored is assigned to the emission from helicenium aggregate species which can be formed in the cytoplasm due to the reduced solubilization of the salt.

To investigate the protonation effect on chiroptical properties of aza helicenes, Inoue and coworkers performed theoretical and experimental studies on the modification of circular dichroism spectroscopy of mono and diazonia[6]helicenes.$^{10}$ The Cotton effects (CE) at the $\mathbf{1B}_{a}$ and $\mathbf{1B}_{b}$ bands shown in Figure 2.4 are responsible for the helical chirality of the helicenes, while the weak CE at $\mathbf{1L}_{b}$ band is responsible to various factors such as electronic and steric effects. After protonation, the insignificant alternations at the major $\mathbf{1B}_{a}$ and $\mathbf{1B}_{b}$ bands were attributed to weak strength of the cation-$\pi$ interaction to reduce the helix pitch, while a large CE enhancement was observed at the $\mathbf{1L}_{b}$ for monoazonia[6]helicenes while less intense for diazonia[6]helicenes due to the repulsive cation-cation-interactions.

Crassous and coworkers exploited the coordination ability of phosphole-modified aza[6]helicenes 53 (see paragraph II.3) to study the complexation impact of metallic ions of the chiroptical properties of these $\pi$-conjugated ditopic ligands.$^{11a}$ They verified the efficiency in
organizing the heteroditopic ligands around the distorted square planar Pd$^{II}$ metal center that showed a profound impact on the chiroptical properties of the assemblies in comparison with the tetrahedral Cu$^I$ center (Figure 2.5).

In addition, their high optical stability and rigid helical framework of azahelicenes makes them promising candidates for the fabrication of chiral catalysts$^{12}$ and ligands in asymmetric synthesis as recently issued by Captain and Takenaka in the first application of N-oxide functionalized-enantiopure 1-aza-[6]helicene 47 as a catalyst for enantioselective ring opening of meso epoxides (Scheme 2.2)$^{12}$.

More recently, Fuchter, Campbell and coworkers demonstrated the first circularly polarized responsive photo-FETs based on enantiopure 1-aza-[6]helicene 51 as a chiral organic semiconductor.$^{13}$ This particular helicene is a hole-transporting material that uniformly distributes across a surface and produces well-behaved OFET characteristics (Figure 2.6a). Indeed, OFETs with a (+)-1-aza[6]helicene semiconductor layer show a response to right-handed ($\sigma^+$) but not to left-handed ($\sigma^-$) circularly polarized light, and OFETs with a (-)-1-aza[6]helicene semiconductor layer show a response to left-handed ($\sigma^-$) but not to right-handed ($\sigma^+$) circularly polarized light (Figure 2.6b).
II.3 Synthesis of azahelicenes

Despite these exciting preliminary applications, one of the key limitations for azahelicene study is access to structural diversity and significant quantities of material. Only limited reports have concerned the synthesis of helicene enantiomers on >1 g scale. As a reason, different synthetic strategies were performed to synthesize aza-[n]-helicenes.

II.3.1 Photocyclization

Stilbene photocyclization is the electrocyclization of stilbenic systems upon ultraviolet irradiation in the presence of an oxidant, usually iodine balls, and that results in fused aromatic systems. This method requires highly diluted solutions to prevent intermolecular interactions such as [2+2] cyclo addition.

The mechanistic pathway is summarized in Scheme 2.3. UV irradiation isomerizes trans-stilbene to cis-stilbene that possesses the necessary geometry for the intramolecular cyclisation, which in turn leads to the formation of dihydrophenanthrene. Finally, the oxidation of dihydrophenanthrene rearomatizes the system. In this step, iodine is generally used in catalytic amount in the presence of oxygen; however, sometimes it can be used equivalently in an inert atmosphere using excess of propylene oxide or THF to capture the iodhydric acid formed during the rearomatization of the system. For our reactions, an immersion mercury lamp was used (either a 150W or a 700W).
Using the photocyclization strategy, Martin and Deblecker reported in 1969 the synthesis 4-aza[6]helicene \(48\)\(^{19}\) and Caronna and coworkers reported in 2005 the synthesis of 6-aza[5]helicene \(49\)\(^{20}\), then Ben Hassine and coworkers reported the synthesis of 3-aza[6]helicene \(50\)\(^{21}\) with 1-aza[6]helicene \(51\) as minor product from the corresponding stilbene as depicted in Scheme 2.4. Note that the nomenclature for helicenes is the one recommended by IUPAC.

More recently, Crassous, Réau and coworkers reported the synthesis of 4-aza[6]helicene bearing diyne \(52\)\(^{11}\). The oxidative coupling of diyne with zirconocene dichloride followed by \([\text{ZrCP}_2]/\text{PPh}\) exchange, or what is known as the Fugan-Nugent route,\(^{22}\) gave an interesting \(\pi\)-conjugated phosphole-azahelicene \(53\) (Scheme 2.5) that acts as P,N chelating ligand\(^{11}\) as previously described.
Stilbenoid precursors are easy to prepare, however they require several synthetic steps. The photocyclization is a convenient method for the synthesis of a variety of helicenes in mild reaction conditions, nevertheless, it is difficult to employ in large scale preparation (one of the key limitations for azahelicene study) and also lacks tolerance to some functional groups, such as NH$_2$ and NO$_2$, which accelerate intersystem crossing and prevent cyclization.$^{23}$

In addition, the nitrogen atom lone pair might quench the reaction due to their proton affinity i.e. capture HI acid formed to form a salt that precipitates during reaction. Moreover, the photochemical approach can fail sometimes with azahelicenes$^{20,24}$ as evidenced by Caronna and coworkers where they failed to prepare 7-aza[5]helicene 54 even under the most drastic conditions,$^{25}$ and all the attempts to prepare the 2-aza[5]helicene gave the 7-azabenzo[ghi]perylene 55 as the only product (Scheme 2.6).

Photocyclization reaction is not totally regioselective, some side products can be obtained from [2+2] cycloaddition or non-ortho position cyclization. Also, it is not enantioselective; the two enantiomers are prepared in equal portions then usually separated by HPLC over chiral
stationary phase. However, it can be diastereoselective. Angela Marinetti and coworkers reported recently that the photocyclization of stilbenic system with diastereomerically pure P-menthyl-substituted phosphindole oxide can be regio- and stereocnemically controlled\textsuperscript{26} to obtain the enantiopure phosphindole-based [6]helicene 56 as summarized in Scheme 2.7. Under the Hg lamp, compound 56 underwent subsequent [2+2] cycloaddition to 56'.

\textbf{Scheme 2.7} Diastereoselective synthesis of a phosphindole-based [6]helicene 56 and [2+2] cycloaddition to 56'

The negative drawbacks of photocyclization derived the attention toward the development of new synthetic routes. Selected examples are presented in the next paragraphs.

\textbf{II.3.2 Metal induced synthesis}

\textit{a- Stille-Kelly coupling}

The Stille–Kelly reaction is the Pd-catalyzed intramolecular aryl dihalide cyclization using ditin reagents.\textsuperscript{27} Following this strategy, Staab and co-workers reported the synthesis 1,16-diaza[6]helicene 57 in 52% yield (Scheme 2.8a),\textsuperscript{24b} and Takenaka and co-workers synthesized 1-azahelicene 58 in 61% yield (Scheme 2.8b).\textsuperscript{12} The precursor is easily prepared by a highly Z-selective Wittig reaction of the halogen substituents. This synthetic strategy is of considerable practical utility, since different helicenes can be easily prepared using different Wittig reaction precursors.

This route can be accessible towards gram scale synthesis of helicenes; however, it has several drawbacks. For example, Takenaka's route involves seven linear steps with the use of significant amounts of hexamethylditin reagent.
b- Metal-catalyzed cycloisomerization

Stary, Stara, and coworkers used the Co(I)-catalyzed [2+2+2] cycloisomerization method to prepare 1- and 2-aza[6] helicenes (51 and 59) and 1,14-diaza[5]helicene 60 by modifying the triyne precursors as summarized in Scheme 2.9. This strategy relies on a [2+2+2] cyclotrimerization of an aromatic triyne in the presence of a Co(I) catalyst to build the helical scaffold, then re-aromatization using MnO₂ in combination with microwave irradiation afforded the aza[n]helicenes (n = 5, 6 ...). However this route comprises of eight linear steps and requires 30 equivalent of MnO₂ as an oxidant.

Recently, Storch and co-workers used double cycloisomerization of the nitrogen-containing biphenylnaphthalene to synthesize aza[6]helicene 60 and 61 in ~80% yield in the presence of PtCl₄ and InCl₃ (Scheme 2.10).
This sequence of reactions provides a synthetic route to helicenes in two steps from simply accessible building blocks. Furthermore, this method enables the introduction of substituents into the hexahelicene skeleton.\(^{30}\)

More recently, Fuchter and coworkers developed a rapid and robust strategy to prepare functionalized 1-aza[6]helicenes\(^{31}\) through PtCl\(_4\)-catalyzed cycloisomerization, in a similar manner as Storch strategy but without using InCl\(_3\) (Scheme 2.11). This method allows the access towards the gram-scale synthesis of helicene molecules, and more importantly it is suitable for the axial to helical chiral relay i.e. the highly hindered biaryl phenanthroline precursor could be isolated as enantiopure axially chiral atropisomers using semipreparative chiral HPLC that were highly stable to racemization. Therefore, using such cycloisomerization chemistry will ensure the high-fidelity transfer of stereochemical information from biaryl to helicene. Interestingly, this intrinsic property can open-up the possibility of an enantioselective synthesis of azahelicenes using this strategy via enantioselective synthesis of biaryles.

**c- Ortho-metalation (metallahelicenes synthesis)**

Away from organic helicenes prepared by C-C bond formation, Crassous and coworkers recently developed a short and efficient strategy to synthesize helicene derivatives with a transition metal incorporated into their ortho-annulated \(\pi\)-conjugated backbones,\(^{32}\) where the construction of the helical backbone is achieved using simple and practical ortho-metalation reaction with [4]helical ligand comprising phenyl-pyridine-like functionality. (Scheme 2.12)
The peculiarity of metallahelicenes comes from 1) π-conjugated helical structure with huge chiroptical properties,
2) distinctive properties of transition metals (redox behavior, ligand exchanges, metal-metal interactions, metal-ligand interactions, and so on), that can provide the helicene with unusual photophysical properties for example, and 3) structural engineering of the helicene scaffolds can be performed by varying either the ligands or the nature of the metal.

II.4 Towards Helicenes bearing bipyridine functionality

After the development of metallahelicenes and phosphole-azahelicenes by our group, and emphasizing the huge impact of metal coordination on their chiroptical properties, we were interested in synthesizing a new class of helicenes bearing the 2,2’-bipyridine functionality. 2,2’-Bipyridine has received unprecedented attention as a ligand due to its remarkable chemistry and high stability against moisture and oxygen, unlike many other common systems such as cyclopentadienyls and phosphines. It was classified as the “most widely used ligand” because of its exceptional coordination chemistry, where 2,2’-bipyridine complexes of virtually every metal in the periodic table have been described. This \(N^N’\) chelating ligand presents two nitrogen atoms coordinated to the metal center through their lone pairs that results in extremely stable species even with more labile ions. Indeed, the two excellent primary σ-dative interactions are further enhanced by the opportunities for overlapping between the aromatic π-system and the d orbitals of coordinated transition metal ions.

The diversity of \(N\)-heterocyclic structures had driven many interests towards the development of different synthetic approaches to provide chiral derivatives. Chiral bipyridine ligands have revealed potential interests as chiral inducers especially in asymmetric catalysis. On the other hand, helicenes display chiral environment through their helical shape and display high chiroptical activity due to their extended π-conjugated helical backbone formed of ortho-fused aromatic rings. Thus, helicenes bearing bi-pyridine functionalization are interesting compounds because they posses different characteristic properties within the same molecule; chirality, coordinating ability, and π-extended system that can yield unprecedented chiral coordination or organometallic complexes combining strong chiroptical properties with emission or redox activities furnished by the metallic ion.

Scheme 2.12 Synthesis of platinum helicenes through ortho-metalation
Very few examples of helicenes bearing bi-pyridine are known in the literature. The first [9]helicene-2,2’-bipyridine (Scheme 2.13a) was reported by Diederich and coworkers in 1991, and the second one was issued recently by Takenaka and coworkers who synthesized [6]helical chiral 2,2’-bipyridine N-monoxide (Scheme 2.13b) as a catalyst for enantioselective propargylation of aldehydes. On the other hand, Katz reported in 1999 the synthesis of [7]helicene with 1,10-phenanthroline as $N^N'$ chelating ligand (Scheme 2.13c).

Scheme 2.13 Helical 2,2’-bipyridine examples reported in the literature.

In this chapter, the synthesis of 3-pyridyl-4-aza[4]helicene (62), 3-pyridyl-4-aza[6]helicene (63), 3,14-dipyrildyl-4,13-diaza[6]helicene (64), are described. The ligands were fully characterized by multinuclear NMR spectroscopy and elemental analysis. In case of [6]helicenes, they were resolved into their (+) and (-) enantiomers by using HPLC over chiral stationary phase. The photophysics (UV/vis and luminescence) and chiroptical properties (optical rotation, electronic and vibrational circular dichroism) of the enantiopure pure helicenes were measured experimentally.
II.5 Results and discussion

Scheme 2.14 summarizes the retro-synthetic routes to prepare the different [n]helicene-bipyridines 62-64.

Scheme 2.15 Synthesis of 2,2'-bipyridine-6-carbaldehyde 68

2,2'-Bipyridine-6-carbaldehyde was prepared in two steps according to a known procedure as described in Scheme 2.15: 1) The Negishi coupling\textsuperscript{41} between 2,6-dibromopyridine 65 and 2-pyridyl-zinc(II) bromide 66 in the presence of Pd(PPh\textsubscript{3})\textsubscript{4} as a catalyst at room temperature for 24 hours yielded 73% of 6-bromo-2,2'-bipyridine 67, then 2) the formylation of 67 was achieved by \textit{n}-BuLi / DMF at low temperature to obtain 2,2'-bipyridine-6-carbaldehyde 68 in 81% yield.\textsuperscript{42}

II.5.1 3-(2-Pyridyl)-4-aza[4]helicene (62)

\textit{a)- Synthesis}

The synthesis of 3-(2-pyridyl)-4-aza[4]helicene 62 takes place in two steps (Scheme 2.16). The first step is a Wittig reaction between the 2-methyl-naphtalene-triphenyl-phosphonium bromide 69 and 2,2'-bipyridine-6-carbaldehyde 68. In this step, the strong base (\textit{n}-
butyllithium) used will deprotonate the phosphonium salt and forms a phosphorus ylide. THF is used as solvent at -78 °C to avoid the formation of byproducts. The aldehyde is then added to the solution and a mixture of cis and trans isomers of stilbene system 70 are obtained, which is subsequently photocyclized using a 150 W mercury lamp in diluted Toluene/THF (9:1) solution with catalytic I$_2$ to form the ligand 62.

In absence of THF, the HI formed during the reaction progress is captured by the stilbenic system or the precursor before re-aromatization to form a precipitated salt that prevents the formation of the desired product. To circumvent this problem, small amount of THF is used as a proton scavenger.

**b) $^1$H NMR spectroscopic studies**

The structure characterization of the target products was ascertained by $^{13}$C and $^1$H NMR spectroscopy. In the $^1$H NMR spectrum, the formation of stilbenic system 70 is verified by the disappearance of the aldehyde singlet at 10.2 ppm in CDCl$_3$ and the appearance of two $AB$ systems corresponding to trans and cis isomers with $^3J = 12$ and 7 Hz, respectively (See exp. part). The disappearance of these $AB$ systems and the appearance of one set of protons resonances between 7.2 and 9.5 ppm with the loss of 2 protons determined the photocyclization of the 70 and the formation of 62 (Figure 2.7).
Note that $H_1$ and $H_{12}$ appear at deshielded chemical shifts, which is typical for [4]helicenes. The complete assignment was achieved with the help of 2D-COSY NMR.

**c)- X-Ray diffraction studies**

Single crystals of 62 were obtained by slow evaporation of CD$_2$Cl$_2$ with few drops of water in NMR tube. The ligand crystallizes in non-centrosymmetric orthorhombic space group $P2_12_12_1$ with one molecule in the asymmetric unit (Figure 2.8). The helicity (dihedral angle between the two terminal aromatic rings) of 62 is 25.13º, and the distortion$^{43}$ of its molecular structure, which is defined by the sum of the two torsion angles of $C_1$-$C_{12c}$-$C_{12b}$-$C_{12a}$ and $C_{12c}$-$C_{12b}$-$C_{12a}$-$C_{12}$, is 32.54º is consistent with a helical structure and comparable with aza[4]helicenes.$^{44}$

![Figure 2.8 X-ray molecular structure of azahelicene 62](image)

The 2 pyridyl moieties are in mutual *trans* positions. Moreover, it is noteworthy to mention that in the bulk solid, the [4]helicenes are right-handed ($P$) and they stack on top of each others in infinite columns in which short intermolecular distances are observed between the ligands (intermolecular $\pi$-distances c.a. 3.47-3.7 Å) revealing $\pi$-$\pi$ interaction. (Figure 2.9)

![Figure 2.9 (a) Columnar stacks of 62; (b) Intermolecular $\pi$-$\pi$ interaction between ligands](image)

II.5.2 3-(2-Pyridyl)-4-aza[6]helicene (63)

**a)- Synthesis**

Ligand 63 is synthesized by using the same strategy followed in 62 but using 2-methylbenzophenanthrenetriphenylphosphonium bromide$^{45}$ salt 71 to prepare the *cis-trans*
stilbenoid precursor (Scheme 2.17). Photocyclization of 72 with a 150 W mercury lamp yielded ~40% of [6] helicene but contaminated with starting material. The purification of 63 over silica gel column chromatography was difficult since the helicene possesses the same R_f value as that for stilbene system. However, using a 700 W mercury lamp (with 80% efficiency) yielded >90% of [6] helicene 63 without contamination of stilbenoid precursor.

**Scheme 2.17 Synthesis of [6]helicene 63 bearing 2,2’-bipyridine functionality**

b) - \(^1\)H NMR spectroscopic studies

\(^1\)H NMR spectrum of 63 shows one set of 18 protons resonances between 6.5 and 8.7 ppm (Figure 2.10). In addition to the disappearance of the AB systems corresponding to cis-trans stilbene system, the appearance of ddd proton signal at ~6.6 ppm referred to H\(_{15}\) characterizes the formation of the [6]helicene moiety.

**Figure 2.10** \(^1\)H NMR of ligand 63 in CD\(_2\)Cl\(_2\) (400 MHz).

II.5.3 3,14-Di-(2-pyridyl)-4,13-diaza[6]helicene (64)

a)- Synthesis

The synthesis of diaza[6]helicene 64 is done in two steps (Scheme 2.18). Double Wittig reaction involving 2,7-bismethylnaphtalenebistriphenylphosphonium dibromide\(^{46}\) 73 and two equivalents of 68 yielded 74 with 92% yield The second step is a double photocyclization using
700 W mercury lamp (80 % efficiency) to obtain 64 in ~83% yield, in contrast to the low efficiency of the 150 W lamp (~20 % yield product with difficulty in purification).

\[
\text{Scheme 2.18 Synthesis of [6]helicene 64 with bis-bipyridine.}
\]

**b) - \textbf{1}H NMR spectroscopic studies**

The complicated \textsuperscript{1}H NMR of the stilbene system due to the presence of different \textit{cis}/\textit{trans} isomers (see exp. part) is simplified to one set of protons resonances between 7.0 and 8.7 ppm (Figure 2.11). The 10 protons integration is due to the \textit{C}_2-symmetry.

\[
\text{Figure 2.11 1}H \text{ NMR of ligand 64 in CD}_2\text{Cl}_2 (400 MHz).}
\]

**c) - X-Ray diffraction studies**

Single crystals of racemic 64 were obtained by slow diffusion of pentane in a dichloromethane solution (Figure 2.12) and their study by X-ray diffraction allowed us to confirm their structure.

Ligand 64 crystallized in a centro-symmetric space group (\textit{C}2/c). Its X-ray structure shows \textit{i}) the helical 4,13-diaza[6]helicene part (helicity, \textit{i.e.} dihedral angle between the two terminal rings 61.87°), \textit{ii}) the two grafted 2-pyridyl groups that are almost coplanar with the helicene part (dihedral angles -11.98,-10.73°) and \textit{iii}) the nitrogen atoms of each bipy in mutual \textit{trans} positions.
In the bulk solid, the [6]helicenes 64 are stack on top of each others in infinite columns where short intermolecular distances are observed between the bipyridine moiety and the helical core (intermolecular $\pi$-distances c.a. 3.1-3.7 Å) revealing $\pi-\pi$ interactions (Figure 2.13).

**Figure 2.13** Stacking of 64 showing intermolecular $\pi-\pi$ interaction between bipyridine and the helical core


The photophysical studies concerning prepared [n]helicene-bipyridine ligands were investigated. The UV/Vis absorption spectra were measured at room temperature in dichloromethane, and the emission spectra were measured in dichloromethane at room temperature and in EPA glass at 77K. The absorption and emission data are summarized in Table 2.1.

#### II.6.1 Absorption studies

The UV/Vis absorption spectra of ligands 62, 63, and 64 in CH$_2$Cl$_2$ (5x10$^{-5}$ M) are shown in Figure 2.14. 3-(2-Pyridyl)-4-Aza[4]helicene ligand 62 displays a strong band ($\varepsilon > 50 \times 10^3$ M$^{-1}$ cm$^{-1}$) at 295 nm, accompanied with several structured bands of lower intensity between 300-400
nm. 3-(2-Pyridyl)-4-Aza[4]helicene ligand 63 displays a strong band ($\varepsilon > 50 \times 10^3$ M$^{-1}$ cm$^{-1}$) at 266 nm, and several structured broad bands around 330, 350 and 393 nm. 3,14-Di-(2-pyridyl)-4,13-diaza[6]helicene 64 displays a strong band ($\varepsilon > 60 \times 10^3$ M$^{-1}$ cm$^{-1}$) at 272 nm, and several structured bands of lower intensity around 344 and 398 nm. Overall ligands 63 and 64 have redshifted and stronger UV/vis spectra than ligand 62 due to the increased $\pi$-conjugated system.

![Figure 2.14](image1)

**Figure 2.14** Experimental UV/Vis absorption spectra of ligands 62, 63, and 64 in CH$_2$Cl$_2$ (5 x 10$^{-5}$) at 298 K.

### II.6.2 Emission Studies

The ligands have a typical emission of organic $\pi$-conjugated molecules. At room temperature, ligands 62, 63, and 64 emit pure blue fluorescence in CH$_2$Cl$_2$. The emission peaks of 62 at 385 (λ$_{\text{max}}^\text{fluoro}$), 406 and 431 nm (vibronic progression ~1400 cm$^{-1}$) are significantly redshifted in 63 and 64 (421 (λ$_{\text{max}}^\text{fluoro}$), 445, 473 nm in 63, and 422 (λ$_{\text{max}}^\text{fluoro}$), 488, 476 nm in 64) due to the increase in the $\pi$-conjugation (Figure 2.15).

![Figure 2.15](image2)

**Figure 2.15** Experimental emission spectra of ligands 62, 63, and 64 in CH$_2$Cl$_2$ at 295±3 K.
The fluorescence of the ligands at room temperature was characterized by lifetime in the ns scale and relatively high quantum yields (up to 8.6%) for such organic π-systems (Table 2.1).

### Table 2.1 Absorption and Emission data of ligands in DCM at 298 K and in EPA at 77 K

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Absorption: $\lambda_{\text{max}}$ / nm ($\varepsilon$ / M$^{-1}$ cm$^{-1}$)</th>
<th>Emission 298 K</th>
<th>$\Phi_{\text{lum}}$</th>
<th>Emission 77 K</th>
</tr>
</thead>
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<tr>
<td>$62$</td>
<td>295 (57800), 309sh (33800), 331 (19600), 347 (17900), 363 (8880), 383 (7640)</td>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>$\tau$ (ns)</td>
<td>$\lambda_{\text{max}}$ (nm)</td>
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<td></td>
<td></td>
<td>385, 406, 431, 456</td>
<td>$\textbf{3.8}$</td>
<td>383, 392sh, 405, 428, 456</td>
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<td></td>
<td>FLUOR</td>
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<td></td>
<td></td>
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<td>512, 524, 555, 599, 654</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>PHOS</td>
</tr>
<tr>
<td>$63$</td>
<td>240 (35000), 266 (55800), 322 (27000), 353 (14400), 372 (10200), 393 (2630), 417 (1800)</td>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>$\tau$ (ns)</td>
<td>421, 445, 473, 508</td>
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<tr>
<td></td>
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<td></td>
<td>$\textbf{0.084}$</td>
<td>417, 442, 471</td>
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<td>531, 542sh, 577, 624</td>
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<td></td>
<td></td>
<td></td>
<td>PHOS</td>
</tr>
<tr>
<td>$64$</td>
<td>242 (35100), 272 (60300), 286 (65300), 344 (26500), 366sh (20200), 398 (3500), 420 (2750)</td>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>$\tau$ (ns)</td>
<td>422, 488, 476, 510</td>
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<td></td>
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<td>$\textbf{0.086}$</td>
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<tr>
<td>$75$</td>
<td>282 (33700), 308sh (17600), 351 (13600), 418 (4630)</td>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>$\tau$ (ns)</td>
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<td></td>
<td>$\textbf{0.082}$</td>
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<td>530, 577, 621</td>
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<td>PHOS</td>
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In a rigid EPA glass {EPA = diethyl ether/isopentane/ethanol 2:2:1 v/v} at 77 K, the fluorescence of the 3 ligands is accompanied by long-lived green phosphorescence that is ascribed to vibrational structure from the triplet state (populated by intersystem crossing ISC) both because of the large Stokes shift and because of their very long lifetime. The long-lived green phosphorescence at low temperature of $62$ ($\lambda_{\text{max}}$\text{phos} = 512 nm; $\tau = 1.6$ s) is bathochromically shifted with the increase of π-conjugation in $63$ ($\lambda_{\text{max}}$\text{phos} = 531 nm; $\tau = 1.3$ s) and $64$ ($\lambda_{\text{max}}$\text{phos} = 532 nm; $\tau = 1.5$ s) (Figure 2.16).
II.7 Chiroptical Properties

In order to investigate the chiroptical properties of enantiopure [6]helicenes 63 and 64, HPLC separations were carried out using chiral stationary phase Chiralpak IC (250 x 10 mm) to afford $P$-(+)- / $M$-(−)-63 and $P$-(+)- / $M$-(−)-64 (Figure 2.17) with $ee$ 93-99%. This was performed in the group of C. Roussel and N. Vanthuyne (Chirosciences, Marseille). The helical chirality of these enantiomers was stable and the optical rotation (OR), circular dichroism (CD), and circular polarized luminescence (CPL) were measured.

![Enantiopure Structures of 63 and 64](image)

**Figure 2.17** Enantiopure Structures of 63 and 64.
II.7.1 Optical rotation (OR)

OR is the rotation of the plane of linearly polarized light about the direction of motion by a specific angle as the light travels through a chiral (optically active) substance. It is usually measured using a polarimeter, as summarized in Figure 2.18, which consists of a light source, polarizing lens, sample tube and analyzing lens.

Figure 2.18 The principle of measuring OR with a polarimeter.

The quantified rotation viewed is defined as observed rotation “α” that is affected by the path length “l” and the sample concentration “c”. When these effects are eliminated i.e. path length of 1 dm and sample concentration 1 g/ml, then it is defined as specific rotation \([\alpha]_D^{23} = \alpha / l . c\) with formal unit deg dm\(^{-1}\)cm\(^3\) g\(^{-1}\). In order to compare molecules of different structures, the molecular weight must be taken into account and we define the molar rotation \([\phi]_D^{23} = [\alpha]_D^{23} \ast Mw/100\) with formal unit 10\(^{-2}\) deg dm\(^{-1}\)cm\(^3\) mol\(^{-1}\). 

The [6]Helicene-bipy ligand \(P-63\) has high specific and molar rotations \{\(P- (+)-63; [\alpha]_D^{23} = 1800, [\phi]_D^{23} = 7320 \ (\pm \ 5\%) \ (C = 5 \times 10^{-5} \ M, \ CH_2Cl_2)\}\}. Interestingly, \(P-64\) shows almost three times higher optical rotation \{\(P- (+)-64; [\alpha]_D^{23} = 4300, [\phi]_D^{23} = 20830 \ (\pm 5\%) \ (C = 4 \times 10^{-5} \ M, \ CH_2Cl_2)\}\}.

Theoretical TD-DFT calculations are currently being performed by the group of Autschbach in order to understand such an increase. Most probably, this comes from the more extended π-conjugated system in 64.

II.7.2 Circular Dichroism (CD)

The phenomenon of CD involves the absorption of light and it can be considered as a special type of absorption spectroscopy. CD is the difference in the absorption of left-handed and right-handed circularly polarized light and is defined as:

\[ \Delta \varepsilon(\lambda) = \varepsilon_L(\lambda) - \varepsilon_R(\lambda) \]
where $\varepsilon_L$ and $\varepsilon_R$, respectively, are the molar extinction coefficients for the left- and right-handed circularly polarized components at wavelength $\lambda$. The units for CD, when defined as $\Delta \varepsilon$, are $\text{M}^{-1}\cdot\text{cm}^{-1}$, where $M$ is the molar concentration.

The difference in absorbance of left-handed and right-handed circularly polarized light is the basis of circular dichroism. A molecule that absorbs LCP and RCP differently is optically active, or chiral.

Molar ellipticity is another measure for CD, and is defined as:

$$[\theta] = 100 \theta / C l$$

where $C$ and $l$ are the molar concentration and path length (cm) of the sample and $\theta$ the ellipticity of the light. Molar ellipticity is reported either as $\text{deg} \cdot \text{cm}^2 \cdot \text{dmole}^{-1}$ or as $\text{deg} \cdot \text{M}^{-1} \cdot \text{m}^{-1}$, and these two units are equivalent. Molar ellipticity and molar CD (as it is called when expressed in $\Delta \varepsilon$) are interconvertible by a factor

$$[\theta] = 3298 \Delta \varepsilon$$

Unlike optical rotation, circular dichroism only occurs at wavelengths of light that can be absorbed by a chiral molecule. At these wavelengths left-handed and right-handed circularly polarized light will be absorbed to different extents.

The chiroptical properties of 63 and 64 in the form of the CD spectrum were also measured. Figure 2.19 shows the electronic circular dichroism (ECD) spectra of (+) and (-)-63 and 64 in CH$_2$Cl$_2$ at ambient temperature where the mirror-image values for the corresponding (+) and (-) enantiomers are well displayed. The ECD of $P$-(+)-63 displays the typically strong positive band at ca. 330 nm ($\Delta \varepsilon = +232 \text{ M}^{-1} \text{ cm}^{-1}$) and the strong negative band around 265 nm ($\Delta \varepsilon = -154 \text{ M}^{-1} \text{ cm}^{-1}$). These values are similar to other azahelicene derivatives and enable to establish their $P$-(+) and $M$-(-) absolute configurations.$^1$ Ligand 64 that displays much higher specific and molar rotations, displays also a stronger and red-shifted ECD spectrum ($P$-(+)-64: positive band at 341 nm; $\Delta \varepsilon = +342 \text{ M}^{-1} \text{ cm}^{-1}$, and negative band at 288 nm; $\Delta \varepsilon = -329 \text{ M}^{-1} \text{ cm}^{-1}$), compared to $P$-(+)-63.
II.8 3-Pyridinium-4-azonia[6]helicene 75

In addition to the unique chemical properties of azahelicenes such as coordination ability and solubility, their enhanced proton affinity (for example 51 and 59 are referred as superbases due to their high proton affinity ~1000 kJ mol\(^{-1}\) as issued by Stary and coworkers\(^{49}\)) has been recently of particular interest either as chiral scaffold for hydrogen-bond-donor catalysts,\(^{50}\) or to gain insights into the chiroptical property change upon protonation, and its effect on the CD spectra of helicenes.\(^{10}\)

Nitrogen ligands containing N-H bonds are described as "ligands with multiple personalities"\(^{51}\) where they have the ability to respond to changes in the solution environment, such as variations in pH, and consequently the properties can be fine-tuned.

Therefore, to study the impact of protonation on photophysical and chiroptical properties of the [6]helicene bearing bipyridine 63, 3-pyridinium-4-azonia[6]helicene 75 was prepared from 63 when adding excess of 18-crown-6.HBF\(_4\).H\(_2\)O acid\(^{52}\) to DCM solution mixture (Scheme 2.19). 75 was purified by ether precipitation after evaporating DCM to a small volume.

The structural characterization of 75 was verified by multinuclear NMR spectroscopy, where one set of peaks is resolved in \(^{13}\)C and \(^{1}\)H NMR (Figure 2.20). Moreover, the photophysical and chiroptical properties were also investigated.

Figure 2.19 CD spectra of M-(−)-63 (red dashed line), P- (+)-63 (blue solid line), M-(−)-64 (violet dashed line P- (+)-64 (green solid line) in CH\(_2\)Cl\(_2\) (5×10\(^{-5}\) M and 4×10\(^{-5}\) M, respectively).
Figure 2.21 shows the UV/Vis absorption spectrum in CH\(_2\)Cl\(_2\) at ambient temperature of azoniahelicene 75 (blue solid line) that is characterized by several bands between 230 and 530 nm. In comparison with that of azahelicene 63 (\(\lambda_{\text{max}} = 282\) nm; \(\varepsilon = 55800\) M\(^{-1}\)cm\(^{-1}\)), a bathochromic shift is observed with a decrease in molar absorption coefficient (\(\varepsilon = 33700\) M\(^{-1}\)cm\(^{-1}\)) for \(\lambda_{\text{max}} = 282\) nm. Moreover, a new broad band appeared between 380 and 530 nm, centered at 419 nm with \(\varepsilon = 4633\) M\(^{-1}\)cm\(^{-1}\). The photophysical impact of protonation agrees well with recent TD-DFT calculations on similar azoniahelicenes.\(^{10}\)

Figure 2.20 \(^1\)H NMR of ligand 75 (red) in CD\(_2\)Cl\(_2\) (400 MHz), compared to 63 (blue)

Scheme 2.19 Synthesis of 3-pyridinium-4-azonia[6]helicene 75
The room temperature emission of the protonated [6]helicene ligand 75 is strongly red-shifted (~170 nm) compared to the non-protonated [6]helicene 63. The emission spectrum is characterized by a structureless band between 530 and 830 nm (Figure 2.22) with $\lambda_{\text{max}} = 590$ nm and with almost the same quantum yield and lifetime ($\Phi = 0.082$, and $\tau = 5.2$ ns) as compared to 63.

On the contrary, the low temperature emission of 75 in rigid EPA glass at 77 K showed a pure blue fluorescence ($\lambda_{\text{max}} = 396, 416, 441, 470, 501$; $\tau = 9.8$ ns) accompanied with long-lived green phosphorescence ($\lambda_{\text{max}} = 530, 577, 621$) (Figure 2.23) characterized by long lifetime ($\tau = 1.43$ s). The emission spectrum of 75 is fully congruent with that of 63 in terms of energy transitions,
$\lambda_{\text{max}}$, and lifetimes. This probably means that at low temperature the acid-base equilibrium goes in favor of non protonated 63.

Figure 2.23 Experimental emission spectra of 75 (blue solid line) compared with 63 (red dashed line) in EPA at 77 K.

Figure 2.24 shows the different emitted colors between 63 and 75. Interestingly, the protonation / deprotonation reaction is very effective and fast upon acid-base addition to an acetone solution. For example, upon addition excess Na$_2$CO$_3$ to the acetone solution of 75, the transition to 63 is clearly observed within 1-2 min through the disappearance of the yellow color and the appearance of the blue color.

Figure 2.24 Acid-base luminescent switch
In our purpose to investigate the chiroptical consequences of protonation, enantiopure $P$-$(+)$- and $M$-$(−)$-$75$ were prepared respectively from enantiopure $P$-$(+)$- and $M$-$(−)$-$63$ using the same procedure for the racemic one.

The enantiopure 3-pyridinium-4-azonia[6]helicene ligand $P$-$(+)$-$75$ has high specific and molar rotations \((+)-75: [\alpha]_D^{23} = 1700, [\beta]_D^{23} = 10000 \ (± 5\%) \ (C = 1.7\times10^{-4} \ M, CH_2Cl_2)\). The similar specific rotations between $P$-$(+)$-$75$ and $P$-$(+)$-$63$ reveals that the protonation interaction does not appreciably affect the helicene. Nevertheless, the protonation shows an electronic effect as revealed by the UV/Vis and CD spectra.

The experimental CD spectra of $P$-$(+)$- and $M$-$(−)$-$75$ enantiomers exhibited mirror-imaged CD spectra that consisted of 3 successive positive-positive-negative cotton effect (CE) extrema for $P$ helicene assignable to bands A, B, and C and the oppositely signed series of extrema for the $M$ helicene (Figure 2.25).

![Figure 2.25 CD spectra of $M$-$(−)$-$75$ (green dashed line), $P$-$(+)$-$75$ (blue solid line) in CH$_2$Cl$_2$ (5×10$^{-5}$ M) compared to $P$-$(+)$-$63$.](image)

C and B bands are found in a wavelength range very similar to that found for the corresponding neutral helicene but with significant decrease in $\Delta\varepsilon$ values (C: $\lambda_{\text{max}} = 264 \ \text{nm}, \ \Delta\varepsilon = -80.8 \ \text{M}^{-1}\text{cm}^{-1}$; B: $\lambda_{\text{max}} = 347 \ \text{nm}, \ \Delta\varepsilon = +44.6 \ \text{M}^{-1}\text{cm}^{-1}$), thus they are assigned to the same transitions in the neutral helicene. This is also supports the fact that these bands originate from the helical structure, and thus there is no significant effect in the helix structure upon protonation.

The CE intensity is a direct function of the scalar product of electric ($\mu_e$) and magnetic ($\mu_m$) transition dipole moments \(^{53}\) with their relative angle ($\theta$). The CE of A band that is very weak or
probably forbidden in neutral azahelicene 63, was fairly strong in azonia[6]helicene 75 \(P-(+): \lambda_{\text{max}} = 419 \text{ nm}, \Delta\epsilon = +14 \text{ M}^{-1} \text{cm}^{-1}\) compared to \(P-(+)\)-63.

More recent inspection of the transition dipole moments \(\mu_e\) and \(\mu_m\) on similar azonia[6]helicenes done by Inoue and co-workers\(^\text{10}\) revealed that this may be due to the solved degeneracy of molecular orbitals in azonia[6]helicene. In neutral helicenes, the HOMO and HOMO−1, as well as LUMO and LUMO+1, are almost degenerated, and all of these MOs contribute to the A band. Therefore, the magnitudes of \(\mu_e\) and \(\mu_m\) are largely canceled out, and moreover, their relative angle (\(\theta\)) is close to 90° (thus, cos \(\theta\) \(\approx\) 0). In contrast, all of the parameters |\(\mu_e|, |\mu_m|,\) and \(\theta\) positively contribute to the enhancement of CE in azonia[6]helicene because the A band is composed of almost pure HOMO-to-LUMO transition, which most likely bears some charge-transfer character.\(^\text{10}\) The reduced CE intensity in B and C bands originate from the smaller magnitudes of both moments, while the angle between the moments in these azonia[6]helicenes probably becomes slightly smaller (thus cos \(\theta\) became larger) than that in the corresponding neutral aza[6]helicenes.\(^\text{10}\)

II.9 Circularly Polarized Luminescence (CPL) Spectroscopy

CPL spectroscopy gives information about the chiral properties of molecules in their excited state. It specifically measures the differential spontaneous emission of left- and right-handed circularly polarized light by a chiral luminescent system, and may be regarded as the emission equivalent of circular dichroism (CD).\(^\text{54}\) The experimentally observed quantities in CPL spectroscopy are the difference in intensity of the left-handed \(I_L\) and right-handed \(I_R\) circularly polarized components of the emitted radiation (i.e. \(I_L - I_R\)) and the total luminescence intensity (i.e. \((I_L + I_R)/2\)). At a particular emission wavelength, the degree of CPL is reported in terms of the emission dissymmetry factor, \(g_{\text{em}}\) (sometimes denoted as \(g_{\text{lum}}\)), which is defined by the following equation:

\[
g_{\text{em}} = \frac{2(I_L - I_R)}{I_L + I_R}
\]

The measurement of CPL, in many cases, has some advantages over the measurement of CD as well as some inherent limitations. The most serious limitation is, quite obviously, that the optically active molecule under study must contain a luminescent chromophore with a reasonable quantum yield. Some of the more important advantages of the technique are: i) CPL provides a direct probe of the chirality of molecular excited states (more specifically, the emitting states), and ii) comparative CPL/CD studies can yield specific information concerning geometry differences between ground and excited states.\(^\text{54}\) This field has been dominated by chiral lanthanide complexes so far.\(^\text{55}\) In recent years, there has been a growing interest in developing organic molecules capable of emitting CPL towards their potential applications in optoelectronic devices.\(^\text{56}\)
To investigate the protonation impact on CPL spectroscopy, especially because the protonation/deprotonation reaction is appreciably reversible in the presence of Na$_2$CO$_3$ base, the CPL properties of the enantiopure P-(+)-/M-(−)-63 and P-(+)-/M-(−)-75 were measured in 1 mM degassed dichloromethane solution at 295 K upon excitation at 400 nm for 63 and 450 nm for 75 (Figure 2.26). These measurements were performed in the group of Gilles Muller in San Jose University (USA).

As shown in Figure 2.26, ligands 63 and 75 exhibited CPL activities, and the CPL spectra of P-(+)- and M-(−)- helicenes are mirror images. The degree of CPL is given by the luminescence dissymmetry ratio $g_{\text{lum}}$. The $g_{\text{lum}}$ values are $+3.4 \times 10^{-3}$ and $-3 \times 10^{-3}$ for P-(+)-/M-(−)-63 isomers around the emission maximum ($\lambda_{\text{em}} = 426$ nm), and of $+3.2 \times 10^{-3}$ and $-2.5 \times 10^{-3}$ for P-(+)-/M-(−)-75 isomers around the emission maximum ($\lambda_{\text{em}} = 568$ nm), respectively. The $g_{\text{lum}}$ values for 63 are comparable to the values observed to other azahelicenes, $^8$a,e and ~10-folds smaller than values observed in aggregating helicenes. $^8$b,d

**Figure 2.26 left:** CPL (upper curve) and total luminescence (lower curve) for M-(−)-75 (red) and P-(+)-75 (black) in 1 mM DCM solution at 295 K, upon excitation at 450 nm

**Figure 2.26 right:** CPL (upper curve) and total luminescence (lower curve) for M-(−)-63 (red) and P-(+)-63 (black) in 1 mM DCM solution at 295 K, upon excitation at 400 nm.

To our knowledge, no CPL was measured for azonia[n]helicenes, and this is probably the first example in switching chemically the circularly polarized luminescence wavelength within helicenes through acid-base interaction.
Interestingly, the fine tuning of photophysical and chiroptical properties upon protonation accompanied by the possibility to switch from one transition to another through acid–base interaction (protonation–deprotonation) makes it possible to obtain a helicenic acid–base CD switch in terms of absorption, and acid–base fluorescence CPL switch during emission.

In fact, there is a very nice example in the literature of triggering CPL demonstrated by T. Kawai and coworkers as the first example of chemical-stimuli-responsive chiroptical properties (CD and CPL) using anion-responsive π-conjugated molecules. The intrinsic feature of BINOL-boron moiety to dipyrroldiketones is the ability to induce a chiral conformation due to the functionalization of boron with chiral diol, and the inversion of pyrrole rings by anion binding enables the induction of conformation changes that modifies the electronic and electrooptical properties. As shown in Figure 2.27, the conformational change in the π-conjugated system enhances the CD anisotropy factor $g_{\text{abs}}$. Interestingly, the anion-binding triggers also the negligibly small CPL in the anion-free π-conjugated system to observe an off/on switching of $g_{\text{lum}}$ that is enhanced to higher extent than $g_{\text{abs}}$.

![Figure 2.27 CD and CPL spectra changes upon Cl⁻ ion sensing by the pyrrole rings.](image)

**II.10 Conclusion**

We have prepared new [4] and [6]helicenes bearing 1 or 2 bipyridine functionalities. They were characterized by multinuclear NMR spectroscopy and X-ray crystallography. The photophysical studies on these helicenes showed that they absorb in the visible region and emit as fluorescent light at room temperature accompanied with phosphorescence at 77 K. The enantiopure [6]helicenes showed high specific and molar optical rotation and the preferential absorption of left- and right-handed circularly polarized light shown in the CD spectra are identical in magnitude and opposite in sign for the corresponding enantiomers which is an indicative of chromophores with opposite chirality. Moreover, the protonation of 63 showed a significant effect on the photophysical and chiroptical properties, where a new band appears in the absorption and CD spectra, and a bathochromic shift ($\Delta\lambda \approx 170$ nm) within the emission and
CPL spectra. The easy reversible reactivity between 63 and 75 through protonation – deprotonation made it possible to obtain an efficient acid – base chiroptical switch.

We will investigate in the next two chapters the coordinating abilities of these helicenes as $N^N$ and $N^C$ chelates to transition metals and study the effect on their photophysical and chiroptical properties.
References


Experimental Part

Most experiments were performed using standard Schlenk techniques. Solvents were freshly distilled under argon from sodium/benzophenone (THF) or from phosphorus pentoxide (CH$_2$Cl$_2$). Starting materials were purchased from Aldrich. Column chromatography purifications were performed in air over silica gel (Merck Geduran 60, 0.063–0.200 mm). Irradiation reactions were conducted using a Heraeus TQ 150 or 700 mercury vapor lamp. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AM300 and 400. Chemical shifts were reported in parts per million (ppm) relative to Si(CH$_3$)$_4$ as external standard and compared to the literature. Elemental analyses were performed by the CRMPO, University of Rennes 1. Specific rotations (in deg cm$^2$ g$^{-1}$) were measured in a 1 dm thermostated quartz cell on a Perkin Elmer 341 polarimeter. Circular dichroism (in M$^{-1}$ cm$^{-1}$) was measured on a Jasco J-815 Circular Dichroism Spectrometer (IFR140 facility - Université de Rennes 1). UV/vis/NIR spectroscopy was conducted on a Varian Cary 5000 spectrometer. Compounds 67$^1$ and 68$^2$ were prepared according to literature.

CPL measurements

The circularly polarized luminescence (CPL) and total luminescence spectra were recorded on an instrument described previously,$^3$ operating in a differential photon-counting mode. The light source for excitation was a continuous wave 1000 W xenon arc lamp from a Spex Fluorolog-2 spectrofluorimeter, equipped with excitation and emission monochromators with dispersion of 4 nm/mm (SPEX, 1681B). To prevent artifacts associated with the presence of linear polarization in the emission,$^4$ a high quality linear polarizer was placed in the sample compartment, and aligned so that the excitation beam was linearly polarized in the direction of emission detection (z-axis). The key feature of this geometry is that it ensures that the molecules that have been excited and that are subsequently emitting are isotropically distributed in the plane (x,y) perpendicular to the direction of emission detection. The optical system detection consisted of a focusing lens, long pass filter, and 0.22 m monochromator. The emitted light was detected by a cooled EMI-9558B photomultiplier tube operating in photo-counting mode. All measurements were performed with quartz cuvettes with a path length of 1.0 cm.

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1. Y.-Q. Fang, G. S. Hanan, *Synlett* 2005, 6, 852.
6-(2-(naphthalen-2-yl)vinyl)-2,2'-bipyridine 70:

A solution of 2-methylnaphtyltriphenylphosphonium bromide 69 (433 mg, 0.89 mmol) in 15 ml of anhydrous THF was placed in a Schlenk tube under argon and cooled to -78 °C. To the stirred suspension was added n-butyllithium (1.6N solution in hexanes, 0.58 ml, 0.93 mmol) dropwise. The reaction mixture turned deep red then warmed to room temperature slowly. After 45 minutes, the reaction mixture was cooled again to -78 °C. Then 2,2'-bipyridine-6-carbaldehyde 68 (157 mg, 0.85 mmol) was added in one portion; the reaction mixture was warmed to room temperature and the color turned yellow white with stirring overnight. The reaction mixture was filtered over celite and concentrated under vacuum, and the crude oily product was purified by column chromatography (silica gel, heptane / ethyl acetate 8:2) to give 215 mg (82%) of 70 as a yellow solid (cis and trans mixture).

\[1^1H\text{ NMR (400 MHz CDCl}_3\] \(\delta\) 8.63 (1 H, d, \(J=4.0\) Hz), 8.51 - 8.58 (2 H, m), 8.22 (1 H, d, \(J=8.0\) Hz), 8.14 (1 H, d, \(J=8.0\) Hz), 7.85 - 7.95 (3 H, m), 7.70 - 7.84 (7 H, m), 7.59 - 7.69 (2 H, m), 7.53 (1 H, t, \(J=7.9\) Hz), 7.34 - 7.48 (7 H, m), 7.23 - 7.34 (2 H, m), 7.11 - 7.17 (2 H, m), 6.96 (1 H, d, \(J=12.3\) Hz), 6.76 (1 H, d, \(J=12.3\) Hz)

Elemental analysis, calcd. (%) for C\(_{22}\)H\(_{16}\)N\(_2\): C, 85.69; H, 5.23; N, 9.08; found C 84.50, H 5.19, N 9.03.

3-pyridyl-4-aza[4]helicene 63

The mixture of cis and trans olefin 6-(2-(benzo[c]phenanthren-2-yl)vinyl)-2,2'-bipyridine 70 (500 mg) in 700mL toluene/THF (9:1) was irradiated for 15 hrs in the presence of catalytic amount of iodine using a 150W mercury vapor lamp. Then the solvent was stripped off and the crude product was purified over silica gel (heptane / ethyl acetate; 9:1) to give 370 mg (75%) of 63 as yellow solid product.

\[1^1H\text{ NMR (400 MHz CDCl}_3\] \(\delta\) 9.41 (1 H, d, \(J=9\) Hz, H\(^1\)), 8.98 (1 H, d, \(J=8.1\) Hz, H\(^12\)), 8.59 - 8.68 (3 H, m, H\(^6\), H\(^2\), H\(^5\)), 8.00 – 8.12 (2H, AB, \(J=8.7\) Hz, H\(^3\), H\(^6\)) 7.98 (1 H, dd, \(J=7.9, 1.7\) Hz,
1H NMR (300 MHz, CD$_2$Cl$_2$) δ 9.26 (1H, s), 9.20 (1H, d, J = 8.5 Hz), 9.17 (0.45H, s), 8.75 (1H, d, J = 3.6 Hz), 8.72 (0.5H, s), 8.65 (1.4H, d, J = 7.8 Hz), 8.33 (1.4H, t, J = 7.4 Hz), 8.15-7.73 (14.5H, m), 7.68 (2H, t, J = 7.8 Hz), 7.53 (1H, dd, J = 14.4, 7.3 Hz), 7.48-7.31 (4H, m), 7.28 (0.3H, s), 7.26-7.19 (0.4H, m), 7.16 (0.4H, d, J = 12.3 Hz), 6.93 (0.4H, d, J = 12.2 Hz).

Elemental analysis, calcd. (%) for C$_{30}$H$_{20}$N$_2$: C, 88.21; H, 4.93; N, 6.86; found C 87.98, H 4.85, N 6.80.

A solution of (benzo[c]phenanthren-3-ylmethyl)triphenylphosphonium bromide 71 (1.465 g, 2.5 mmol) in 40 ml of anhydrous THF was placed in a Schlenk tube under argon and cooled to -78 °C for 5 minutes. To the stirred suspension was added dropwise n-butyllithium (2.5 solution in hexanes, 1 ml, 26 mmol). The reaction mixture turned deep red then warmed to room temperature slowly. After 45 minutes, the reaction mixture was cooled again to -78 °C. Then 2,2'-bipyridine-6-carbaldehyde 68 (440 mg, 2.39 mmol) was added in one portion; the reaction mixture was warmed to room temperature and the color turned yellow white with stirring for 3 hours. The reaction mixture was filtered over celite and concentrated under vacuum, and the crude oily product was purified by column chromatography (silica gel, heptane / ethyl acetate 7:3) to give 72 as a yellow solid product (cis and trans mixture) with 92% yield (890 mg).

13C NMR (75 MHz CD$_2$Cl$_2$) δ 156.46 (C), 155.23 (C), 149.67 (CH), 148.95 (C), 137.28 (CH), 136.67 (CH), 133.98 (C), 131.53 (C), 131.11 (CH), 130.56 (C), 129.43 (CH), 129.20 (CH), 128.67 (CH), 127.86 (CH), 127.31 (C), 127.15 (CH), 127.08 (CH), 126.75 (CH), 125.87 (C), 124.45 (CH), 121.80 (CH), 118.36 (CH)

Elemental analysis, calcd. (%) for C$_{22}$H$_{14}$N$_2$: C, 86.25; H, 4.61; N, 9.14; found C 86.12, H 4.55, N 9.05.
The mixture of cis and trans olefin 6-(2-(benzo[c]phenanthren-2-yl)vinyl)-2,2'-bipyridine 72 (100 mg) in 1 L toluene/THF (9:1) was irradiated for 5 hrs in the presence of catalytic amount of iodine using a 700W mercury vapor lamp. Then the solvent was stripped off and the crude product was purified over silica gel (heptane / ethyl acetate 8:2) to give 63 (90 mg, 90%) as a yellow solid.

\[ \text{\textsuperscript{1}H NMR (400 MHz, CD}_{2}\text{Cl}_{2}) \delta \text{ } 8.56 \text{ (1 H, m, H\textsubscript{3}'}), 8.49 - 8.53 \text{ (1H, m, H\textsubscript{6}')}, 8.14 \text{ (2 H, s), 7.94 - 8.03 (4 H, m), 7.90 (2H, s), 7.86 (1H, d, J=8.9 Hz), 7.80 (1H, d, J=8 Hz, H\textsubscript{13}), 7.79-7.74 (m, 1H, H\textsubscript{4'}), 7.65 (1 H, d, J = 8.7 Hz), 7.57 (d, J = 9 Hz, 1 H, H\textsubscript{16}), 7.22 (1 H, ddd, J = 7.3, 4.8, 1.1 Hz, H\textsubscript{5'}), 7.15 (1 H, ddd, J= 8, 6.9, 1.1 Hz, H\textsubscript{14}), 6.64 (1 H, ddd, J=8.5, 6.9, 1.4 Hz, 1 H, H\textsubscript{15}).}\]

\[ \text{\textsuperscript{13}C NMR (101 MHz CDCl}_{3}) \delta \text{ } 156.33 \text{ (C), 154.86 (C), 149.45 (CH), 147.54 (C), 137.13 (CH), 135.94 (CH), 133.69 (C), 132.59 (C), 132.07 (C), 131.74 (C), 130.63 (CH), 129.88 (C), 129.81 (CH), 128.61 (CH), 128.31 (CH), 128.12 (CH), 128.04 (CH), 128.03 (CH), 127.97 (C), 127.60 (CH), 127.42 (CH), 126.54 (CH), 126.15 (CH), 125.77 (C), 125.58 (CH), 124.39 (C), 124.27 (CH), 121.54 (CH), 116.94 (CH).}\]

Elemental analysis, calcd. (%) for C\textsubscript{30}H\textsubscript{18}N\textsubscript{2}: C, 88.64; H, 4.46; N, 6.89; found C 88.45, H 4.39, N 6.83.

\[ \text{\textsuperscript{2,7-bis(2-(2'-bipyridin)-6-yl)vinyl)naphthalene 74}\]

A solution of 2,7-dimethylnaphtyl-bis-triphenylphosphonium bromide 73 (1 g, 1.2 mmol) in 30 ml of anhydrous THF was placed in a Schlenk tube under argon and cooled to -78 °C for 5 minutes. To the stirred suspension was added n-butyllithium (2.5 N solution in hexanes, 0.53 ml,
1.3 mmol) dropwise. The reaction mixture turned deep red then warmed to room temperature slowly. After 45 minutes, the reaction mixture was cooled again to -78 °C. Then 2,2'-bipyridine-6-carbaldehyde 68 (440 mg, 2.4 mmol, 2 eq) was added in one portion; the reaction mixture was warmed to room temperature and the color turned yellow white with stirring overnight. The reaction mixture was filtered over celite and concentrated under vacuum, and the crude oily product was purified by column chromatography (silica gel, heptane / ethyl acetate 7:3) to give (530 mg, 92%) 74 as a yellow solid (cis and trans mixture).

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 8.45 - 8.61 (3 H, m), 8.19 - 8.25 (1 H, m), 8.11 - 8.18 (2 H, m), 7.66 - 7.89 (8 H, m), 7.45 - 7.62 (3 H, m), 7.18 - 7.45 (6 H, m), 7.06 - 7.17 (3 H, m), 6.93 (1 H, d, $J=12.6$ Hz), 6.88 (1 H, d, $J=12.30$ Hz), 6.74 (d, $J=12.30$ Hz), 6.69 (1 H, d, $J=12.6$ Hz).

Elemental analysis, calcd. (%) for C$_{34}$H$_{24}$N$_4$: C, 83.58; H, 4.95; N, 11.47; found C 83.42, H 4.84, N 11.38.

3,14-di(pyridin-2-yl)naphtho[1,2-f:8,7-f']diquinoline 64

The mixture of cis and trans olefin 2,7-bis(2-([2,2'-bipyridin]-6-yl)vinyl)naphthalene 74 (100 mg, 0.2 mmol) in 700mL toluene/THF (9:1) was irradiated for 5 hrs in the presence of catalytic amount of iodine using a 700W mercury vapor lamp. Then the solvent was stripped off and the crude product was purified over silica gel (heptane/ethyl acetate; 8:2 as eluents) to give 64 (83 mg, 83%) as a yellow solid.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 8.57 (1 H, d, $J=7.9$ Hz, H$^1$), 8.43 (1 H, d, $J=3.0$ Hz, H$^6$), 8.19 (2 H, s, H$^{5,6}$), 8.00 - 8.07 (3 H, m, H$^{7,8,3'}$), 7.72 - 7.79 (2 H, m, H$^{2,4'}$), 7.16 - 7.21 (1 H, m, H$^5$)

$^{13}$C NMR (101 MHz, CD$_2$Cl$_2$) $\delta$ 156.55 (C), 155.60 (C), 149.87 (CH), 148.33 (C), 137.58 (CH), 136.60 (CH), 134.33 (C), 132.56 (C), 131.09 (CH), 130.71 (CH), 128.66 (CH), 128.59 (CH), 128.27 (C), 125.87 (C), 124.76 (CH), 122.10 (CH), 118.08 (CH)

Elemental analysis, calcd. (%) for C$_{34}$H$_{20}$N$_4$: C, 84.28; H, 4.16; N, 11.56; found C 83.12, H 4.05, N 11.42.
3-pyridinium-4-azonia[6]helicene 75

10 mg of 63 (0.024 mmol) was dissolved in 4 ml DCM then 18-crown-6.HBF$_4$.H$_2$O (0.053 mmol, 20 mg) was added and the reaction mixture was stirred for 2 hours at room temperature. DCM was evaporated to small volume, and then ether was added to observe yellow precipitate that was filtrated and washed with ether to remove the excess acid. Finally, the precipitate was dried under vacuum to obtain 75 as yellow-orange powder (12.6 mg, 90%).

$^1$H NMR (300 MHz, CD$_2$Cl$_2$) $\delta$ 9.08 - 9.15 (1 H, m, H$_6^6$), 8.47 - 8.59 (2 H, AB, $J = 9.1$ Hz), 8.34 - 8.43 (2 H, m), 8.27 (2 H, d, $J =$8.3 Hz), 8.12 - 8.19 (3 H, m), 8.02 - 8.09 (2 H, m), 7.94 (1 H, dd, $J =$8.10, 0.8 Hz, H$_{13}$), 7.88 (1 H, ddd, $J =$7.6, 5.4, 1.1 Hz, H$_{5'}$), 7.65 (1 H, 6, $J =$ 8.6 Hz, H$_{16}$), 7.47 (1 H, d, $J =$9.0 Hz), 7.29 (1 H, ddd, $J =$8, 6.9, 1.1 Hz, H$_{14}$), 6.83 (1 H, ddd, $J =$8.5, 7.0, 1.4 Hz, H$_{15}$).

$^{13}$C NMR (75 MHz, CD$_2$Cl$_2$) $\delta$ 147.07 (C), 146.53 (CH), 144.34 (CH), 144.25 (C), 140.42 (CH), 135.39 (CH), 134.28 (C) 132.78 (C), 132.68 (C), 132.62 (C), 130.30 (1 CH), 129.19 (CH), 129.18 (CH), 129.06 (C), 128.68 (CH), 127.99 (CH), 127.70 (CH), 127.68 (CH), 127.56 (CH), 127.40 (C), 127.26 (C), 126.80 (C), 126.66 (CH), 126.61 (CH), 126.30 (CH), 125.81 (CH), 124.10 (C), 123.55 (CH), 116.10 (CH). One C is missing
Analytical chiral HPLC separation for compound 63

- The sample is dissolved in a mixture ethanol/chloroform (1/1), injected on the chiral columns, and detected with an UV detector at 254 nm and a polarimeter. The flow-rate is 1 ml/min.

<table>
<thead>
<tr>
<th>Column</th>
<th>Mobile Phase</th>
<th>t1</th>
<th>k1</th>
<th>t2</th>
<th>k2</th>
<th>α</th>
<th>Rs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chiralpak IC</td>
<td>Hexane/ethanol/chloroform 90/5/5</td>
<td>6.33 (+)</td>
<td>1.11</td>
<td>7.98 (-)</td>
<td>1.66</td>
<td>1.50</td>
<td>2.76</td>
</tr>
</tbody>
</table>
Semi-preparative separation for compound 63:

- Sample preparation: About 600 mg of compound 63 are dissolved in 280 ml of chloroform/hexane 1/1.

- Chromatographic conditions: Chiralpak IC (250 x 10 mm), thermostated at 30 °C, hexane/ethanol/chloroform 90/5/5 as mobile phase, flow-rate = 5 ml/min, UV detection at 385 nm.

- Injection: 350 times 800 µl, every 12 minutes.

- Collection: the first eluted enantiomer is collected between 6 and 7.7 minutes and the second one between 8.2 and 10 minutes.

- First fraction: 273 mg of the first eluted ((+)-enantiomer) with ee > 99%

- Second fraction: 257 mg of the second eluted ((-)enantiomer) with ee > 99%

- Chromatograms of the collected enantiomers:
Analytical chiral HPLC separation for compound 64

- The sample is dissolved in chloroform, injected on the chiral columns, and detected with an UV detector at 254 nm and CD 254nm. The flow-rate is 1 mL/min.

<table>
<thead>
<tr>
<th>Column</th>
<th>Mobile Phase</th>
<th>t1</th>
<th>k1</th>
<th>t2</th>
<th>k2</th>
<th>α</th>
<th>Rs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chiralpak IA</td>
<td>Hexane / 2-PrOH with 0.1% triethylamine / chloroform (7/1/2)</td>
<td>4.52 (+)</td>
<td>0.51</td>
<td>4.87 (-)</td>
<td>0.62</td>
<td>1.21</td>
<td>0.86</td>
</tr>
<tr>
<td>Chiralpak IB</td>
<td></td>
<td>4.31</td>
<td>0.44</td>
<td></td>
<td></td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Chiralpak IC</td>
<td></td>
<td>5.17 (-)</td>
<td>0.72</td>
<td>8.05 (+)</td>
<td>1.68</td>
<td>2.33</td>
<td>4.95</td>
</tr>
<tr>
<td>Chiralpak ID</td>
<td></td>
<td>5.35 (+)</td>
<td>0.78</td>
<td>8.16 (-)</td>
<td>1.72</td>
<td>2.19</td>
<td>6.43</td>
</tr>
<tr>
<td>Chiralpak IE</td>
<td></td>
<td>10.40 (-)</td>
<td>2.47</td>
<td>14.06 (+)</td>
<td>3.69</td>
<td>1.49</td>
<td>3.87</td>
</tr>
<tr>
<td>Chiralpak IF</td>
<td></td>
<td>5.59 (+)</td>
<td>0.86</td>
<td>6.13 (-)</td>
<td>1.04</td>
<td>1.21</td>
<td>1.30</td>
</tr>
</tbody>
</table>
Semi-preparative separation for compound 64:

- **Sample preparation**: About 470 mg of compound 64 are dissolved in 120 mL of chloroform.

- **Chromatographic conditions**: Chiralpak IC (250 x 10 mm), thermostated at 30 °C, hexane / 2-ProOH with 0.1% triethylamine / chloroform (7/1/2) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.

- **Injections**: 400 times 300 μL, every 10 minutes.

- **Collection**: the first eluted enantiomer is collected between 4 and 6.8 minutes and the second one between 7.8 and 10 minutes.

- **First fraction**: 210 mg of the first eluted (-(+, CD 254 nm)-enantiomer) with ee > 93%

- **Second fraction**: 230 mg of the second eluted ((+, CD 254 nm)-enantiomer) with ee > 98%
• Chromatograms of the collected enantiomers:

Chiralpak IC Hexane / 2-PrOH with 0.1% triethylamine / chloroform (7/1/2)

1: 254 mm, 4 mm

Results

Retention Time | Area   | Area % | Capacity factor | Relative RT | Resolution (USP)
--- | --- | --- | --- | --- | ---
5.19 | 61043829 | 96.73 | 0.73 | 1.00 | 0.00
8.17 | 2063451 | 3.27 | 1.72 | 2.36 | 5.13

Chiralpak IC Hexane / 2-PrOH with 0.1% triethylamine / chloroform (7/1/2)

1: 254 mm, 4 mm

Results

Retention Time | Area | Area % | Capacity factor | Relative RT | Resolution (USP)
--- | --- | --- | --- | --- | ---
5.19 | 243141 | 0.84 | 0.73 | 1.00 | 0.00
8.05 | 28704404 | 99.16 | 1.68 | 2.31 | 5.05
III.1 Introduction

The field of photophysics and photochemistry of coordination complexes of transition metals has received great interest since the last few decades especially for understanding excited state properties, photochemical reactions, as well as exploring and exploiting the potential applications.

Luminescent d$^6$ rhenium (I) tricarbonyl complexes with chelating N,N’-diimine ligands of general formula fac-[Re(CO)$_3$(N$^\text{N'}$)X]$^{n+}$ (N$^\text{N'}$ = 1,10-phenanthroline, 2,2’-bipyridine, etc … and X = monodentate ligands such as halides for n=0, and pyridines, phosphines, or isocyanides for n=1) has been extensively studied and continue to attract much attention ever since their excited states was first recognized in 1974 by Wrighton and Morse.

The advantages of using Re (I) complexes over other d$^6$ transition metals are:

- Ease of preparation
- Visible light excitation and emission
- Large Stokes shifts
- Large luminescent lifetime
- Ease of emission color tuning
- Resistance to photobleaching
- Heavy Metal with strong, spin-orbit coupling

Due to these advantages, Re (I) tricarbonyl systems have been explored in different fields of application which include photoredox chemistry, chemi- or electrochemi-luminescence, chemical and biological sensing, bioconjugation, and used as phosphorescent dopants for organic light emitting diodes (OLEDs).

III.2 Re(CO)$_3$(N$^\text{N'}$)Cl complexes

III.2.1 Synthesis of neutral Re(CO)$_3$(N$^\text{N'}$)Cl complexes

Re(I) complexes of the form fac-[Re(CO)$_3$(N$^\text{N'}$)] where N,N’ is a polypyridine type ligand, can be readily synthesized by the reaction of the appropriate ligand with an equimolar amount of Re(CO)$_3$Cl under reflux in non polar solvents (typically hexane or toluene). (Eq 3.1)

$$\text{Re(CO)}_3\text{Cl} + 2,2'\text{-bpy} \xrightarrow{\text{Toluene, Reflux}} \text{Re(CO)}_3(\text{bpy})\text{Cl} + 2\text{CO}$$ (Eq 3.1)
The desired product often precipitates from solution and can be isolated and purified easily. Moreover, these complexes can crystallize very easily and show very good thermal and air stability.

Rhenium tricarbonyl complexes usually possess octahedral molecular geometry which describes the shape of compounds wherein six atoms or groups of atoms or ligands are symmetrically arranged around a central atom, defining the vertices of an octahedron. When two or more types of ligands are coordinated to an octahedral Re centre, the complex can exist as isomers. The naming system for these isomers depends upon the number and arrangement of different ligands.

For rhenium tricarbonyl complexes with the general formula \([\text{Re(CO)}_3(L)X]\) two isomers are possible (Scheme 3.1) - a **facial** isomer (\textit{fac}) in which each set of three identical ligands occupies one face of the octahedron surrounding the metal atom, so that any two of these three ligands are mutually \textit{cis}, and a **meridional** isomer (\textit{mer}) in which each set of three identical CO ligands occupies a plane passing through the metal atom and the (\textit{N\textsuperscript{N'}}) ligand.

\[
\begin{array}{cc}
\text{Facial isomer (\textit{fac})} & \text{Meridional isomer (\textit{mer})} \\
\end{array}
\]

\textbf{Scheme 3.1} \textit{Fac} and \textit{mer} Re(I) isomers.

Note that there is no evidence in the literature for the formation of rhenium(I) tricarbonyl complexes in a \textit{mer} isomeric form by the normal thermal substitution. This is due to the strong \(\pi\)-accepting ability associated with carbonyl ligands, thus they can compete with other ligands, in particular the trans-ligand (\textit{N\textsuperscript{N'}}), for \(\pi\)-back-bonding interaction with the metal center.\textsuperscript{2a} However, Osamu Ishitani and his co-workers reported recently the photochemical synthesis of \textit{mer}-[Re(bpy)(CO)\textsubscript{3}Cl] through irradiation of the \textit{fac} isomer by a high-pressure Hg lamp (500 W) under CO pressure \textsuperscript{13} (Scheme 3.2).

\[
\begin{array}{cc}
\text{fac} & \text{mer} \\
\end{array}
\]

\textbf{Scheme 3.2} Photochemical synthesis of \textit{mer}-[Re(bpy)(CO)\textsubscript{3}Cl] isomers.
III.2.2 Photophysical Properties

III.2.2.1 UV/vis absorption spectroscopy

Examining the ground state UV/vis absorption properties of such Re(I) complexes, they were found to display a number of different absorption bands as shown in the absorption spectra of Re(CO)$_3$(bpy)Cl$^3$ (Figure 3.1).

![Absorption Spectra](image)

*Figure 3.1*: UV/vis absorption spectra of [Re(CO)$_3$(bpy)Cl] in DCM at 298 K. Reproduced from reference 3.

The intense high-energy feature at 295 nm in the absorption spectra of Re(CO)$_3$bpyCl is associated with intraligand (IL) or ligand-centered (LC) bipyridyl $\pi$-$\pi^*$ transition.$^{3,14,15}$ The ligand-centered transition in the free ligand is found at similar energy and shows very little change on complexation to the Re metal. The broad band observed at 390 nm is assigned to $d\pi$(Re) $\rightarrow$ $\pi^*$(bpy) metal-to-ligand charge transfer (MLCT) transitions, and these transitions are found to be analogous in a wide variety of similar diimine Re(I) complexes.$^{3,16}$ The MLCT character of the 340-390 nm is further supported by their strong sensitivity to solvents$^{16b}$ where it shifts to lower energy with decreasing solvent polarity due to characteristic solvatochromism$^{17}$ (Table 3.1).

The photophysics of Re diimine complexes are dominated by the nature of the polypyridine ligands with less importance in the axial ligand. Thus, the nature of the substituents on polypyridine ligand, electron withdrawing or donating, can affect the band shifts of the MLCT transitions in the absorption spectra of Re(CO)$_3$(N$^\text{N'}$)Cl complexes (Table 3.1).

Comparing the electronic environment of different diimine ligands, the electron donating substituents on bipyridyl increase the energy of the $\pi^*$ acceptor to a greater degree than they do for the $d\pi$ (Re) orbitals which leads to a blue shift in the $\lambda_{\text{max}}$, while the electron withdrawing group stabilizes the $\pi^*$ level of bipyridyl ring causing red shift in the $\lambda_{\text{max}}$. 

127
Table 3.1 Absorption maxima data for the complexes [Re(CO)₃(4,4'-X₂-bpy)Cl] at 298 K, (bpy = 2,2’-bipyridine). For [Re(CO)₃(4,4’-(COOCH₃)₂-bpy)Cl], data was only available in dichloromethane.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>CH₂Cl₂</th>
<th>CH₃CN</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,2’-bipyridyl (bpy)¹⁴</td>
<td>387</td>
<td>370</td>
</tr>
<tr>
<td>4,4’-(CH₃)₂-bpy¹⁴</td>
<td>380</td>
<td>364</td>
</tr>
<tr>
<td>4,4’-(phenyl)₂-bpy</td>
<td>396¹⁸</td>
<td>384¹⁹</td>
</tr>
<tr>
<td>4,4’-(NH₂)₂-bpy</td>
<td>360</td>
<td>350</td>
</tr>
<tr>
<td>4,4’-(NO₂)₂-bpy</td>
<td>475</td>
<td>448</td>
</tr>
<tr>
<td>4,4’-(COOCH₃)₂-bpy</td>
<td>433¹⁹</td>
<td>—</td>
</tr>
<tr>
<td>4,4’-(Cl)₂-bpy¹⁹</td>
<td>410</td>
<td>390</td>
</tr>
</tbody>
</table>

III.2.2.2 Emission spectroscopy

Rhenium(I) tricarbonyl complexes are one of the few classes of metal carbonyl complexes that emit in fluid solution. In 1974, Wrighton and Morse observed that Re(CO)₃bpyCl possesses a broad and structureless emission at room temperature with λ<sub>max</sub> centered at 610 nm (Figure 3.2).

The emission energies of these systems depend heavily on the π* orbital of the bipyridine ligand, and have been found to originate from ³MLCT phosphorescence [π*(N²N’) → dπ(Re)]. This luminescent character of Re complexes depends significantly on the environment. The Re(CO)₃(bpy)Cl emission from ³MLCT at 298 K decays with lifetime of 51 ns, that increases to 2.68 μs in rigid polyester resins or in EPA glass at 77 K. Moreover, the emission maxima exhibit a blue shift from 610 nm at 298 K to 535 nm at 77 K. These rigidochromic shifts are characteristics of emission originating from ³MLCT.

As described before for the absorption spectra, the emission maxima are sensitive to the nature of the polypyridine ligand at 298 K and 77 K (Table 3.2).
The emission maxima (compared to \([\text{Re(CO)}_3(\text{bpy})\text{Cl}]\)) are blue-shifted in the presence of an electron donating group (-CH\(_3\)) and are red-shifted in the presence of an electron withdrawing group (-Cl). An electron donating group leads to a blue shift in the emission maximum due to the increased energy of the LUMO which increases the \(t_2g - \varepsilon^{\text{MLCT}}\) energy gap. On the other hand, an electron withdrawing group results in a red shift in the emission maximum due to the decreased energy of the LUMO, which decreases the \(t_2g - \varepsilon^{\text{MLCT}}\) energy gap.

In 2004, theoretical calculations have led to a similar conclusion. Yang and coworkers have applied DFT studies to analyze the excited-state properties of \([\text{Re(CO)}_3(\text{bpy})\text{Cl}]\), \([\text{Re(CO)}_3(5,5'\text{-dibromo-bpy})\text{Cl}]\) and \([\text{Re(CO)}_3(4,4'\text{-dimethylbpy})\text{Cl}]\). For these complexes, the excited state responsible for the luminescence was of MLCT nature.

### III.3 Re(I)(CO)\(_3\)(N\(^\text{N}^\text{'})-core complexes

Generally Re(I) tricarbonyl complexes are MLCT emitters having broad and structureless bands that are sensitive to changes in the environment. Thus variations in the structure of the non-carbonyl bidentate as well as the ancillary ligands produce considerable effects on luminescence energies, lifetimes, and quantum yields that can be fine-tuned. This can be explained by the possible presence of close lying non-radiative ligand field (LF) excited states in \(d^6\) and \(d^8\) complexes that compete within the population of the emissive MLCT states. Thus by changing the spectator ligand, the population of the MLCT can be improved to generate the emissive behavior either by raising the d-d LF excited states energy through the incorporation of strong \(\sigma\)-donor ligands, or lower MLCT energy through the introduction of strong \(\pi\)-acceptor ligand.\(^1\)

<table>
<thead>
<tr>
<th>Ligand</th>
<th>(\lambda_{max}) (nm) 298 K</th>
<th>(\lambda_{max}) (nm) 77 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2,2'\text{-bipyridyl (bpy)})(^{14})</td>
<td>610(^a)</td>
<td>535(^b)</td>
</tr>
<tr>
<td>(4,4'\text{-}(\text{CH}_3)_2\text{-bpy})(^{21})</td>
<td>601(^c)</td>
<td>510(^b)</td>
</tr>
<tr>
<td>(4,4'\text{-}(\text{phenyl})_2\text{-bpy})(^{19})</td>
<td>647(^d)</td>
<td>560(^b)</td>
</tr>
<tr>
<td>(4,4'\text{-}(\text{COOCH}_3)_2\text{-bpy})(^{22})</td>
<td>600(^e)</td>
<td>555(^f)</td>
</tr>
<tr>
<td>(4,4'\text{-}(\text{Cl})_2\text{-bpy})(^{19})</td>
<td>700(^g)</td>
<td>580(^b)</td>
</tr>
<tr>
<td>(4,4'\text{-}(\text{NCH}_3)_2\text{-bpy})(^{22})</td>
<td>532(^e)</td>
<td>472(^f)</td>
</tr>
</tbody>
</table>

\(^a\) Dichloromethane. \(^b\) Ethanol / methanol (4:1) v/v). \(^c\) Acetonitrile. \(^d\) Methyl THF. \(^e\) DMF. \(^f\) DMF/CH\(_2\)Cl\(_2\) (9:1) v/v)
III.3.1 Synthesis

Different methods have been employed to substitute the chloride ion with different electron donating or accepting groups such as acetylides\textsuperscript{24,25} to prepare neutral Re(I) complexes, or pyridines\textsuperscript{26} substituted pyridines,\textsuperscript{2c,4b,27} isocyanides,\textsuperscript{28} phosphines or phosphites,\textsuperscript{29} etc... to prepare cationic Re(I) complexes through the removal of Cl ligand by silver salts, filtration of AgCl, then coordination of the monodentate ligand that substitutes the coordinated solvent used in the reaction mixture, as summarized in Scheme 3.3.

III.3.2 Photophysical properties

III.3.2.1 Re-acetylides

The alkynyl group with its linear geometry, rigid structure, extended π-electron delocalization, and its ability to interact with metal centers via p\textsubscript{x}-d\textsubscript{x} overlap which can effectively strengthen the metal-carbon bonds,\textsuperscript{30} is an attractive building block for the construction of carbon-rich containing materials which may possess potential applications as
nonlinear optical materials, molecular wires, and molecular electronics. In 1995, Vivian Yam and her co-workers reported the synthesis of the first luminescent Re(I)-acetylide complex in solution, solid state, and at room temperature (Scheme 3.4).

In general, the electron absorption spectrum of these complexes in acetone shows an intense low energy absorption at c.a. 391-440 nm attributed to a MLCT dπ(Re) → π*(tBu2bpy) which is relatively red-shifted compared to the chloro counterpart Re(CO)3(tBu2bpy)Cl. This red shift in MLCT is consistent with the σ-donating ability of the acetylide, being stronger than that of the chloro moiety, that renders Re(I) center more electron-rich, raising the Re(I) d-d states energy, and thereby improving the population of MLCT.

Upon excitation at λ>350 nm, the Re-acetylide complexes show intense and long-lived orange-red luminescence in solution and solid state ascribed to 3MLCT emissions which occurs at lower energy (red shifted) compared to the chloro counterpart, and this is again consistent with the good σ-donating ability of the acetylide, which would render Re(I) center more electron rich and hence lower the MLCT transition energy.

![Scheme 3.4: Synthesis of Re(I)(CO)3(tBu2bpy)acetylide complexes.](image)

**Figure 3.3** Emission spectra of [Re(CO)3(tBu2bpy)Cl] (—), R=tBu (---) and R=H (· · · ·) in degassed THF at 298 K. Reproduced from reference 30.
One of the interesting applications for such complexes reported by Yam and her coworkers is their incorporation into organogel systems to form luminescent metallogels.\textsuperscript{32} By designing the polypyridine bidentate ligand and the acetylide ancillary ligand, both complexes Re-A and Re-B (Scheme 3.5) showed gelation properties in DMSO, and also in \textit{n}-hexane and acetone respectively with low critical gelation concentration (Figure 3.4).

Moreover, the solution (sol)-gel transformation is found to be thermally stable with detectable color and emission changes. Upon excitation at the absorption maxima, the DMSO metallogels emit strongly at 580-650 nm, however it was almost “turned off” in the solution state (Figure 3.5). This explains the importance of the rigidity in the gel state that reduces molecular vibration and motions and hence slows down the nonradiative deactivation pathways.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.4.png}
\caption{Representative images of (a) the gel formed from Re-A in hexane (10 wt \%) and (b) the gel formed from Re-B in DMSO (9 wt \%). Reproduced from reference 32.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.5.png}
\caption{Corrected emission spectra of the DMSO gel of Re-B at 25 °C (s) and the DMSO sol at 75 °C (-- -). Reproduced from reference 32.}
\end{figure}

\textit{Scheme 3.5} Re tricarbonyl diimine complexes that possess gelation properties.
III.3.2.2 Re-isocyanides

Recently, attention was paid on the design of rhenium tricarbonyl complexes with isocyanides as ancillary monodentate ligands, i.e. \([\text{N}^\text{N'}\text{Re}(\text{CO})_3\text{CNR}]^+\), that can finely tune the photophysical properties through high quantum yields (>0.7) and long excited-state lifetimes (>100μs).\(^\text{16e,33-36}\) Isocyanides (R-NC:) are isoelectronic to carbonyl ligand (OC:), and their coordination abilities are similar. However, one of the advantages of using isocyanide ligands is that the physical, steric, and electronic properties of metal isocyanide complexes can be effectively tuned through the modification of the substituent on the N atom.\(^\text{2a,33}\)

The photophysical properties of complexes of the general formula \([\text{Re}(\text{CO})_3(\text{N}^\text{N'})(\text{CNR})]^+\) (\(\text{N}^\text{N'} = 2,2'-\text{bipyridine, or substituted phenanthroline; R = t-Bu, n-alkyl, 2,6-dimethylphenyl, or 2-methoxybenzene}\)) have been examined.\(^\text{2a,16ec,e,28,34-36}\)

All complexes display intense UV/vis absorption bands at c.a. 230-350 nm corresponding to the spin allowed IL \(\pi-\pi^*\) transitions of isocyanides and diimine ligands. This assignment is based on the striking similarity in energy, extinction coefficient, and band shapes to the transitions observed in the free ligand. In addition, several moderately intense bands or shoulders in the lower energy region 330-450 nm are also observed in the absorption spectra of these complexes which are ascribed to MLCT \(d(\pi)\text{Re} \rightarrow \pi^*(\text{CNR})\) and MLCT \(d(\pi)\text{Re} \rightarrow \pi^*(\text{N}^\text{N'})\) transitions and probably mixed with LLCT \(\pi(\text{CNR}) \rightarrow \pi^*((\text{N}^\text{N'})\) transitions.

For the series of complexes \([\text{Re}(\text{CO})_3\text{LCN}-\text{tBu}]^+\) (L = bpy, 1,10 phenanthroline, 4,7-dimethyl-1,10-phenanthroline or 3,4,7,8-tetramethyl-1,10-phenanthroline) the lowest excited state was controlled by varying L or temperature. At room temperature the emission spectra show a clear progression from broad structureless \(^3\text{MLCT}\) to highly structured \(^3\text{IL}\) emission on going from bpy, to 1,10-phenanthroline to 4,7-dimethyl-1,10-phenanthroline to 3,4,7,8 tetramethyl-l,10-phenanthroline (Figure 3.6).\(^\text{16c-e}\)

![Figure 3.6 Room temperature emission spectra of LRe(CO)\(_3\) (CN-\('\text{tBu}')\) in CH\(_2\)Cl\(_2\). The appearance of the structured spectra reveals the \(^3\text{IL}\) (\(\pi-\pi^*\) phosphorescence) emission property. Reproduced from reference 16e.](image)
The trend in $^3$IL character revealed in the emission spectra was paralleled by the increase in lifetimes. Lifetimes of 1.97, 10.6, 68.9 and 120.7 μs were obtained for the bpy, 1,10-phenanthroline, 4,7-dimethyl-1,10-phenanthroline and 3,4,7,8-tetramethyl-1,10-phenanthroline complexes respectively. The trend in $\pi$-$\pi^*$ character revealed in the emission spectra, paralleled by the changes in the substituents, arises from the rigidity of the environment that prevents relaxation of the MLCT state and keeps it at higher energy relative to the ligand $\pi$-$\pi^*$ triplet state. At 77 K, all of the complexes showed increased $^3$IL $[^3(\pi-\pi^*)]$ character as evidenced by the increase in structure of emission spectra. Most notably at 77 K, [Re(CO)$_3$(bpy)(CN-tBu)]$^+$ emits from both $^3$IL and $^3$MLCT states (Figure 3.7) whereas at room temperature only $^3$MLCT based emission was observed (Figure 3.6).

![Graph showing structured and structureless emission](image)

**Figure 3.7** Low temperature (77 K) emission spectra of bpyRe(CO)$_3$(CN-tBu)$^+$ in 9:2 DMF/CH$_2$Cl$_2$. The appearance of the structured spectra reveals the $^3$IL ($\pi-\pi^*$ phosphorescence) emission property. Reproduced from reference 16e.

Similar trends were also observed for the series of complexes [Re(CO)$_3$(s-phen)(CNR)]$^+$ where s-phen = 1,10-phenanthroline, 4,7-dimethyl-1,10 phenanthroline or 3,4,7,8- tetramethyl-1,10-phenanthroline and CNR = 2,6 dimethylphenylisocyanide, or 2-methoxybenzene. The 1,10-phenanthroline complex was classed as a MLCT emitter at room temperature whereas both MLCT and IL based emission were observed from the 4,7-dimethyl-1,10-phenanthroline and 3,4,7,8-tetramethyl-1,10-phenanthroline complexes at room temperature. This could be due to the fact that at 77 K the $^3$MLCT shifts up to a much higher energy than $^3$IL, and under these conditions, the emission would likely to occur as ligand-centered character.

### III.3.2.3 Re-pyridines

There has been extensive work carried out over decades in synthesizing rhenium tricarbonyl complexes of the form $\text{fac-[Re(CO)}_3(N^N')(L)]^+$ where L = pyridine / substituted...
pyridine (Scheme 3.3). The replacement of the weak field Cl\(^-\) with a stronger ligand field pyridine can modify the photophysical properties of rhenium complexes from single to multiple emissions as investigated by Wrighton and his coworkers in 1979.\(^{37}\) They reported the synthesis and characterization of a set of cationic Re(I) complexes where systematic variations in charge density on Re(I) resulted in systematic variation in the \(^3\)MLCT energy emissive state and consequently another emission state is obtained assigned to \(^3\)(\(\pi-\pi^*\)) transition that can be controlled and manipulated depending on the energetic separation of \(^3\)MLCT and \(^1\)(\(\pi-\pi^*\)) states.

The photophysical properties of different fac-\([(N^N')(\text{Re(CO)}_3(L))]^+ (N^N'= 2,2'-bipyridine, 1,10-phenanthroline, 5 phenyl-1,10-phenanthroline, etc… and L = substituted pyridine or quinoline) were studied. Their absorption and emission spectra at room and low temperature coincide properly with Re complexes possessing isocyanides as ancillary ligands.\(^{16b,d,38,39}\)

The fine tuning of the photophysical properties of fac-\[[\text{Re(CO)}_3(L-L)(\text{py})]^+\) as well as the easy functionalization of pyridine ligands with different substituents broaden the prospects in different fields of applications such as cell imaging,\(^{40,41}\) biological probes,\(^{42-45}\) photocatalytic H\(_2\) production from water,\(^{46}\) C-C coupling,\(^{47}\) etc… Moreover, the different applications of rhenium(I) tricarbonyl complexes have been reviewed recently by K. K.-W. Lo and coworkers.\(^{2c}\)

### III.4 Chiral Re(I) tricarbonyl diimine complexes

Very few examples of Re(I) tricarbonyl complexes coordinated to chiral bipyridine ligands have been reported in the literature. In 1999, Katz and coworkers\(^{48}\) prepared rhenium(I) complex Re-C coordinated to [7]helicene bearing 1,10-phenanthroline functionality (Scheme 3.6). The \(^1\)H NMR spectrum of the pure fraction revealed the symmetrical structure of the complex. However, the photophysical properties of this complex were not reported.
In 2012, Réau, Hissler, Crassous and coworkers issued the synthesis of different chiral Rhenium complexes bearing phosphole–pyridine chelates\(^{49}\) (Scheme 3.7), where the different diastereoisomers were separated by HPLC over chiral stationary phase. They demonstrated that the large dissymmetric environment around the heavy Re center resulted from the coordinated (2-pyridyl)phosphole ligands leads surprisingly to large chiroptical properties as shown in Figure 3.8.

More recently, Zheng and coworkers\(^{50}\) reported the synthesis and characterization of chiral rhenium(I) complex **Re-F** based on the chiral \((-\)\)-4,5-pinene-2,2\'-bipyridine ligand (Scheme 3.8). Its emission spectrum shows efficient MLCT phosphorescence with a photoluminescence
quantum efficiency of 0.035, and represents the first rhenium-based complex reported with ferroelectricity.

Consequently, the rare examples of chiral rhenium complexes attracted our attention to:

- Prepare enantiopure Re complexes of H6-bipy.
- Tune the chiroptical properties.
- Look for efficient luminescence properties.
- Obtain the first CPL active rhenium complexes.

**III.5 Results and discussion**

In this chapter, the synthesis of helicenes coordinated to one or two Re(CO)$_3$Cl units through their $N^N'$ chelating moiety are described. The structure of the complexes has been determined by multinuclear NMR spectroscopy and X-ray crystallography.

The photophysics and chiroptical properties of the enantiopure pure Re(I) complexes have been measured experimentally. We will show also that the incorporation of one or two Re atoms within an extended $\pi$-conjugated system significantly impacts the properties of these helicenes derivatives.

It is worth to mention that octahedral complexes can be chiral; in the case of rhenium(I) tricarbonyl diimine complexes: if the two pyridyl rings are identical, such as 2,2’-bipyridine, then the octahedral complex possesses $C_5$ symmetry, which means Re is not a stereogenic center. However, the difference in the two pyridyl rings breaks the $C_5$ symmetry and therefore rhenium becomes a stereogenic center that attributes two mirror images absolute configurations, clockwise designated by “C” and anti-clockwise designated by “A”.\footnote{59}
The absolute configuration is described by the steering-wheel system, a principle put by Cahn, Ingold, and Prelog\textsuperscript{51} consisting of an oriented plane (or circle) traversed by a vector oriented perpendicularly to the plane. The orientation in the plane or around the circle, both to the right or to the left, is unambiguous and will be called “C” and “A” (Figure 3.9).

The priority rules (sequence rule) allow the oriented plane and axis to be defined as $C$ or $A$. The priority rules are the same in coordination chemistry as in organic chemistry.\textsuperscript{52}

\begin{center}
Priority 1 2 3, the oriented plane $P$ is:
\end{center}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{steering_wheel_system.png}
\caption{The steering-wheel system.}
\end{figure}

In the case of octahedrons (except those bearing several bis-chelate ligands for which the $\Delta,\Lambda$ is more appropriate),\textsuperscript{59} the oriented axis goes from the ligand with the highest priority (1) towards the trans ligand with the lowest possible priority. The ligands situated in the perpendicular plane are numbered according to the priority rules. The sense of rotation is then which goes from the ligand with the highest priority towards its immediate neighbor with the lowest priority.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{octahedral_system.png}
\caption{Priority $a$, $b$, $c$}
\end{figure}

III.5.1 Synthesis and characterization of $[\text{LRe(CO)}_3\text{X}]^n$ with $\text{L}=[4]\text{helicene-bipy}$

All $\text{fac}$-diimine rhenium(I) tricarbonyl chloride complexes were prepared following the same procedure; the free ligand is mixed with commercially available $\text{Re(CO)}_5\text{Cl}$ and thermal substitution of two CO ligands occurs in refluxing toluene.
In addition, in our aim to fine tune the chiroptical properties of Re(I) tricarbonyl systems, the rigorous design of the ancillary ligand (electron donating / withdrawing) and its possibility to influence the MLCT excited states can interestingly yield unprecedented results. The Cl coordinated ligand in the axial position was modified by phenyl acetylene, and pyridine as electron donating ligands, and 2,6-dimethylphenyl isocyanide as electron accepting ligand.

*a*- (H$_4$-bpy)Re(CO)$_3$Cl [Re-1] complex

The reaction was first optimized with H$_4$-bpy 62 that was added to refluxing toluene solution with 1 eq. of Re(CO)$_5$Cl (Scheme 3.9). The color directly changes to red, and the reaction mixture was refluxed for 5 hours during which the product precipitates as yellow-orange solid that was isolated by filtration then washed with ether to obtain one product Re-1 as identified by $^1$H-NMR (Figure 3.11) and $^{13}$C-NMR spectroscopy (one set of peaks). It was also characterized by elemental analysis and UV/Vis spectroscopy.

\[ \text{62} + \text{Re(CO)}_3\text{Cl} \rightarrow \text{Toluene \ Reflux-6 hrs \ 85\%} \]

Scheme 3.9: Reaction of Rhenium pentacarbonyl chloride with H$_4$-bpy 62.

The numbering system employed in the assignment of $^1$H NMR peaks is shown in Figure 3.10, and the assignment of protons resonances were made by comparison with the model [Re(CO)$_3$(bpy)Cl] complex, free ligand, and with the aid of two dimensional (COSY) spectra.

It is worth to mention that the chemical shifts of the protons of the ligands are influenced by three factors:

(i) The electron density on the ligands diminishes upon coordination, inducing a downfield shift.

(ii) Steric effects lead to a downfield shift

(iii) Alignment of a proton above an adjacent aromatic ring leads to a dramatic upfield shift.
The free H$_4$-bpy ligand 62 and the H$_4$bpy rhenium tricarbonyl complex Re-1 display signals between 7.2 and 9.7 ppm as shown in Figure 3.10. Except for H$_{12}$, H$_{6'}$, and H$_2$ that were shielded after complexation, all other protons peaks are found to be downfield shifted with remarkable deshielding of H$_{3'}$, H$_{4'}$, H$_5'$, and H$_5$ (Figure 3.11). The difference between the shifts of protons resonances after coordination with respect to the free ligand (c.i.s. = $\delta_{\text{complex}} - \delta_{\text{ligand}}$) are listed in Table 3.3. The positive c.i.s. values have been attributed to ligand-to-metal $\sigma$-donation when a ligand coordinates to a metal center.$^{54,55}$

The positive c.i.s values corresponding to the downfielded protons can be explained by the reduction of electron density on the ligand after coordination, and electron delocalization between pyridine ring and the ortho fused aromatic rings. The highest c.i.s. of H$_5$ (0.8 ppm) can be also due to the additional steric effect of the Re metal after coordination. The slight shift of H$_{12}$, H$_{6'}$, and H$_2$ can be probably due to an increase in electron density.

Figure 3.10: Structures of bipyridine-helicenes with corresponding rhenium(I) tricarbonyl discussed in this section. Numbering employed in the assignment of the $^1$H NMR peaks.
**Table 3.3:** Coordinated-induced shifts in Re-1 relative to the free ligand 62.

<table>
<thead>
<tr>
<th>c.i.s</th>
<th>H_{Nb}</th>
<th>H_1</th>
<th>H_3'</th>
<th>H_5</th>
<th>H_{12}</th>
<th>H_6'</th>
<th>H_2</th>
<th>H_6</th>
<th>H_5'</th>
<th>H_9</th>
<th>H_7</th>
<th>H_8</th>
<th>H_{10}</th>
<th>H_{11}</th>
<th>H_4'</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.2</td>
<td>0.4</td>
<td>7</td>
<td>0.8</td>
<td>-0.13</td>
<td>-0.26</td>
<td>-0.29</td>
<td>0.2</td>
<td>7</td>
<td>0.3</td>
<td>0.11</td>
<td>0.17</td>
<td>0.11</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

**Figure 3.11:** $^1$H NMR spectra of H$_4$-bpy 62 (red) and (H$_4$-bpy)Re(CO)$_3$Cl Re-1 (blue) in CD$_2$Cl$_2$ (400 MHz)

**b)- (H$_4$-bpy)Re(CO)$_3$(CCPh) \{Re-2\} complex**

Re-2 was synthesized following a reported procedure$^{56}$ by refluxing the suspension of Re-1, AgOTf, phenyl acetylene, and Et$_3$N in THF (Scheme 3.10). After filtration of AgCl, the crude reaction mixture was purified by column chromatography using CH$_2$Cl$_2$ as the eluent to recover Re-2 as a red solid. However, the negative feedback of this nucleophilic substitution is the low yielded product. Re-2 is well determined by $^1$H NMR spectroscopy through the appearance of 5 protons corresponding to the aromatic region of the phenyl group between 6.5 and 7 ppm (Figure 3.12).

![Scheme 3.10 Synthesis of Re-2: Nucleophilic substitution of Cl ligand with phenyl acetylene.](image-url)
In addition to neutral Re(I) tricarbonyl complexes, cationic Re(I) complexes can be prepared by substitution the Cl ancillary ligand with neutral 2 electron donor ligands such as pyridines and isocyanides.

c) \((H_4-bpy) Re(CO)_3(py)\) \{Re-3\} complex

Re-3 was prepared from Re-1 by removing the Cl ligand using AgBF₄ in refluxing acetonitrile that coordinates to the cationic Re as evidenced by the appearance of a singlet at 2.04 ppm in the \(^1\)H NMR spectra. After filtration of AgCl precipitate, substitution of the coordinated CH₃CN with pyridine takes place in refluxing THF reaction mixture. Re-3 was observed as yellow precipitate with high yield after filtration over celite and drying under vacuum (Scheme 3.11).

![Scheme 3.11 Synthesis of cationic Re-3.](image)

Single crystals of complex Re-3 were grown from slow diffusion of pentane vapors in a DCM solution and crystallized in a centrosymmetric space group \(P2_1/n\) (Figure 3.13). The coordination sphere of the rhenium unit can be described as a slightly distorted octahedron in which the three carbonyl ligands are arranged in a facial geometry. The equatorial plane is described by the chelate bipyridine ligand and two \textit{trans} carbonyls. A third carbonyl and the pyridine are placed in the apical plane. Moreover, the pyridine ligand is directed in the same sense as the helical backbone of \([4]\)helicene-bpy that has a helical degree of \(34.62^\circ\).
Following the same principle, Cl was removed by reacting AgOTf in a refluxing EtOH/THF mixture. Re-4 was obtained with high yield by substitution of coordinated triflate to Re with isocyanide, another 2 e⁻ neutral donating ligand and isoelectronic to carbonyl (Scheme 3.12).

The complex was isolated as a yellow precipitate and crystallized by slow diffusion of pentane vapors in a DCM solution to obtain single crystals with Fdd2 space group where it possesses the same geometry as the previously reported Re complexes (Figure 3.14). Moreover, the isocyanide ligand is directed in the same sense as the helical backbone of [4]helicene-bpy that has a helical degree of 34.57°.
III.5.2 Synthesis and characterization of LRe(CO)₃Cl with L=[6]helicene-bipy

\textit{a)- (H₆-bpy)Re(CO)₃Cl complex}

The same synthetic procedure to prepare Re-1 was followed with racemic H₆-bpy 63 and Re(CO)₅Cl, however, taking a look at ¹H NMR (Figure 3.15), two sets of peaks are resolved that correspond to two diastereomeric Re(I) complexes Re-5 and Re-6 (Scheme 3.13) distinguished by the position of the Cl group in the axial position, either directed towards or outward the helical core.

![Scheme 3.13: Reaction of Rhenium pentacarbonyl chloride with racemic H₆-bpy (±)-63.](image)

Multinuclear NMR spectroscopy especially ¹H-NMR has been widely effectively used for the structural characterization of Rhenium tricarbonyl complexes due to their diamagnetic low spin d⁶ configuration.⁵⁷,⁵⁸ The crude ¹H NMR of the reaction mixture in Scheme 3.13 showed two sets of peaks between 6.7 and 9.2 ppm with unequal proportion and different from the starting material (free ligand) that were ascribed as the two diastereomeric Re complexes Re-5 and Re-6 due to the similarity in the proton resonances (Figure 3.15). The diastereoselectivity comes from the non-planar helical structure of the H₆-bpy moiety. Upon complexation, the Cl group in the axial position of the \textit{fac-(H₆-bpy)Re(CO)₃Cl} can be directed in the same or opposite sense to the helical core. This also explains the presence of one (H₄-bpy)Re(CO)₃Cl product due to the average planar structure of H₄-bpy.
After the separation of the two diastereomers by the aid of silica gel column chromatography (ethyl acetate / heptane), the $^1$H NMR was recorded, showing the difference in shifts of proton resonances between them and relative to the free ligand (Figure 3.16).

Figure 3.15: $^1$H NMR spectra of H$_6$-bpy 63 (red) and crude (H$_6$-bpy)Re(CO)$_3$Cl Re-5,6 (blue) in CD$_2$Cl$_2$ (400 MHz)

Figure 3.16: $^1$H NMR spectra of H$_6$-bpy 63 (red), Re-6 (green), and Re-5 (blue) in CD$_2$Cl$_2$ (400 MHz).
The major difference between the two diastereomeric Re(I) tricarbonyl complexes, as referred to the proton NMR, is H_{15} that is more deshielded in Re-5 (fraction-1) than Re-6 (fraction-2) due to the orientation of Cl / CO groups. In the two complexes, there is a remarkably downfield shift for all the protons of the two pyridyl rings after coordination due to the decrease in electron density and delocalization between the fused rings, except for H_{6} that is found upfield shifted and coincides with the results of (bpy)Re(CO)_{3}Cl and Re-1.

Single crystals of complex Re-5 were grown from slow diffusion of a DCM solution and crystallized in a non-centrosymmetric space group (P2_{1}/C) in which two enantiomeric structures are presented in the unit cell, namely (M,C^{Re})- and (P,A^{Re})-Re-5^{59} that assemble into heterochiral dimers due to π–π interaction (interplanar distance 3.2 – 3.6 Å, Figure 3.17). The Re atom adopts a distorted octahedral geometry, with three carbonyl groups being fac-oriented around the Re(I), as classically seen in such rhenium(I) tricarbonyl diimine complexes.

Note that a substantial distortion comes from the bite angles between the chelating N atoms of the helicenic ligand, the rhenium center, and the chlorine ligand ranging between 82.58-84.30°. In complex Re-5 the chlorine atom is directed inwards the helicene moiety, whereas it therefore directs outwards the helicene core in the enantiomeric complexes (M,A^{Re}) and (P,C^{Re})-Re-6.

![Figure 3.17: (a) X-ray structure of Re-5; (b) (M,C^{Re})-Re-5 and (P,A^{Re})-Re-5 assembly (π-π stacking).](image)

The helicity of the aza[6]helicene moiety ranges between 47.04-66.15°, classical values for aza[6]helicene derivatives.^{60} Finally, complexation with Re allows an extended π-conjugation over the whole molecule, as evidenced by the small NCCN dihedral angles between the two chelating pyridine moieties (-3.07-6.01°). This is also evidenced in the UV/vis spectrum (see below).

\[b)- (\text{H}_6\text{-bis-bpy})\text{Re(CO)}_3\text{Cl complex}\]

Racemic H_{6}-bis-bpy (±)-64 was reacted with 2 eq. of Re(CO)_{3}Cl in refluxing toluene, yielding after purification by column chromatography a mixture of dinuclear Re(I) diastereomers (Re-7, 84%) and (Re-8, 16%) (Scheme 3.14), as evidenced by \textsuperscript{1}H NMR (Figure 3.18) and X-ray diffraction. (Figure 3.19)
The diastereoselectivity between **Re-7** and **Re-8** can be easily interpreted by $^1$H NMR spectroscopy where **Re-7** displays a symmetric $^1$H spectrum since the two Re centers have the same stereochemistry (clockwise; $C^{Re},C^{Re}$ or $A^{Re},A^{Re}$), while fraction 2 (**Re-8**) displays dissymmetric spectra due to the dissymmetry in the stereochemistry of Re centers; one Re center displays “C” configuration while the other displays the “A”. The $^1$H NMR spectra is characterized by the downfield shift of approximately all the protons after coordination (Figure 3.18), which can be explained by the reduction of electron density on the ligand after coordination, and electron delocalization between pyridine rings and the ortho fused aromatic rings. Note that the Re complex consisting of the 2 Cl placed outward the helix was not observed in the reaction mixture.

**Scheme 3.14:** Reaction of Rhenium pentacarbonyl chloride with racemic H$_6$-bis-bpy (±)-64.

**Figure 3.18:** $^1$H NMR spectra of H$_6$-bis-bpy 64 (red), Re-7 (blue) and Re-8 (green), in CD$_2$Cl$_2$. 
Single crystals of complexes Re-7 and Re-8 were grown by slow diffusion of pentane vapors in DCM solution and crystallized in a non-centrosymmetric space groups (Re-7: \( P2_1/n \); Re-8: \( P2_1/c \)) in which two enantiomeric structures are presented, namely \((M, C^\text{Re}, C^\text{Re})\) and \((P, A^\text{Re}, A^\text{Re})\)-Re-7 and \((M, C^\text{Re}, A^\text{Re})\) and \((P, A^\text{Re}, C^\text{Re})\)-Re-8 (Figure 3.19).

Each Re atom adopts a distorted octahedral geometry, with three carbonyl groups being fac-oriented around the Re(I). In complex Re-7, each chlorine atom is directed inwards the helicene moiety, thus it possesses a \( C_2 \) symmetry as each Re atom has “C” or “A” configuration with helical degree 39.13°, while in Re-8 chlorine atoms are directed inwards and outwards the helicene core with subsequent Re “C” and “A” configurations, respectively. The symmetry is broken, and the helical degree is 46.39°.

**Figure 3.19:** X-ray structure of dinuclear Re(I) complexes (a) \((M, C^\text{Re}, C^\text{Re})\)-Re-7; (b) \((M, C^\text{Re}, A^\text{Re})\)-Re-8 (only one enantiomer shown).

### III.5.3 Photophysical Studies

The photophysical studies concerning the UV/vis absorption and emission properties of the prepared complexes were investigated in comparison with the free ligands.

#### III.5.3.1 Absorption Studies

The UV-absorption spectra of all complexes synthesized in this chapter were recorded in dichloromethane solutions at 295±3 K. Their absorption data are summarized in Table 3.4.

**Figure 3.20:** shows the absorption spectra of Re-1 in comparison with the free ligand H₄-bpy 62. This spectrum illustrates the considerable effect of the metal on optical properties especially in the 380-510 nm region. The absorption bands of Re-1 lying at high energy between 230-370 nm and centered at \( \lambda_{\text{max}} = 330 \text{ nm} \) (\( \varepsilon = 43200 \)) can be clearly assigned to IL \( \pi-\pi^* \) (H₄-bpy) which is very similar in energy, extinction coefficient, and band shape to the free ligand.
The electronic absorption spectra of complexes Re-2,3, and 4 shown in Figure 3.21 in comparison with Re-1 show intense high-energy absorption bands at about 230-370 nm, ascribed to an admixture of IL $\pi \rightarrow \pi^*$ transitions of the diimine and alkynyl, pyridyl, and isocyanide ligands. The low energy absorptions at about 370-530 nm are ascribed to MLCT $d\pi(\text{Re}) \rightarrow \pi^*$ (H$_4$-bpy) for the three complexes accompanied with other transitions. In particular, the low-energy absorptions for Re-2 complex between 370-430 nm and tailed down to about 430-530 nm, centered at 451 nm ($\varepsilon = 2970 \text{M}^{-1}\text{cm}^{-1}$), are assigned to the $[d\pi(\text{Re}) \rightarrow \pi^*(\text{diimine})]$ metal-to-ligand charge transfer (MLCT) transition, probably mixed with some $[\pi(\text{CCPh}) \rightarrow \pi^*(\text{H}_4\text{-bpy})]$, alkynyl-to-diimine ligand-to-ligand charge transfer (LLCT) character. On the other hand, the bathochromic low-energy absorption bands at $\lambda>$370 nm and tailed to ~480 nm corresponding to Re-3 and Re-4 with extinction coefficients greater than Re-1 are ascribed to $[d\pi(\text{Re}) \rightarrow \pi^*(\text{diimine})]$, $[d\pi(\text{Re}) \rightarrow \pi^*(\text{L})]$ (where L = pyridine or isocyanide), and probably mixed with LLCT $[\pi(\text{CNR}) \rightarrow \pi^*(\text{H}_4\text{-bpy})]$ and $[\pi(\text{py}) \rightarrow \pi^*(\text{H}_4\text{-bpy})]$ transitions.
Table 3.4: Absorption data of ligands and complexes in DCM at 298 K.

<table>
<thead>
<tr>
<th>Ligand / Complex</th>
<th>$\lambda_{\text{max}}$ / nm ($\epsilon$ / M$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_4$-bpy 62</td>
<td>295 (57800), 309sh (33800), 331 (19600), 347 (17900), 363 (8880), 383 (7640)</td>
</tr>
<tr>
<td>Re-1</td>
<td>243 (34500), 273 (30300), 318 (30300), 330 (43200), 398 (12700)</td>
</tr>
<tr>
<td>Re-2</td>
<td>243 (37800), 273 (44200), 316 (33000), 328 (41500), 381 (10100), 402 (9670), 451 (2970)</td>
</tr>
<tr>
<td>Re-3</td>
<td>248 (35700), 280 (34200), 327sh (27300), 338 (37700), 408 (13500), 422 (13900)</td>
</tr>
<tr>
<td>Re-4</td>
<td>251 (54900), 273 (51900), 326sh (35900), 337 (46600), 403 (14600), 422 (15200)</td>
</tr>
<tr>
<td>H$_6$-bpy 63</td>
<td>240 (35000), 266 (55800), 322 (27000), 353 (14400), 372 (10200), 393 (2630), 417 (1800)</td>
</tr>
<tr>
<td>Re-5</td>
<td>237 (59800), 278 (65000), 305sh (36300), 344 (26300), 418 (11000), 445 (10200)</td>
</tr>
<tr>
<td>Re-6</td>
<td>236 (45900), 277 (49900), 307 (28200), 339 (21300), 420 (7960), 444 (7300)</td>
</tr>
<tr>
<td>Re-7</td>
<td>283 (46500), 299 (51400), 361 (15500), 387 (15400), 450 (6080)</td>
</tr>
<tr>
<td>Re-8</td>
<td>283 (33700), 299 (37900), 359 (12700), 389 (11300), 450 (5090)</td>
</tr>
<tr>
<td>H$_6$-bis-bpy 64</td>
<td>242 (35100), 272 (60300), 286 (65300), 344 (26500), 366sh (20200), 398 (3500), 420 (2750)</td>
</tr>
</tbody>
</table>
**b) Re(I) complexes with [6]helicene-bipy 63 and 64**

Figure 3.22 shows the absorption spectra of the two diastereomeric **Re-5** and **Re-6** in comparison with the free ligand H$_6$-bpy 63. The two complexes possess same absorption bands but with smaller absorption coefficient for **Re-6**. The high energy absorption bands between 230-370 nm centered at $\lambda_{\text{max}} = 278$ nm for **Re-5** and $\lambda_{\text{max}} = 277$ nm for **Re-6**, and red-shifted compared to the free ligand, are ascribed as IL $\pi-\pi^*$ (H$_6$-bpy).

At the low energy level between 370-480 nm, the absorption bands are assigned as MLCT d$_{\pi}(\text{Re}) \rightarrow \pi^*$ (H$_6$-bpy) in the two diastereomeric Re(I) complexes. However, looking deeply to the spectra, the two complexes possess two absorption bands in the MLCT region, centered at 418 nm and 445 nm for **Re-5**, and 420 nm and 444 nm for **Re-6**. These may correspond to a vibronic progression (**Re-5**: 1452 cm$^{-1}$, **Re-6**: 1287 cm$^{-1}$, 21; 1465 cm$^{-1}$).

The incorporation of two Re metal centers to the helicenic ligand H$_6$-bis-bpy 64 (**Re-7** and **Re-8**) shows an increase in extinction coefficient with red-shift in the absorption spectra at high energy ($\lambda_{\text{max}} = 299$ nm (51400 M$^{-1}$cm$^{-1}$) for **Re-7**, and 299 nm (37900 M$^{-1}$cm$^{-1}$) for **Re-8**) as shown in Figure 3.23, which are assigned to IL $\pi-\pi^*$ (H$_6$-bis-bpy). At lower energy ($\lambda > 370$ nm), the new bands in the absorption spectra of **Re-7** and **Re-8** ($\lambda_{\text{max}} = 387$ (15400 M$^{-1}$cm$^{-1}$), and 389 nm (11300 M$^{-1}$cm$^{-1}$), respectively) tailing down to c.a. 500 nm are ascribed as MLCT d$_{\pi}$(Re) $\rightarrow \pi^*$ (H$_6$-bis-bpy).
III.5.3.2 Emission Studies

The complexes were excited at their low energy bands (MLCT), and their emission spectra were recorded in deoxygenated dichloromethane at 298 K and in EPA glass at 77 K (EPA = diethyl ether / isopentane / ethanol 2:2:1 v/v). The emission data are summarized in Table 3.5.

At 298 K, all Re(I) tricarbonyl diimine complexes show similar broad and structureless emission spectra that are assigned as $^3$MLCT emission since the position and shape of the emission bands are consistent with that previously reported to [(diimine)Re(CO)$_3$(L)]$^{0/+1}$ complexes (L = Cl, phenylacetylene, pyridine, CNR).

As shown in Figure 3.24a, b, and c, the emission maxima for Re-1, 5, 6, 7, and 8 at 298 K are red shifted compared to (bpy)Re(CO)$_3$Cl ($\lambda_{\text{max}}$ = 610 nm), and they are as follows: Re-1, 678 nm; Re-5, 673 nm; Re-6, 680 nm; Re-7, 664 nm; Re-8, 678 nm. These Re(I) complexes with Cl ancillary ligand are characterized by low quantum yield and lifetime in ns (Table 3.5). Upon exchanging Cl ligand with phenylethynyl in Re-2, the emission is blue shifted in comparison to Re-1 (Figure 3.24a), but a low impact is observed on the quantum yield and lifetime (Table 3.5). On the contrary, the coordination of pyridine and isocyanide in Re-3 and Re-4, respectively, showed a significant effect on the blue shift on the emission spectra (Figure 3.24a); a strong increase in quantum yield from 0.11% in Re-1 to 8.3 % and 16 % in Re-3, and Re-4, respectively. Moreover, their lifetime increases toward the $\mu$s scale (Table 3.5) demonstrating the phosphorescence-type emission.

Figure 3.23: Absorption spectra of H$_6$-bis-bpy 64 (green), Re-7 (blue), and Re-8 (red) in dichloromethane at room temperature.
However, the emissions at 77 K for the all Re complexes, except Re-2, exhibit a spectacular change in character from broad and structureless band only at 298 K to vibrational structured emission features at higher energy (Figure 3.24 and 3.25b).

![Emission spectra of Re-1: blue at 298 K and red at 77 K](image1)
![Emission spectra of (H_{6}-bis-bpy)ReCOCl; Re-5: blue at 298 K and red at 77 K, Re-6: orange at 298 K and green at 77 K](image2)

The broad structureless emission is assigned to $^{3}$MLCT emission. On the other hand, the striking similarity of the highly structured emission at 77K with the $^{3}$IL [$^{3}(\pi-\pi^*)$] phosphorescence (Section II.6.2) leaves no doubt that these structured emissions are ascribed as ligand-centered phosphorescences of the coordinated ligands ($^{3}$IL). The sharp increase in radiative lifetimes also supports these assignments. However, the absence of long-lived $\pi-\pi^*$ component may be due to mixing of MLCT character into a $\pi-\pi^*$ state to make it more allowed. This is not surprising as it coincides with earlier results.\textsuperscript{16}
Table 3.5 Emission data of Re complexes in comparison with free ligand at room temperature at 77 K.

<table>
<thead>
<tr>
<th>Ligand / Complex</th>
<th>Emission 298 K</th>
<th>Φ_lum</th>
<th>Emission 77 K</th>
<th>Φ_lum</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>λ_{max} (nm)</td>
<td>τ (ns)</td>
<td>λ_{max} (nm)</td>
<td>τ (ns)</td>
</tr>
<tr>
<td>H₄-bpy 62</td>
<td>385, 406, 431, 456</td>
<td>3.8</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>Re-1</td>
<td>678</td>
<td>25</td>
<td>383, 392sh, 405, 428, 456</td>
<td>FLUOR</td>
</tr>
<tr>
<td>Re-2</td>
<td>643</td>
<td>24</td>
<td>512, 524, 555, 599, 654</td>
<td>PHOS</td>
</tr>
<tr>
<td>Re-3</td>
<td>595, 623</td>
<td>11500</td>
<td>553, 599, 649</td>
<td>74000</td>
</tr>
<tr>
<td>Re-4</td>
<td>585, 618</td>
<td>67000</td>
<td>553, 600, 649</td>
<td>101000</td>
</tr>
<tr>
<td>H₆-bpy 63</td>
<td>421, 445, 473, 508</td>
<td>6.6</td>
<td>417, 442, 471</td>
<td>FLUOR</td>
</tr>
<tr>
<td>Re-5</td>
<td>673</td>
<td>33</td>
<td>531, 542sh, 577, 624</td>
<td>PHOS</td>
</tr>
<tr>
<td>Re-6</td>
<td>680</td>
<td>27</td>
<td>554, 601, 654sh</td>
<td>43000</td>
</tr>
<tr>
<td>Re-7</td>
<td>664</td>
<td>38</td>
<td>560, 605, 654sh</td>
<td>46000</td>
</tr>
<tr>
<td>Re-8</td>
<td>678</td>
<td>32</td>
<td>557, 604, 624sh, 657</td>
<td>43000</td>
</tr>
<tr>
<td>H₆-bis-bpy 64</td>
<td>422, 488, 476, 510</td>
<td>5.1</td>
<td>421, 447, 476, 509</td>
<td>FLUOR</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>532, 546, 575, 626, 683</td>
<td>PHOS</td>
</tr>
</tbody>
</table>

Figure 3.25 (a): Emission spectra of Re(I) complexes with [4]helicene at 298 K.

Figure 3.25 (b): Emission spectra of Re(I) complexes with [4]helicene at 77 K.
The diagrams in Figure 3.26 explain the emission changes with temperature. At 298 K all emissions are MLCT in character, and the lowest excited state is MLCT. At 77 K all the emissions are blue-shifted and show significant change consistent with the $^3\pi-\pi^*$ being the lowest one. The greatly increased ligand emission components relative to the 298 K arises from the rigidity of the environment that prevents relaxation of the MLCT state and keeps it at higher energy relative to the ligand $^3\pi-\pi^*$. So at 77 K, inversion between the IL and MLCT energy states takes place that appears to be due to a smaller IL-MLCT state gap.

![Figure 3.26: State diagram for [(N^N')Re(CO)$_3$L]$^{n=1}$ complexes as function of temperature.](image)

### III.5.4 Chiral (N^N')Re(CO)$_3$Cl Complexes

Helicenes are fascinating chiral compounds since they possess a series of interesting chiral, physical, electronic and optical properties. Thus coordination with transition metals tunes finely the optical properties as discussed in Section III.2.3 and it can also tune the chiroptical properties.

Enantiopure “chiral at rhenium” complexes are still very rare.$^{48-50}$ The purpose after preparation of racemic complexes was to investigate the effect on chiroptical properties of the enantiopure complexes.

Before going on the synthesis, it is noteworthy to mention that (L)Re(CO)$_3$Cl are chiral with Re being a stereogenic center. They are identified as “clock wise” (C) or “anticlock wise” (A) configuration as previously explained.

So, (H$_6$-bpy)Re(CO)$_3$Cl can exist in 4 different stereoisomers (2 chiral elements; $2^2$): (P,A$^{Re}$) and (M,C$^{Re}$), i.e. (+)-Re-5, (-)-Re-5, (P,C$^{Re}$) and (M,A$^{Re}$) i.e. (+)-Re-6, (-)-Re-6, where M and P are designated for the H$_6$-bpy helicene moiety; A$^{Re}$ and C$^{Re}$ are designated for anticlockwise or clockwise orientation of stereogenic Re center (Figure 3.27).
Enantiopure complexes \((M,A^{\text{Re}})^{(-)}-\text{Re-5}\) and \((M,A^{\text{Re}})^{(-)}-\text{Re-6}\) were then prepared from enantiopure \(M^{(-)}-\text{H}_6\text{-bpy} \ 63\) (Scheme 3.15) and their mirror images \((P,C^{\text{Re}})^{(+)}-\text{Re-5}\) and \((P,A^{\text{Re}})^{(+)}-\text{Re-6}\) were obtained from \(P^{(+)}-\text{H}_6\text{-bpy}\) with the same synthetic procedure and purification as racemic complexes. These chiral at rhenium complexes can be obtained enantiomerically pure as evidenced and characterized by optical rotation (OR) and circular dichroism (CD).

On the contrary, no formation of enantiopure diastereomer \((+)^{-}\) and \((-)^{-}\)Re-8 was observed upon reaction of either \(M^{(-)}\)- or \(P^{(+)}-\text{H}_6\text{-bis-bpy}\) ligand with Re(CO)\(_5\)Cl. This phenomenon can be explained by the combined higher solubility of enantiopure \((-)^{-}\) and \((+)^{-}\)Re-8 in toluene with their lower stability at 110°C compared to Re-7, leading to their easy epimerization into \((-)^{-}\) and \((+)^{-}\)Re-7. In other words, the precipitation of \((\pm)^{-}\)Re-8 from the reaction mixture enables to isolate it despite its lower stability (and epimerization to) as compared to Re-7. Thus, the two enantiomers observed were \((M,C^{\text{Re}},C^{\text{Re}})^{(-)}-\text{Re-7}\) and \((P,A^{\text{Re}},A^{\text{Re}})^{(+)}-\text{Re-7}\) (Scheme 3.16).
Scheme 3.16 Synthesis of enantiopure (-) and (+)-Re-7 complexes.

### III.5.4.1 Optical Rotation (OR)

Complexes \((P, C^\text{Re})\)-Re-5 and \((P, A^\text{Re})\)-Re-6 display experimentally high specific and molar rotations \{\((P, C^\text{Re})\): \([\alpha]_D^{23} = 1440; \phi_D^{23} = 10250 (\pm 5\%); \}\{(P, A^\text{Re})\): \([\alpha]_D^{23} = 1200; \phi_D^{23} = 8550 (\pm 5\%); (C = 5 \times 10^{-5} \text{ M, CH}_2\text{Cl}_2)\}. The molar rotations are higher than the free ligand \((P-63;\phi_D^{23} = 7320)\).

Surprisingly, complex \((P, A^\text{Re}, A^\text{Re})\)-(+) Re-7 displays a much lower MR value \{\([\phi]_D^{23} = 4500 (\pm 5\%); (C = 5 \times 10^{-5} \text{ M, CH}_2\text{Cl}_2)\} than the free ligand \((P-64;\phi_D^{23} = 20830)\) and complexes (+)-Re-5 and 6. This might be due to the negative effect produced by the stereochemistry on Re center i.e. the stereogenic Re center and the helicene orient the polarized light in different directions, thus producing a subtraction effect on the final optical rotation.

### III.5.4.2 Circular Dichroism (ECD)

The ECD of enantiopure Re(I) complexes were investigated and were recorded on solutions of samples in CH\(_2\)Cl\(_2\) at ambient temperature and concentration around \(5 \times 10^{-5}\) M. In all
cases, they display mirror-image values for the (+) and (-) enantiomers within the experimental errors.

The ECD spectra of \((P, C^{Re})-(+)\text{-Re-5}\) and \((P, A^{Re})-(+)\text{-Re-6}\) complexes assigned by solid blue and green curves respectively (Figure 3.28) show a strong negative band at 274 nm for \((+)-\text{Re-5}\) with \{\(\Delta \varepsilon = -173 \text{ M}^{-1} \text{ cm}^{-1}\)\} and 264 nm for \((+)-\text{Re-6}\) \{\(\Delta \varepsilon = -116 \text{ M}^{-1} \text{ cm}^{-1}\)\} that have similar transitions to that of the free ligand but with slight increase in \(\Delta \varepsilon\) for \((+)-\text{Re-5}\), and decrease for \((+)-\text{Re-6}\). At \(\lambda > 300 \text{ nm}\), both complexes show red shifted strong positive ones with decrease in \(\Delta \varepsilon\) compared to free ligand at 352 nm \{(+)-\text{Re-5}: +123 \text{ M}^{-1} \text{ cm}^{-1}; \text{(+)-Re-6}: +85 \text{ M}^{-1} \text{ cm}^{-1}\}\} and 369 nm \{(+)-\text{Re-5}: +130 \text{ M}^{-1} \text{ cm}^{-1}; \text{(+)-Re-6}: +77 \text{ M}^{-1} \text{ cm}^{-1}\}\} accompanied with weaker ones between 380-450 nm \(\Delta \varepsilon = 20-50 \text{ M}^{-1} \text{ cm}^{-1}\) that are related to the MLCT character of Re.

On the other hand, the mirror image ECD spectra of \((-)-\text{Re-7}\) show several bands of medium intensities (Figure 3.29) where the high decrease in OR is observed again in \(\Delta \varepsilon\) of ECD as compared to the free ligand; \((+)-\text{Re-7}\) \(\Delta \varepsilon = -115, -50, +54, +35, -26 \text{ M}^{-1} \text{ cm}^{-1}\) at 270, 306, 360, 410 and 458 nm respectively) and this can be explained again probably by the difference in absorption between the left and right polarized light for asymmetric Re and chiral helicene.

Figure 3.28 CD spectra of enantiopure \(P-(+)-\text{H}_{6}\text{-bpy 63}\) (plain red) and their corresponding enantiopure Re(I) complexes \((M, A^{Re})-(+)\text{-Re-5}\) (dotted light blue) and \((M, C^{Re})-(+)\text{-Re-6}\) (dotted dark blue) and \((P, C^{Re})-(+)\text{-Re-5}\) (plain light blue) and \((P, A^{Re})-(+)\text{-Re-6}\) (plain dark blue).
III.6 Conclusion and perspectives

Rhenium(I) tricarbonyl diimine complexes of general formula \( \text{fac-}[(N^N)'\text{Re(CO)}_3X]^{0/+1} \) are easy to prepare via thermal substitution between the diimine and CO ligands, show reasonable stability, and are used majorly in cell imaging due to their resistance to photobleaching.

New series of rhenium(I) tricarbonyl complexes bearing [4] and [6]helicenes-bpy were synthesized and characterized by multinuclear NMR and X-ray crystallography. Their photophysical properties were investigated where their phosphorescent luminescence was derived from \( ^3\text{MLCT} \) transition state at room temperature and from \( ^3\text{LL} \) transition state at 77 K. The quantum yield of neutral complexes is very low (~0.1%), nevertheless, modifying the Cl ligand with 2e\(^-\) donor ligands such as pyridine and isocyanide to prepare cationic Re(I) complexes lead to a significant increase in the quantum yield to 8% and 16%, respectively.

The chiroptical properties of rhenium complexes bearing [6]helicenes-bpy were also studied. Re-5 and Re-6 showed high specific and molar rotation, and mirror-imaged ECD spectra of the corresponding enantiomers that are red-shifted compared to the free ligand with slight decrease in the \( \Delta\varepsilon \) values. While Re-7 and Re-8 showed a significant decrease in specific and molar rotations as well as the ECD spectra which is explained due to the opposite effects derived from the chirality of helicenes and the chirality on Re center.
Recently we were able to prepare *rac*-rhenium(I) tricarbonyl complex **Re-9** bearing [6]helicene-bpy and isocyanide as ancillary ligand (Scheme 3.17). Prospectively, we would like to synthesize the enantiopure (-)- and (+)-**Re-9** complexes and investigate their CPL spectroscopy due to the good quantum yield they showed to exhibit with [4]helicene-bpy and trying to obtain the first example on CPL active rhenium complexes.

![Scheme 3.17 Rac-rhenium(I) tricarbonyl complex Re-9.](image-url)
References


164


Experimental Part

Most experiments were performed using standard Schlenk techniques. Solvents were freshly distilled under argon from sodium/ benzophenone (THF) or from phosphorus pentoxide (CH\textsubscript{2}Cl\textsubscript{2}). Starting materials were purchased from Aldrich. Column chromatography purifications were performed in air over silica gel (Merck Geduran 60, 0.063–0.200 mm). 1H and 13C NMR spectra were recorded on a Bruker AM300 and 400. Chemical shifts were reported in parts per million (ppm) relative to Si(CH\textsubscript{3})\textsubscript{4} as external standard and compared to the literature. Specific rotations (in deg cm\textsuperscript{2} g\textsuperscript{-1}) were measured in a 10 cm thermostated quartz cell on a Jasco P1010 polarimeter. Circular dichroism (in M\textsuperscript{-1} cm\textsuperscript{-1}) was measured using a Jasco J-815 Circular Dichroism Spectrometer (IFR140 facility, Rennes 1 University).

Re-1:

42.5 mg of 3-(pyridin-2-yl)naphtho[1,2-f]quinoline 62 (0.138 mmol) and (50.2 mg, 1 eq) of Re(CO)\textsubscript{5}Cl were heated to reflux in 3 mL distilled toluene for 5 hours where an orange precipitate is observed. Later, the reaction mixture was cooled then vacuum filtrated, and washed with pentane and ether, to provide Re-1 (76 mg, 90%) as an orange powder.

\textsuperscript{1}H NMR (400 MHz, CD\textsubscript{2}Cl\textsubscript{2}) \(\delta\) 9.61 (1 H, d, \(J=9\) Hz, H\textsubscript{1}), 9.14 (1 H, ddd, \(J=5.6, 4.8, 0.8\) Hz, H\textsubscript{6}), 8.90 (1 H, d, \(J=9.3\) Hz, H\textsuperscript{5}), 8.77 (1 H, d, \(J=8.1\) Hz, H\textsuperscript{12}), 8.38 (1 H, d, \(J=8.1\) Hz, H\textsuperscript{3}), 8.32 (1 H, d, \(J=9.3\) Hz, H\textsuperscript{8}), 8.27 (1 H, d, \(J=9.3\) Hz, H\textsuperscript{6}), 8.02 - 8.15 (3 H, m, H\textsuperscript{4,9,7}), 7.90 (1 H, d, \(J=8.7\) Hz, H\textsuperscript{8}), 7.66 - 7.77 (2 H, m, H\textsuperscript{10,11}), 7.55 (1 H, ddd, \(J=7.6, 5.5, 1.3\) Hz, H\textsuperscript{3}).

\textsuperscript{13}C NMR (101 MHz CD\textsubscript{2}Cl\textsubscript{2}) \(\delta\) 160.39 (C), 157.82 (C), 153.59 (CH), 149.67 (C), 139.93 (CH), 139.55 (CH), 134.51 (C), 134.19 (CH), 132.35 (C), 130.70 (C), 130.63 (CH), 129.97 (C), 129.85 (CH), 129.59 (CH), 128.00 (CH), 127.95 (C), 127.80 (CH), 127.70 (CH), 127.31 (CH), 126.61 (CH), 124.86 (CH), 118.59 (CH). 3 CO not seen.

Elemental analysis, calcd. (%) for C\textsubscript{25}H\textsubscript{14}ClN\textsubscript{2}O\textsubscript{3}Re: C, 49.06; H, 2.31; found C 48.97, H 1.98.
Re-2:

A reaction mixture of Re-1 (0.1 mmol, 61 mg), AgOTf (0.11 mmol), Et3N (0.11 mmol), phenyl acetylene (0.14 mmol) and THF (20 ml) was allowed to reflux under an inert atmosphere of nitrogen in the dark for 24 h. After cooling to room temperature, the dark brown suspension was filtered and the orange-red filtrate was reduced in volume under reduced pressure. The residue was then purified by column chromatography on silica gel using CH2Cl2 as eluent to afford Re-2 (13 mg, 20%) as red powder.

1H NMR (400 MHz, CD2Cl2) δ 9.59 (1 H, d, J=8.8 Hz, H1), 9.19 (1 H, d, J=4.5 Hz, H5), 8.97 (1 H, d, J=9.0 Hz, H5'), 8.78 (1 H, d, J=8.5 Hz, H12), 8.37 (1 H, d, J=8.8 Hz, H3'), 8.32 (1 H, d, J=8.8 Hz, H8), 8.26 (1 H, d, J=9.0 Hz, H8), 7.98 - 8.12 (3 H, m, H3,9,7, 7.90 (1 H, d, J=8.8 Hz, H8), 7.64 - 7.78 (2 H, m, H10,11), 7.48 - 7.55 (1 H, m, H3'), 6.79 - 6.94 (3 H, m), 6.72 (2 H, d, J=6.8 Hz).

Re-3:

To a solution of Re-1 (63 mg, 0.103 mmol) in acetonitrile (20 ml) was added silver tetrafluoroborate (20 mg, 0.103 mmol). The mixture was heated at reflux overnight in the dark and under nitrogen atmosphere. The solution mixture was then filtrated over celite to remove AgCl salt and the solvent was removed at high vacuum to give (H4-bpy)Re(CO)3NCCH3[BF4]. 15 ml THF and 25 μL pyridine (0.31 mmol) were added and the mixture was and heated at 50°C.
for 20 hours. The resultant solution was subsequently filtered through celite prior to the removal of the solvent in vacuum to furnish Re-3 (61 mg, 80%) as an orange precipitate.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 9.76 (1 H, d, $J$=9.3 Hz, H$^1$), 9.25 (1 H, m, H$^6$), 8.84 (1 H, d, $J$=9.3 Hz, H$^5$), 8.78 (1 H, d, $J$=8.4 Hz, H$^{12}$), 8.64 (1 H, d, $J$=8.1 Hz, H$^3$), 8.52 (1 H, d, $J$=9.3 Hz, H$^2$), 8.40 (1 H, dd, $J$=9.3 Hz, H$^6$), 8.29 - 8.37 (1 H, m, H$^4$), 8.06 - 8.15 (2 H, m, H$^{9,7}$), 7.95 (1 H, d, $J$=8.7 Hz, H$^8$), 7.66 - 7.81 (6 H, m, H$^{5,11,12}$py), 7.05 - 7.13 (2 H, m, H$^{py}$).

$^{13}$C NMR (101 MHz CD$_2$Cl$_2$) $\delta$ 196.50 (CO), 195.26 (CO), 191.71 (CO), 157.38 (C), 156.07 (C), 153.39 (CH), 151.88 (2CH), 149.24 (C), 142.17 (CH), 141.98 (CH), 140.33 (CH), 135.83 (CH), 134.64 (C), 132.51 (C), 131.52 (CH), 129.81 (C), 129.67 (CH), 129.33 (CH), 128.87 (C), 128.69 (CH), 128.30 (2CH), 128.27 (CH), 127.82 (CH), 127.37 (CH), 127.16 (C), 127.03 (CH), 126.35 (CH), 120.06 (CH).

Elemental analysis, calcd. (%) for C$_{30}$H$_{19}$BF$_4$N$_3$O$_3$Re: C, 48.53; H, 2.58; found C 48.42, H 2.52.

**Re-4:**

53 mg of Re-1 (0.087 mmol) and AgOTf (22.3 mg, 0.087 mmol) were dissolved in ethanol / THF (25:10 ml) solution mixture and refluxed in dark for 6 hours. The solution was then filtrated over celite prior to the removal of THF solvent by vacuum pump. Later on, 2,6-dimethylphenyl isocyanide (11.3 mg, 0.087 mmol) dissolved in ethanol was added and the reaction mixture was refluxed overnight. The ethanol solvent was evaporated to a small volume (c.a. 3~4 ml) then 7 ml of saturated NH$_4$PF$_6$ aq. solution was added. A yellow precipitate directly observed than was isolated by vacuum filtration, washed with water, pentane, and ether, then dried at 50 ºC for several hours to obtain Re-4 (59 mg, 80 %) as an orange precipitate.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 9.78 (1 H, d, $J$=9.3 Hz, H$^1$), 9.17 (1 H, dd, $J$=5.6, 0.8 Hz, H$^6$), 8.78 (1 H, d, $J$=8.4 Hz, H$^{12}$), 8.72 (1 H, d, $J$ = 8.1 Hz, H$^3$), 8.69 (1 H, d, $J$=9 Hz, H$^5$), 8.62 (1 H, d, $J$=9 Hz, H$^2$), 8.30 - 8.39 (2 H, m, H$^{4,6}$), 8.05 - 8.11 (2 H, m, H$^{7,9}$), 7.92 (1 H, d, $J$=8.7 Hz, H$^8$), 7.78 - 7.85 (1 H, m, H$^{11}$), 7.68 - 7.76 (2 H, m, H$^{10,5}$), 7.07 (1 H, t, $J$=7.57 Hz, H$_{isocyanide}$), 6.92 (2 H, d, $J$=7.57 Hz, H$_{isocyanide}$), 1.89 (6 H, s, H$_{Me(isocyanide)}$)
$^{13}$C NMR (101 MHz, CDCl$_3$) δ 191.80 (CO), 191.35 (CO), 188.57 (CO), 157.91 (C), 156.34 (C), 154.12 (C), 154.07 (CH), 150.13 (C), 141.78 (CH), 141.73 (CH), 136.03 (C), 135.93 (C), 135.73 (C), 135.32 (C), 134.62 (C), 131.48 (CH), 130.85 (CH), 129.79 (C), 129.68 (CH), 128.99 (CH), 128.79 (CH), 128.73 (CH), 128.63 (CH), 128.56 (2CH), 128.28 (CH), 127.69 (CH), 126.95 (C), 126.62 (CH), 126.29 (CH), 119.57 (CH), 18.33 (2 CH$_3$).

Elemental analysis, calcd. (%) for C$_{34}$H$_{23}$F$_6$N$_3$O$_3$PRe: C, 47.89; H, 2.72; found C 47.79, H 2.72.

Re-5 and Re-6:

3-(2-Pyridyl)-4-aza[6]helicene 63 (30 mg, 0.0738 mmol) and Re(CO)$_5$Cl (27 mg, 0.0246 mmol) were heated to reflux in 2 mL distilled toluene for 5 hours. Toluene was evaporated under reduced pressure and the mixture was purified over silica gel column chromatography (heptane/ethyl acetate 4:6 as the eluent) to provide two different Re complexes Re-5 (34 mg, 65%) and Re-6 (18 mg, 35%) as red orange solids.

Re-5: $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 9.06 (1 H, m, H$_6'$), 8.84 (1 H, d, J=9 Hz, H$^1$), 8.33 (1 H, d, J=9 Hz, H$^2$), 8.13 - 8.20 (2 H, m), 8.01 - 8.08 (3 H, m), 7.92 - 7.96 (2 H, m, H$^4'$, H$^3'$), 7.89 (2 H, s), 7.71 - 7.79 (1 H, m, H$^{13}$), 7.56 (1 H, d, J=8.70 Hz, H$^{16}$), 7.36 - 7.48 (1 H, m, H$^5$), 7.26 (1 H, d, J=9.26 Hz), 7.17 (1 H, ddd, J=8.13, 7.01, 1.12 Hz, H$^{14}$), 6.92 (1 H, ddd, J=8.41, 7.01, 1.40 Hz, H$^{15}$).

Re-5: $^{13}$C NMR (75 MHz, CD$_2$Cl$_2$): δ 198.30 (CO), 197.87 (CO), 190.40 (CO), 171.19 (s, 1 C), 157.53 (s, 1 C), 155.72 (s, 1 C), 153.27 (CH), 148.14 (s, 1 C), 139.42 (CH), 138.79 (CH), 134.47 (s, 1 C), 133.89 (CH), 132.59 (s, 1 C), 132.55 (s, 1 C), 130.21 (CH), 130.03 (CH), 129.21 (CH), 129.08 (CH), 128.76 (s, 1 C), 128.33 (CH), 128.27 (CH), 127.66 (CH), 127.51 (s, 1 C), 127.37 (CH), 127.00 (CH), 126.92 (CH), 126.89 (s, 1 C), 126.70 (CH), 126.39 (CH), 124.60 (CH), 124.38 (s, 1 C), 116.86 (CH)

Re-6: $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 9.06 (1 H, m, H$_6'$), 8.91 (1 H, d, J=9.3 Hz, H$^1$), 8.36 (1 H, d, J = 9.3 Hz, H$^2$), 8.18 (1 H dd, J=8.8, 1 Hz), 8.15 (1 H, d, J=8.4 Hz), 8.03 - 8.06 (3 H, m), 7.89 - 7.98 (4 H, m), 7.78 - 7.82 (1 H, m, H$^{13}$), 7.51 - 7.55 (1 H, m, H$^{15}$), 7.46 - 7.51 (1 H, m, H$^5$),
7.29 (1 H, d, J=9 Hz), 7.14 (1 H, ddd, J=8.1, 6.9, 1.3 Hz, H\textsuperscript{14}), 6.73 (1 H, ddd, J=8.5, 6.9, 1.4 Hz, H\textsuperscript{15})

**Re-6:** \textsuperscript{13}C NMR (75 MHz, CD\textsubscript{2}Cl\textsubscript{2}) \(\delta\) 198.03 (CO), 197.49 (CO), 189.52 (CO), 157.14 (C), 155.27 (C), 153.32 (CH), 148.34 (C), 139.43 (CH), 138.71 (CH), 134.33 (C), 133.88 (CH), 132.81 (C), 132.48 (C), 132.18 (C), 130.12 (CH), 129.80 (CH), 129.04 (CH), 128.99 (CH), 128.94 (C), 128.51 (CH), 128.07 (CH), 127.79 (C), 127.71 (CH), 127.40 (CH), 127.33 (CH), 126.77 (C), 126.68 (CH), 126.52 (CH), 125.82 (CH), 124.38 (CH), 124.10 (C), 116.89 (CH) One C not seen.

Elemental analysis, calcd. (%) for C\textsubscript{33}H\textsubscript{18}Cl\textsubscript{2}N\textsubscript{2}O\textsubscript{3}Re: C, 55.65; H, 2.55; found C 55.46, H 2.68.

**Re-7 and Re-8:**

![Re-7 and Re-8 structures](image)

3,14-Bis(2-Pyridyl)-4,13-diaza[6]helicene 64 (26.6 mg, 0.055 mmol) and Re(CO)\textsubscript{5}Cl (41.7 mg, 0.115 mmol) were heated to reflux in 4 mL of distilled toluene for 5 hours. Toluene was evaporated under reduced pressure and the mixture was purified over silica gel column chromatography (heptane/ethyl acetate 4:6 as the eluent) to provide two different Re complexes Re-7 (50 mg, 84%) and Re-8 (10 mg, 16%) as red orange solids.

**Re-7:** \textsuperscript{1}H NMR (400 MHz, CD\textsubscript{2}Cl\textsubscript{2}) \(\delta\) 8.97 - 9.02 (1 H, m, H\textsuperscript{6'}), 8.78 (1 H, d, J=9.3 Hz, H\textsuperscript{1}), 8.30 (1 H, d, J=9.3 Hz, H\textsuperscript{6'}), 8.25 (2 H, d, J=8.4 Hz, H\textsuperscript{3',7}), 8.16 (1 H, d, J=8.4 Hz, H\textsuperscript{6}), 8.10 (1 H, d, J=9 Hz, H\textsuperscript{5}), 7.79 (1 H, d, J=9 Hz, H\textsuperscript{6}), 7.75 (1 H, td, J=7.9, 1.5 Hz, H\textsuperscript{4}), 7.36 (1 H, ddd, J=7.6, 5.5, 1.3 Hz, H\textsuperscript{6'})

**Re-8:** \textsuperscript{1}H NMR (300 MHz, CD\textsubscript{2}Cl\textsubscript{2}) \(\delta\) 9.14 (1 H, d, J=4.5 Hz, H\textsuperscript{6'}), 9.08 (1 H, d, J=4.90 Hz, H\textsuperscript{6''}), 9.03 (1 H, d, J=8.7 Hz, H\textsuperscript{1}), 8.90 (1 H, d, J=9.0 Hz, H\textsuperscript{16}), 8.46 (2 H, m, H\textsuperscript{2,15}), 8.2 - 8.4 (7 H, m), 7.90 – 7.98 (4 H, m), 7.47 - 7.57 (3 H, m)

Because of solubility problems, \textsuperscript{13}C NMR spectra were difficult to observe.

Elemental analysis, calcd. (%) for C\textsubscript{40}H\textsubscript{20}Cl\textsubscript{2}N\textsubscript{4}O\textsubscript{5}Re\textsubscript{2}: C, 43.84; H, 1.84; found C 43.72, H 1.78.
IV.1 Introduction “Roll-Over” Cyclometalation

C-H bond activation, similarly to different approaches, such as directed orthometalation,\(^1\) remote functionalization,\(^2,3\) or cyclometalation,\(^4\) is the precoordination of the substrate to a metal center, followed by the activation of geometrically accessible C–H bonds, which can be adjacent or remote, to generate a template for further functionalization.

In particular, cyclometalation has attracted much attention\(^4\) and the popularity of this reaction type, in particular, of cyclopalladation,\(^5\) is due to the facts that:

i) The outcome of the reaction is highly predictable because predominantly five-membered rings are formed in a strictly intramolecular process

ii) The resulting compounds are versatile intermediates for further transformations, e.g. carbonylations, alkenylations, acylations, isocyanations, or halogenations.

If the substrate exhibits more than one coordination site, a special variant of the classical course may become accessible, which is “roll-over” cyclometalation. A comparison between both reaction types is depicted in Scheme 4.1 where the roll-over type reaction is historically connected with the enormously popular 2,2’-bipyridine ligand.

Among nitrogen donors, 2,2’-bipyridines are very attractive ligands, mainly due to their rich and intriguing coordination chemistry, enriched by the easiness of functionalization of the pyridine ring and by the high stability of their complexes against moisture and oxygen. The range of applications is so wide that bipyridines have been recently defined as “the most widely used ligands”.\(^6\) 2,2’-Bipyridines, despite their abundant and well-documented coordination chemistry, have received attention as chiral inducers only in recent times.\(^7\) Generally, 2,2’-bipyridines act as

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**Scheme 4.1** Classical cyclometalation versus “roll-over” cyclometalation for a metal complex containing 6-phenyl-2,2’-bipyridine as a ligand.
$N^\text{N^'}$ chelating ligands. Only recently, new coordinating behavior, called “roll-over” cyclometalation, have appeared in the literature as described in Scheme 4.1.8

“Roll-Over” cyclometalation was first observed in 1983 in iridium (III) complex 9 (Scheme 4.2), or what was known as “Watts Complex” synthesized in 1974.10 With the aid of the crystal structure reported by Wickramasinghe, Bird, and Serpone for the perchlorate salt of [Ir(bipy)$_2$(H$_2$O)(bipy)]$^{3+}$11 and further studies based on $^1$H and $^{13}$C-NMR, supported the Ir-C bond formation and confirmed the structural suggestion [Ir(bipy)$_2$(bipy – H)]$^{3+}$ for this complex also in solution. (Note that the notation (bipy – H) stands for (bipy-C3,N’).

(a)

(b)

Scheme 4.2 (a) Initially proposed structural representations of the monodentate and the “covalently hydrated” form of “Watts complex”, as suggested in ref. 11 together with (b) the actual “roll-over” cyclometalated structure.

In 1985 it was first observed with platinum derivatives by Young and co-workers12 through the thermal rearrangement of diaryl(bipyridyl)platinum (II) complexes that proceeded via rotation of one pyridyl ring followed by consecutive 3-metallation of the bipyridyl ligand or C(3)-H activation at the metal center. So, hydrogen migration from bipyridyl to aryl ligands leads to the elimination of arene (Ar-H) upon heating in toluene. In the presence of a large excess free pyridine, the dinuclear roll over cyclometalated pyridine adduct was isolated with the determination of the structure via X-ray crystallography.12 (Scheme 4.3)

Scheme 4.3: Synthesis of first dinuclear “roll-over” cyclometalated-pyridine complex produced in the thermal rearrangement of [Pt(bipy)(C$_6$H$_5$)$_2$] in the presence of an excess of 4-tert-butylypyridine.

Trying to understand this phenomenon, bipyridine has two possible coplanar conformations, cis and trans (Figure 4.1, a and b), which differ in several aspects such as dipole moment and charge distribution. It is well-known that the most stable form, both in the solid state and in solution, is
the trans species, b. The cis coplanar form may be disfavored by H- - H steric interactions and Coulombic repulsions of the nitrogen lone pairs.

The common graphic representation of 2,2'-bipy is that corresponding to the cis conformation, (a), because as a neutral ligand 2,2'-bipy almost invariably acts as an \(N,N'\) chelating ligand (c), whereas the type b conformation may play a role favoring, with an appropriate metal intermediate, activation of a C-H bond of a pyridine ring, forming an \(N'-C(3)\) five-membered cyclometalated ring, (d). (Fig 4.1, c and d)

The rare behavior of roll-over cyclometalated complexes with 2,2'-bipyridine brought the attention towards understanding the major causes of this phenomenon. Thus depending on the nature of the components M, X, and the bidentate ligands in complexes like in Scheme 4.1, rotation around the C(2)-C(2') bond can be quite energetically demanding; moreover the choice of the reaction conditions has proved crucial.

Antonio Zucca, Giovanni Minghetti and their co-workers gave a new momentum to the “roll-over” chemistry and they studied all the influences and strategies to be followed in such reactions; the choice of the metal precursor, the role of monodentate ligands (X) and their effect on the electronic environment around the metal, as well as the bidentate ligand and the effect of the substituents.

In 2003, they reported the reaction of \([Pt(Me)_{2}(DMSO)_{2}]\) and \([Pt(Ph)_{2}(DMSO)_{2}]\) derivatives with 6-alkyl-, benzyl-, and aryl-substituted 2,2'-bipyridines, HL\(^0\) (Scheme 4.5), to give new “roll-over” cyclometalated species \([Pt(Me)(L)(DMSO)]\) and \([Pt(Ph)(L)(DMSO)]\) through methane or benzene elimination; highlighting on the importance of the substituents on the 6-position of the pyridyl ring, and on the electronic structure of the Pt precursors.
The reaction of cis-[Pt(Me)₂(DMSO)₂] with the (C-6) substituted ligands has been carried out both in acetone at room or reflux temperature and in toluene at 70-90 °C with a Pt/L 1:1 molar ratio. The reactions were straight-forward, and the yields were fairly good in acetone, but showed partial decomposition of metal when heating in toluene at 70-90 °C, while the reaction of [Pt(Me)₂(DMSO)₂] with 5-methyl-2,2'-bipyridine for example affords only the [Pt(Me)₂(N₄N')] adduct (Scheme 4.6). Hence, the substituents in the “C-6” position is of paramount importance since it seems to dramatically facilitate N',C(3) metalation. However, the nature of the electronic and steric properties of the 6-substituent of HL" does not remarkably affect the reaction, which in most cases, e.g., n = 1, 2, 3, and 6, occurs even at room temperature.

However, in terms of unsubstituted 2,2'-bipyridine, C(3)-H bond activation and metalation in high yields can be forced with carefully optimized reaction conditions; heating in anhydrous toluene at 110° C for 3 hours and under dry nitrogen atmosphere. (Scheme 4.6)

In addition to the basic function of 6-substituted 2,2'-bipyridines in facilitating “roll-over” cyclometalation, Antonio Zucca, Giovanni Minghetti and their co-workers showed that the electronic structure of Pt derivatives possess an indispensible role. So, to point out the role of the substitution of a methyl for a chloride, the behavior of the strictly homologous species [Pt(Me)₂(DMSO)₂], [PtCl(Me)(DMSO)₂], and [PtCl₂(DMSO)₂] toward ligand HL₁ has been compared under the same conditions (Scheme 4.7). As can be seen C(3)-H activation is achieved only with the dimethyl derivative. Thus concluding that N',C(3) metalation seems to be peculiar of electron rich derivatives.
In addition to the electronic environment, the roll-over reactivity can be altered by changing the transition metal species. With the aid of extensive DFT calculations done by Butschke and Schwarz on the C-H bond activation in the sequence \([M(bipy)(X)]^+ \rightarrow [M(bipy-H)]^+ + HX\) (\(M = \text{Vi, Pd, Pt; X = CH}_3, \text{Cl}\)) the potential energy surfaces show a clear preference for an oxidative-addition/reductive-elimination scenario for \(M = \text{Pt}\), while \(\sigma\)-bond metathesis is favored for \(M = \text{Ni}\); also, for \([\text{Pd(bipy)(CH}_3]\]^+\) the latter scenario prevails, while for \([\text{Pd(bipy)(Cl)}]^+\) both mechanisms compete.

The progress of \(N'-C(3)\) metalation was investigated following by \(^1\text{H} \) NMR spectroscopy the reaction of \([\text{Pt(Me)}_2(\text{DMSO})_2]^{-}\) with the ligands \(\text{HL}^1\) and \(\text{HL}^2\) in \(d_6\)-acetone at room temperature, thus they were able to give a plausible pathway for the conversion of the adduct to the \(N',C(3)\) cyclometalated species (Scheme 4.8).\(^{15}\) The steric hindrance due to the substitution in 6 position makes the adduct \((A)\) unstable and allows the cleavage of a Pt-N bond weakened by the strong \(\text{trans}\) influence of the methyl group. Rotation of a pyridine ring around the \(C(2)-C(2')\) bond brings a C-H bond close to the metal, \((B)\). The pseudo coordinateously unsaturated intermediate \(B^{17}\) promotes the \(C(\text{sp}2)-\text{H}\) oxidative addition to yield the pentacoordinated hydridoplatinum(IV), \((C)\).\(^{18,19}\) From \(C\), loss of methane eventually leads to the platinum(II) \(N'-C(3)\) cyclometalated species as the thermodynamically stable isomer \((D)\).

However, for the oxidative addition/reductive elimination scenario, the experimental evidence of this mechanistic study lacks the detection by NMR studies of the hydride intermediates. In contrast, Zuber and Pruchnik reported the NMR-based detection of hydride intermediates when they treated \([\text{Rh(bipy)}_2\text{Cl}]\) with \(\text{CD}_3\text{ONa/ CD}_3\text{OD}\).\(^{20}\) The hydrogen atoms in the 3,3’-positions of the bipy ligand were selectively exchanged for deuterium, and the process is interpreted in terms of a reversible ‘‘roll-over’’/retro-‘‘roll-over’’ cyclometalation process.

\[\text{Scheme 4.7: Role of the electronic environment around the Pt complexes towards Roll Over.}\]
In 2011, the same group reported the synthesis of the first nonracemic cyclometalated “roll-over” complex of platinum(II), \([\text{Pt}(L\text{-H})\text{Me(DMSO)}]\) in good yields by reaction of the chiral pinene-derived ligand (5S,7S)-5,7-methane-6,6-dimethyl-2 (pyridin-2-yl)- 5,6,7,8-tetrahydroquinoline, L, with the electron-rich platinum complex \([\text{Pt(DMSO)}_2\text{Me}_2]\) through the C\_3-H bond activation, which is also favored by the presence of the substituents in the 6 position.\(^2^1\) (Scheme 4.10)

The C-H bond activation is regioselective: no indication was found for the roll-over metalation at the unsubstituted pyridine ring, a sign of the importance of steric factors. This complex was the first chiral roll-over complex reported.

Recently, they have also showed that “roll-over” cyclometalation takes place with another bipyridine derivative: 2-(2’-pyridyl)quinoline,\(^2^2\) a more delocalized ligand that contains an additional fused ring compared to 2,2’-bipyridine. (Scheme 4.12)
The cyclometalated complex is also obtained with high yield and in regiospecific C-H activation following the same synthetic strategy of substituted bipyridines i.e. in acetone at 50˚ C. This also indicates that roll-over is extremely sensitive to steric factors where roll-over of unsubstituted 2,2’-bipyridine takes place only under harsh conditions as previously described, while the presence of the condensed ring on one of the pyridine rings in 2-(2’-pyridyl)quinoline facilitates the reaction.

IV.2 Reactions of “roll-over” cyclometalated complexes

The labile peculiarity of DMSO ligand makes the “roll-over” chemistry versatile. It can be easily exchanged by various 2 e’ neutral donating ligand e.g. PPh₃, PCy₃, CO, 3,5-dimethyl pyridine, quinoline, or CH₃CN to produce a variety of mononuclear “roll-over” species under very mild conditions. In addition to mononuclear complexes, homobimetallic or heterobimetallic “roll-over” cyclometalated derivatives can also be achieved by using two eq. of the Pt(II) precursor or reacting the mononuclear species, under the same synthetic strategies, with different transition metal precursors that can undergo C-H activation such as Pd(II).

Moreover, in such “Roll-Over” cyclometalated Pt(II) complexes, the Pt-C(sp³) bond was cleaved with HCl without affecting the Pt-N-‘C(3) bond inside the five membered cycle, and the formation of one isomer also (Scheme 14.3). This reaction is likely to occur through oxidative addition of HCl followed by fast reductive elimination of CH₄ with no detection of hydrido-alkyl species. The different trans influence of the donors accounts for the isomer having a trans Cl-Pt-C arrangement. The chloride containing precursors generated can therefore be used to generate platinum(II)-hydride complexes via treatment with NaBH₄.

In contrast, using 18-crown-6.HBF₄.H₂O acid with weak coordinating counter anion leads selectively to the protonation of the uncoordinated nitrogen; and the proton can be reversibly removed upon treatment with Na₂CO₃. The different modifications on mono and bimetallic species are summarized in Schemes 4.13 and 4.14.
Classically cyclometalated compounds have attracted great attention in synthetic procedures especially for the introduction of functional groups in high regioselective fashion via attacking the M-C bond. The second step was to use such synthetic procedures with the roll-over.
over cyclometalated complexes and this was firstly done by Minghetti and coworkers where they reported the carbonylation of roll-over cyclometalated palladium complexes.\textsuperscript{33}

![Scheme 4.14](image)

Scheme 4.14 Series of heterobimetallic “roll-over” cyclometalated Pt(II) complexes.

Under quite harsh conditions, i.e. 40 bar of CO pressure and 60 °C in ethanol, the cyclometalated palladium complex is transformed into the ethyl ester or the corresponding acid after basic workup (Scheme 4.15). This procedure is interesting as 3,6’-disubstituted 2,2’-bipyridines are produced, which are difficult to synthesize otherwise. Moreover, nicotinic-acid derivatives are of biological and pharmaceutical interest.\textsuperscript{21}

![Scheme 4.15](image)

Scheme 4.15 The procedure for the synthesis of alkyl esters and acids via carbonylation of “roll-over” cyclometalated palladium–bipy\textsuperscript{R} complexes

More recently, Sukbok Chang and coworkers reported the development of a Rh(NHC) catalytic system for the hydroarylation of alkenes and alkynes with 2,2’-bipyridines (bipy) and 2,2’-biquinolines.\textsuperscript{34}

Initially generated (bipy)Rh(NHC) chelates become labile because of the strong \textit{trans} effect of N heterocyclic carbenes, thus weakening a rhodium–pyridyl bond, which is trans to the bound NHC. Subsequent roll-over cyclometalation leads to the C–H bond activation, eventually giving rise to double highly efficient and selective bisfunctionalization of the chelate molecules (2,2’-bipyridines and 2,2’-biquinolines). (Scheme 4.16)
In addition to catalytic applications, Constable and his coworkers issued the first case of a genuine roll-over / retro-roll-over cyclometalation process comprising a 2-(2-thienyl)pyridine coordinated to Ru(terpyridine) complex. As shown in Scheme 4.17, the metal-thienyl bonding was reversibly switchable between Ru-S and Ru-C bonding modes depending on the pH of the solution.

This interesting example urged Wolf and coworkers to synthesize reversible molecular switches comprising similar systems in which ruthenium(II)bis(bipyridyl) is coordinated to oligothiophenes via a diphenylphosphine linker and a thienyl sulfur (P, S bonding). The effect of metal interaction with different bonding modes (P, S and P, C – Scheme 4.18) is reflected by changes in structural, chemical, and physical properties between the two species.
IV.4 Results and Discussion

Based on the results described, “roll-over” cyclometalation chemistry may be applied to our helicene-bipyridines that are substituted with fused rings at the 6-position. In addition to the $N,N'$ chelate that was discussed previously with Re(I) tricarbonyl complexes, we will have the opportunity to investigate the $N$-$C'(H)$ chelating properties of helicenes-bipyridines ligands 62 and 63, which possess additional fused aromatic rings compared to 2,2’-bipyridine, thus potentially able to furnish supplementary electronic, steric, and chiroptical properties.

VI.4.1 Synthesis and NMR characterization of “Roll-over” cyclometalated species

Electron rich $cis$-$DMSO_2Pt(II)Me_2$ was prepared according to the literature\textsuperscript{37,38} a 3-steps synthesis described in Scheme 4.19, then the reactivity towards $H_4$ and $H_6$-bpy was studied.

\begin{center}
\begin{tikzpicture}
\node (a) at (0,0) {\textbf{Scheme 4.19: Synthesis of $cis$-$DMSO_2PtMe_2$}};
\end{tikzpicture}
\end{center}

\textbf{a)- ($H_4$-bpy)$PtDMSOMe$}

The reaction of Pt precursor with $H_4$-bpy 62 in acetone at 50° C results in direct change in color to red then yellow after few hours indicating the formation of the roll over cyclometalated Pt(II) complex, which affords C,N-Pt five membered ring through C(sp$^2$)-H activation and elimination of methane gas. (Scheme 4.20)

\begin{center}
\begin{tikzpicture}
\node (a) at (0,0) {\textbf{Scheme 4.20: Synthesis of “Roll-over” cyclometalated Pt-1.}};
\end{tikzpicture}
\end{center}

The structure Pt-1 complex is mainly based on $^1$H NMR spectrum that provides the formation of one isomer only (Figure 4.2). It confirms the metalation by 13 protons integrated. The absence of
the H$_2$ signal in the aromatic region and the appearance of a singlet at 9.5 ppm flanked by satellites corresponding to H$_4$ demonstrates the formation of the C(2)-Pt bond. The $^{195}$Pt-H$_1$ coupling constant value ($^3J_{Pt-H} = 64.2$ Hz) is consistent with a DMSO coordinated in the trans position to the C$_2$ atom.$^{15}$ Moreover, the coordination of the nitrogen atom is confirmed by the deshielding of H$_6'$ to 9.77 ppm compared to the free ligand at 8.67 ppm (c.i.s. = 1.1 ppm), and by the coupling $^{195}$Pt-H$_6'$ ($^3J_{Pt-H} = 20$ Hz), typical of a pyridine ring coordinated to Pt in cis position to a DMSO moiety.$^{14}$

The coordination sphere of the metal center is completed by the methyl group and the DMSO moiety and the high field $^1$H NMR of the Pt-Me group appears as singlet flanked with satellites ($^2J_{Pt-H} = 82$ Hz) at 0.78 ppm (See Exp. Part) that fits with a methyl group trans to a nitrogen atom.$^{39}$ On the other hand, the small J-coupling constant ($^3J_{Pt-H} = 18.3$ Hz) relative to Pt-DMSO protons at 3.19 ppm is consistent with a ligand trans to a C(sp$^2$).$^{40}$ The C-H bond activation is regioselective as no indications were found for the roll-over metalation at the unsubstituted pyridine ring, a sign of the importance of steric factors.

**b)- (H$_6$-bpy)PtDMSOMe**

Following the same procedure, “roll-over” cyclometalated (H$_6$-bpy)Pt(II)DMSOMe Pt-2 complex was synthesized by reacting the free ligand 63 with electron rich Pt(dmso)$_2$Me$_2$ precursor (Scheme 4.21) in actone at 50°C for 5 hours.
The $^1$H NMR spectroscopy has the great credit for giving the information about the formation of the roll-over Pt(II) complex. As Figure 4.3 shows, only one isomer is observed, with 17 protons due to the loss of H$_2$ proton through the elimination of CH$_4$, and appearance of H$_1$ as a singlet flanked with satellites that demonstrates the formation of the C(2)-Pt bond. The $^{195}$Pt-H coupling constants were comparable to that obtained with Pt-1.

In the aromatic region, H$_6$ is highly dishielded due to the nitrogen atom coordinated to Pt (H$_6$: $\delta$ = 9.56 ppm [c.i.s. = 1.05 ppm], $^3J_{Pt-H} = 20$ Hz; H$_1$: $\delta$ = 9.56 ppm, $^3J_{Pt-H} = 62.5$ Hz).

In the aliphatic region at high field, the Pt-Me signal appears at - 0.34 ppm with $^2J_{Pt-H} = 83$ Hz. However, unlike Pt-1, the two methyl groups of DMSO are diastereotopic due to the presence of the [6]helicene moiety (Figure 4.4; Me$_1$S(O)Me$_2$: $\delta_1$ = 3.02 ppm, $^3J_{Pt-H} = 18.2$ Hz; $\delta_2$ = 2.93 ppm, $^3J_{Pt-H} = 18.2$ Hz).
IV.4.2 Reactivity of “Roll-over” cyclometalated species with acids

The peculiarity of “roll-over” cyclometalated complexes arises from the presence of uncoordinated nitrogen. Taking the advantage of its coordination ability to another transition metal or responding to pH variations through protonation / deprotonation, it is conceivable to tune the photophysical as well as the chiroptical properties of the cyclometalated species.

To shed some light on the nitrogen atom behavior towards protonation, the reaction of Pt complexes Pt-1 and Pt-2 with acids was investigated. Two different types of acids were used with different coordinating properties:

1- 0.1 M HCl that have a coordinating anion, i.e. Cl⁻.
2- [18-crown-6.HBF₄.H₂O] with weakly coordinating anion, i.e. BF₄⁻.

\textbf{a)- Reaction with HCl: non-protonated species}

The reaction of Pt-1 complex with 1 eq. of aqueous 0.1 M HCl in acetone didn’t result in the protonation of the N atom, but in the loss of the coordinated methyl group as evidenced by \(^1\)H NMR (Figure 4.4) with coordination of Cl⁻ anion instead. Hence, the reaction is likely to proceed via Pt-CH₃ bond attack with subsequent loss of methane gas and formation of the corresponding \((H₄-bpy)PtDMSO(Cl)\) Pt-3 complex. (Scheme 4.22)

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4.4}
\caption{\textbf{Figure 4.4}: \(^1\)H NMR signals of Me and DMSO coordinated to Pt in Pt-2 (400 MHz).}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{scheme4.22}
\caption{\textbf{Scheme 4.22}: Synthesis of “Roll-over” cyclometalated \((H₄-bpy)PtDMSOCl\) Pt-3 and \((H₂-bpy)Pt(PPh₃)Cl\) Pt-4.}
\end{figure}
Figure 4.4 $^1$H NMR spectra of Pt-3 (red) in comparison with Pt-1 (blue) in CH$_2$Cl$_2$ (400 MHz).

A clear downfield shift of H$_1$ is observed ($\delta = 10.17$ ppm; c.i.s. = 0.64 ppm; $^3J_{\text{Pt-H}} = 50$ Hz) concomitant with deshielding of the DMSO group ($\delta = 3.61$ ppm; c.i.s. = 0.44 ppm; $^3J_{\text{Pt-H}} = 24$ Hz) and slight shielding of H$_6'$ ($\delta = 9.63$ ppm; c.i.s. = -0.14 ppm). From these NMR data, it can be confirmed that one isomer is formed where DMSO is trans to the nitrogen atom. Indeed, the increase in the coupling constant of DMSO and methyl protons with $^{195}$Pt nucleus to 24 Hz versus 18 Hz for Pt-1 indicates the coordination of DMSO trans to nitrogen atom and in line with the weaker trans influence of N with respect to C.$^{21}$ Moreover, the downfield shift of H$_1$ is attributed to the effect in space of the DMSO ligand.$^{21}$

In our attempts to grow single crystals of the “roll-over” cyclometalated Pt complexes and prove the formation of one isomer after reacting with HCl, we focused on the labile character of DMSO, which can be substituted with 2 electrons donor neutral ligand such as PPh$_3$ and facilitate the crystallization process.$^{14,21}$ The substitution reaction takes place in DCM reaction mixture within 1-2 hours, where it is easily characterized by $^{31}$P NMR spectroscopy; a new peak appears at $\delta = 22.7$ ppm and flanked with satellites due to the coupling with $^{195}$Pt nucleus with high coupling constant $^2J_{\text{Pt-P}} = 4301$ Hz (Figure 4.5) indicating that P is trans to N.$^{21}$

Figure 4.5: $^{31}$P NMR spectra of PPh$_3$ coordinated to Pt in Pt-4 (162 MHz).
Single crystals of Pt-4 were grown by slow diffusion of pentane into DCM solution mixture. It crystallizes in centrosymmetric space group P-1 where the platinum atom displays a square-planar coordination with a slight tetrahedral distortion (Figure 4.6). Selected bond lengths and angles for Pt-4 in comparison with the free ligand and bpyPtClPPh$_3$$^{14}$ are reported in Table 4.1. The values were comparable with the 2,2'-bipyridine complex, while with respect to the free ligand, elongation of N$_1$-C$_5$ and C$_6$-C$_7$ by 0.04 Å and 0.02 Å respectively and shortening of C$_6$-C$_7$ by 0.015 Å are observed. The PPh$_3$ has a conformation fixed by the T-shape $\pi-\pi$ interaction.

![Figure 4.6 X-ray structure of (H$_4$-bpy)Pt(PPh$_3$)Cl Pt-4.](image)

<table>
<thead>
<tr>
<th></th>
<th>Pt-4</th>
<th>bpyPtClPPh$_3$$^{14}$</th>
<th>H$_4$-bpy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-Cl</td>
<td>2.386</td>
<td>2.380</td>
<td></td>
</tr>
<tr>
<td>Pt-P</td>
<td>2.228</td>
<td>2.223</td>
<td></td>
</tr>
<tr>
<td>Pt-N$_1$</td>
<td>2.108</td>
<td>2.097</td>
<td></td>
</tr>
<tr>
<td>Pt-C$_7$</td>
<td>2.002</td>
<td>2.008</td>
<td></td>
</tr>
<tr>
<td>N$_1$-C$_5$</td>
<td>1.355</td>
<td>1.349</td>
<td>1.314</td>
</tr>
<tr>
<td>C$_5$-C$_6$</td>
<td>1.466</td>
<td>1.463</td>
<td>1.481</td>
</tr>
<tr>
<td>C$_6$-C$_7$</td>
<td>1.423</td>
<td>1.416</td>
<td>1.402</td>
</tr>
<tr>
<td>Cl-Pt-P</td>
<td>91.97°</td>
<td>92.75°</td>
<td></td>
</tr>
<tr>
<td>Cl-Pt-N$_1$</td>
<td>92.2°</td>
<td>90.77°</td>
<td></td>
</tr>
<tr>
<td>Cl-Pt-C$_7$</td>
<td>173.02°</td>
<td>170.97°</td>
<td></td>
</tr>
<tr>
<td>P-Pt-N$_1$</td>
<td>175.83°</td>
<td>176.24°</td>
<td></td>
</tr>
<tr>
<td>P-Pt-C$_7$</td>
<td>95.01°</td>
<td>95.80°</td>
<td></td>
</tr>
<tr>
<td>N$_1$-Pt-C$_7$</td>
<td>80.81°</td>
<td>80.77°</td>
<td></td>
</tr>
<tr>
<td>Helical degree</td>
<td>28.8°</td>
<td></td>
<td>25.31°</td>
</tr>
</tbody>
</table>

**b)- Reaction with [18-crown-6,HBF$_4$,H$_2$O]: protonated species**

The reaction of Pt-1 complex in DCM at room temperature for 2 hours with [18-crown-6,HBF$_4$,H$_2$O] acid$^{42}$ possessing weak coordinating anion resulted in the selective protonation of uncoordinated N, as evidenced by the appearance of a broad peak at 13.5 ppm in the $^1$H NMR...
spectra with no loss of methane gas, or in other words the Pt-CH$_3$ bond is not attacked. Hence, it was a good opportunity to apply this reaction with H$_6$-bpy then study the effect of protonation on chiroptical properties of the Pt complex.

The same procedure was applied to Pt-2 and the protonated “roll-over” cyclometalated Pt(II) complex bearing [6]helicene was observed (Scheme 4.23) as evidenced also by $^1$H NMR through the appearance of a broad peak at c.a. 13.5 ppm corresponding to the N$^+$-H proton (Figure 4.7).

![Scheme 4.23: Synthesis of protonated “roll-over” cyclometalated Pt-5 complex.](image)

Several modifications are observed in the $^1$H NMR spectrum in Pt-5 as compared to Pt-2. The broad peak appeared at 13.5 ppm corresponds to N$^-$-H, deshielding of H$_6'$ to 9.8 ppm and H$_1$ to 8.9 ppm, and slight deshielding of DMSO and Me groups coordinated to Pt. Moreover, all the hydrogens coupled with Pt possess the same coupling constant as unprotonated Pt-2 complex indicating that one isomer is formed with DMSO trans to carbon and Me to N, contrary to the reaction with HCl.

![Figure 4.6: Aromatic region $^1$H NMR spectra of protonated “roll-over” cyclometalated Pt-5 complex (blue) in CD$_2$Cl$_2$ (400 MHz), compared to Pt-2 (red).](image)

**IV.4.3 Photophysical Properties**

The photophysical properties of the roll-over cyclometalated Pt(II) complexes (Pt-2 and Pt-5) were measured and summarized in Table 4.2. The absorption spectra were recorded in...
DCM at room temperature \((C = 1.4 \times 10^{-4} \text{ M for Pt-2 and } 1.3 \times 10^{-4} \text{ M for Pt-5})\) and the emission spectra were recorded in deoxygenated acetone at room temperature and in EPA at 77 K.

Figure 4.7 shows the absorption spectra of Pt-2, Pt-5, and the free ligand 21 in DCM at room temperature. By comparison, the higher energy bands are attributable to ligand-centered \(\pi-\pi^*\) transitions with \(~10 \text{ nm red-shifted } \lambda_{\text{max}}\) in the protonated species Pt-5 (green). The lower ones are tentatively assigned to metal-to-ligand charge transfer (MLCT) transitions.\(^{22,43}\) N-protonated cationic derivative Pt-5 shows MLCT absorptions at higher wavelengths \((380 - 510 \text{ nm, } \lambda_{\text{max}} = 467 \text{ nm, } \varepsilon = 8260 \text{ M}^{-1}\text{cm}^{-1})\) than the corresponding neutral species Pt-2 \((380 - 460 \text{ nm, } \lambda_{\text{max}} = 429 \text{ nm, } \varepsilon = 5800 \text{ M}^{-1}\text{cm}^{-1})\). Consequently, it seems that protonation has an effect on the electron density thus suggesting a more effective extension of the charge delocalization on the complex. The lower energy MLCT absorptions are red-shifted in comparison with other roll-over cyclometalated species\(^{22}\), and this can be due to the higher extent in the electronic delocalization originating from the helicenic system.

![Figure 4.7 Absorption spectra of Pt-2 (blue), Pt-5 (green) and H6-bpy 21 (red) in CH\(_2\)Cl\(_2\) at 298 K.](image)

The emission spectra recorded in deoxygenated acetone at 298 K characterized by structureless features reveal that the two Pt species possess a phosphorescent luminescence assigned to \(^3\)MLCT emission. Moreover, the \(\mu\)s lifetimes range for Pt-2 \((8.2 \mu\text{s})\) and for Pt-5 \((8.4 \mu\text{s})\) is in agreement with \(^3\)MLCT emission. Interestingly, the quantum yield of Pt-5 is increased by 5 folds compared to Pt-2 (Table 4.2). At low temperature, Pt-2 and Pt-5 luminescence are characterized by structured emission spectra with a significant increase in the lifetime as shown in Table 4.2. This probably can be due to the incorporation of \(^3\)IL emission; however we have to repeat these measurements.
### Table 4.2 Absorption and Emission data of roll-over cyclometalated complexes in DCM\(^a\) and acetone\(^b\) at 298 K and in EPA\(^c\) at 77 K

<table>
<thead>
<tr>
<th>Complex</th>
<th>Absorption: (\lambda_{\text{max}} / \text{nm} (\varepsilon / \text{M}^{-1} \text{cm}^{-1}))</th>
<th>Emission 298 K</th>
<th>(\Phi_{\text{lum}})</th>
<th>Emission 77 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\lambda_{\text{max}} / \text{nm})</td>
<td>(\tau / \text{ns})</td>
<td></td>
<td>(\lambda_{\text{max}} / \text{nm})</td>
</tr>
<tr>
<td><strong>63(^a)</strong></td>
<td>240 (35000), 266 (55800), 322 (27000), 353 (14400), 372 (10200), 393 (2630), 417 (1800)</td>
<td>421, 445, 473, 508</td>
<td><strong>6.6</strong></td>
<td>0.084</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>FLUOR</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>531, 542sh, 577, 624</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>PHOS</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.3 \times 10^9</td>
</tr>
<tr>
<td><strong>Pt-2(^a)</strong></td>
<td>269 (59200), 316sh (29800), 388 (11600), 429 (5800)</td>
<td>574(^b)</td>
<td><strong>8200(^b)</strong></td>
<td>0.003(^b)</td>
</tr>
<tr>
<td><strong>Pt-5(^a)</strong></td>
<td>274 (55700), 352sh (20600), 395 (8870), 467 (8260)</td>
<td>584(^b)</td>
<td><strong>8400(^b)</strong></td>
<td>0.015(^b)</td>
</tr>
</tbody>
</table>

### IV.4.4 Synthesis and Characterization of enantiopure “Roll-Over” cyclometalated complexes

With the same synthetic strategy and by using enantiopure H\(_6\)-bpy, the following non-protonated and the protonated enantiomers were prepared and their chiroptical properties were investigated by optical rotation (OR), circular dichroism (CD), and circularly polarized luminescence (CPL).
**a)- Optical Rotation**

The optical rotation “α” was measured on solutions of Pt-2 and Pt-5 samples in CH$_2$Cl$_2$ at a concentration around 1mg/20ml using Polarimeter at room temperature. The non-protonated Complexes display much higher experimentally specific and molar rotations than the free ligand: $[\alpha]_{D}^{23} = \pm 2695$, $[\phi]_{D}^{23} = \pm 18700$ (± 5%);

While with the protonated species, the experimentally specific and molar rotations decrease approximately to the half referred to non-protonated: $[\alpha]_{D}^{23} = \pm 1170$, $[\phi]_{D}^{23} = \pm 9144$ (± 5%).

**b)- CD and acid-base chiroptical switching**

The CD spectra have been recorded on solutions of samples in CH$_2$Cl$_2$ at a concentration around 1mg/20ml. In all cases, they display mirror-image values for the (+) and (-) enantiomers within the experimental errors. Comparing the non-protonated complexes with the free ligand (Figure 4.8), it is clear that there is no big effect on the CD spectra. For the (+) enantiomers, these complexes show slightly red shifted intense negative structured bands at 264 and 284 nm ($\Delta\varepsilon = -131$ M$^{-1}$ cm$^{-1}$ and -130 M$^{-1}$ cm$^{-1}$ respectively) and a slightly red shifted strong positive band at maxima 344 nm (213 M$^{-1}$ cm$^{-1}$) accompanied with weaker ones between 380-430 nm ($\Delta\varepsilon = 80-30$ M$^{-1}$ cm$^{-1}$) compared to the free ligand. Where the band centered at 428 nm (28 M$^{-1}$ cm$^{-1}$) is comparable to that in the free ligand centered at 415 nm (9 M$^{-1}$ cm$^{-1}$) with increase in $\Delta\varepsilon$ due to the incorporation of the Pt metal center through metal-to-ligand-charge transfer.

Interestingly, the protonation of the uncoordinated N atom in the “roll-over” Pt-5 complexes formed has a great impact on the optical rotation as was described, and also on the CD spectra (Figure 4.9). In the 230-330 nm regions for the M-(+)-Pt-5, it shows a positive intense band centered at 275 nm with slight decrease in $\Delta\varepsilon$ compared to the non-protonated complex (120 M$^{-1}$ cm$^{-1}$). However at 430 nm $\lambda > 330$ nm, it possesses a negative band centered at 343 nm with...
big decrease, approximately divided by 2, in $\Delta \varepsilon$ compared to the non-protonated complex (−126 M$^{-1}$ cm$^{-1}$ V/S 213 M$^{-1}$ cm$^{-1}$). However, at $\lambda > 430$ nm, a new broad CD band at maxima 471 nm ($\Delta \varepsilon = -35$ M$^{-1}$ cm$^{-1}$) and tailed to 510 nm appeared. This result is in agreement with what we have obtained upon protonation of 63 to prepare the protonated [6]helicene-bipyridine 75 (Section II.7) and can be explained in the same manner as recently reported by Inoue and coworkers.$^{44}$

The protonation / deprotonation process is reversible using Na$_2$CO$_3$ as a base and [18-crown-6.HBF$_4$.H$_2$O] as an acid in acetone. The CD for the different species were studied and summarized in Figure 4.10. So within the same UV cell, we studied the effect of acid / base reaction on the CD spectra to check whether we are able to make a CD switch or not. We recorded the CD spectra of $P$-$(+)$-H$_6$-bpyPtDMSOMe in acetone at $\lambda > 325$ nm, where it shows an intense positive band at maxima 344 nm (213 M$^{-1}$ cm$^{-1}$) accompanied with weaker ones between 380-430 nm (blue spectra). Adding acid to the cell, directly deepens the yellow color of the solution, and upon recording the CD, the spectra coincides with the previously recorded spectra of the protonated spectra (Figure 4.7) where the $\Delta \varepsilon$ decreases and a new band at $\lambda > 430$ nm appears (red spectra). Then adding excess sodium carbonate to the UV-cell and recording the CD, the band at $\lambda > 430$ nm disappears, the $\Delta \varepsilon$ increases again, and the spectra (green spectra) coincides with the blue starting one. Moreover, adding acid again will result also in the protonation and variation in the CD spectra comparable to the protonated species (violet spectra).

As a conclusion, the effective reversibility of protonation / deprotonation process on Pt(II) complexes has a direct impact on their chiroptical properties where the absorption bands are modified, and therefore the CD spectra is modified resulting in a reversible CD switch.
The CPL properties of the enantiopure \( M^\mathrm{(-)}/P^\mathrm{(-)}\)-Pt-2 and \( M^\mathrm{(-)}/P^\mathrm{(+)\text{-}acid}\)-Pt-5 were measured in 1 mM acetone solution at 295 K upon excitation at 447 nm for Pt-2 complexes, and 436/441 nm for Pt-5 complexes. The CPL analysis of \( M^\mathrm{(-)}/P^\mathrm{(-)}\)-Pt-2 and \( M^\mathrm{(-)}/P^\mathrm{(+)\text{-}acid}\)-Pt-5 are shown in Figure 4.9 left and right, respectively.

For enantiomeric pair of Pt-2 complex, it exhibit oscillating structured mirror imaged CPL spectra that confirm the enantiomeric nature of these complexes and characterized by \( g_{\text{lum}} \) values for the \( M^\mathrm{(-)} \) and \( P^\mathrm{(+)\text{-}acid} \) isomers of \(-1\times10^{-3}\) and \(+1.1\times10^{-3}\) around the emission maximum, respectively.

In contrast, the protonated roll-over \((-)\)- and \((+)\text{-}Pt-5\) species exhibit structureless mirror imaged CPL spectra that also confirms the enantiomeric nature of these complexes accompanied by an increase in the \( g_{\text{lum}} \) values as compared to the non-protonated version Pt-2 complex. The CPL spectrum of \((-)\text{-}Pt-5\) is characterized by a negative \( g_{\text{lum}} \) value of \(-2.2\times10^{-3}\) (a greater degree of right CPL) at an emission wavelength of \(~585\text{ nm}\) and with a \( g_{\text{lum}} \) value of \(+1.8\times10^{-3}\) corresponds to \((+)\text{-}Pt-5\).
Figure 4.9 left: CPL (upper curve) and total luminescence (lower curve) for \( M^-(\text{-})\text{-Pt-2 (red)} \) and \( P^-(\text{+})\text{-Pt-2 (black)} \) in 1 mM acetone solution at 295 K, upon excitation at 447 nm.

Figure 4.9 right: CPL (upper curve) and total luminescence (lower curve) for \( M^-(\text{-})\text{-Pt-5 (red)} \) and \( P^+(\text{+})\text{-Pt-5 (black)} \) in 1 mM acetone solution at 295 K, upon excitation at 436/441 nm.
IV.5 Conclusion

In this chapter, we have shown that helicenes-bipyridine can act as \(N^\cdot C'\) chelating ligand through C-H activation by electron-rich Pt(II) precursor. The enantiopure \([6]H\text{-bpyPtDMSOMe Pt-2}\) showed higher specific and optical rotation compared to the free ligand 21, but with insignificant effect on the CD spectra. However, the protonation of the uncoordinated nitrogen induced a significant effect on the photophysical and chiroptical properties compared to non-protonated species. A new band appears in the absorption spectra as well as the CD spectra corresponds to the protonated species \(\text{Pt-5}\) with a sharp decrease in specific and molar rotation compared to \(\text{Pt-2}\). In addition, these roll-over cyclometalated complexes were CPL active with a red-shift in \(\lambda_{\text{max}}\) of the CPL and an increase in the anisotropy factor \(g_{\text{lum}}\) is observed upon protonation. Interestingly, the ease, reversibility, and efficient of protonation – deprotonation enabled us to obtain a metallohelicene based acid-base chiroptical switch comprising the chiroptical changes between the two species.
References


Experimental Part

Most experiments were performed using standard Schlenk techniques. Solvents were freshly distilled under argon from sodium/ benzophenone (THF) or from phosphorus pentoxide (CH$_2$Cl$_2$). Starting materials were purchased from Aldrich. Column chromatography purifications were performed in air over silica gel (Merck Geduran 60, 0.063–0.200 mm). $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AM300 and 400. Chemical shifts were reported in parts per million (ppm) relative to Si(CH$_3$)$_4$ as external standard and compared to the literature. Elemental analyses were performed by the CRMPO, University of Rennes 1. Specific rotations (in deg cm$^2$ g$^{-1}$) were measured in a 1 dm thermostated quartz cell on a Perkin Elmer-341 polarimeter. Circular dichroism (in M$^{-1}$ cm$^{-1}$) was measured on a Jasco J-815 Circular Dichroism Spectrometer (IFR140 facility - Université de Rennes 1). UV/vis/NIR spectroscopy was conducted on a Varian Cary 5000 spectrometer.

CPL measurements

The circularly polarized luminescence (CPL) and total luminescence spectra were recorded on an instrument described previously, operating in a differential photon-counting mode. The light source for excitation was a continuous wave 1000 W xenon arc lamp from a Spex Fluorolog-2 spectrofluorimeter, equipped with excitation and emission monochromators with dispersion of 4 nm/mm (SPEX, 1681B). To prevent artifacts associated with the presence of linear polarization in the emission, a high quality linear polarizer was placed in the sample compartment, and aligned so that the excitation beam was linearly polarized in the direction of emission detection (z-axis). The key feature of this geometry is that it ensures that the molecules that have been excited and that are subsequently emitting are isotropically distributed in the plane (x,y) perpendicular to the direction of emission detection. The optical system detection consisted of a focusing lens, long pass filter, and 0.22 m monochromator. The emitted light was detected by a cooled EMI-9558B photomultiplier tube operating in photo-counting mode. All measurements were performed with quartz cuvettes with a path length of 1.0 cm.

---

Synthesis of (NBD)PtCl$_2$

(NBD)PtCl$_2$ was prepared according to literature. $^3$ A 50 mL flask was charged with 0.2 g of K$_2$PtCl$_4$ (0.48 mmol), 4 mL of H$_2$O, 6.4 mL of glacial acetic acid, and 0.1 mL of concentrated HCl, brought to reflux under N$_2$. A 0.2 mL (1.85 mmol) portion of norbornadiene was added, and the solution was allowed to reflux for 45 min, during which time the red color faded to yellow. The reaction mixture was cooled to 0 °C, and the solids were collected on a frit and washed with copious amounts of ice cold water then with pentane. Drying the resulting tan solid under vacuum for several hours gave 0.127 g (74%) of product, which was judged pure by $^1$H NMR.

Synthesis of (NBD)PtMe$_2$

(NBD)PtMe$_2$ was prepared according to literature. $^4$ 0.2 ml of a 1.6 M methyl lithium solution in ether (0.32 mmol) was added to an ice cold solution of 50 mg of (NBD)PtCl$_2$ (0.14 mmol) in 5 ml of distilled ether under nitrogen. The solution was stirred for 2 h, and then treated at 0°C with an ice-cold solution of ammonium chloride. The ether layer was separated, and the aqueous layer extracted with three 5 ml portions of ether. The combined ether fractions were dried over magnesium sulfate, and a small amount of activated charcoal was added. After filtration, ether was removed under reduced pressure to give 42 mg (94%) colorless crystals.

Synthesis of cis-(DMSO)$_2$PtMe$_2$


Cis-(DMSO)$_2$PtMe$_2$ was synthesized according to literature. 4 37 mg (0.12 mmol) of (NBD)PtMe$_2$ was dissolved in 4 ml of distilled benzene, and 0.08 ml of dimethylsulfoxide was added. After 2 h, the solvent was removed under reduced pressure where a colorless solid began to crystallize. The obtained product was washed several times with pentane and ether then dried under vacuum for several hours to have cis-(DMSO)$_2$PtMe$_2$ in quantitative yield.

Pt-1:

To a solution of cis-(DMSO)$_2$PtMe$_2$ (20 mg, 0.05 mmol) in acetone (5 mL) was added 16 mg of H$_4$-bpy 62 (0.05 mmol). The stirred solution was heated to 50° C and kept under a nitrogen atmosphere. After 5 h the mixture was cooled to room temperature, concentrated to small volume, and treated with pentane to form a precipitate. The solid was filtered off, washed with hot pentane, and vacuum-pumped to give the analytical sample Pt-1 (27 mg, 90%) as an orange solid.

$^1$H NMR (400 MHz CD$_2$Cl$_2$) δ 9.77 (1 H, d, $^1J_{Pt-H}$=6.0 Hz, $^3J_{Pt-H}$=20 Hz, H$^6$), 9.54 (1 H, s, $^3J_{Pt-H}$), 9.04 (1 H, d, $^1J_{Pt-H}$=8.5 Hz, H$^{12}$), 8.53 (1 H, d, $^1J_{Pt-H}$=7.3 Hz, H$^3$), 7.95 - 8.04 (3 H, m, H$^{5,4,9}$), 7.90 - 7.94 (1 H, m, H$^6$), 7.78-7.88 (2 H, AB, $^3J_{Pt-H}$=8.5 Hz, H$^{7,8}$), 7.65 (1 H, t, $^1J_{Pt-H}$=6.9 Hz, H$^{11}$), 7.58 (1 H, t, $^1J_{Pt-H}$=7.3 Hz, H$^{10}$), 7.39 (1 H, t, $^1J_{Pt-H}$=5.8 Hz, H$^5$), 3.15 - 3.25 (6 H, s, $^3J_{Pt-H}$=18 Hz, H$_{DMSO}$), 0.78 (3 H, s, $^3J_{Pt-H}$=83 Hz, H$_{Me-Pt}$)

$^{13}$C NMR (101 MHz CD$_2$Cl$_2$) δ 164.75 (C), 161.97 (C), 150.64 (CH), 146.61 (C), 141.42 (C), 138.93 (CH), 138.56 (CH), 133.51 (C), 131.15 (C), 130.48 (C), 128.98 (CH), 128.75 (CH), 128.60 (CH), 128.08 (CH), 127.58 (CH), 127.02 (C), 126.72 (CH), 126.24 (CH), 126.09 (C), 125.98 (CH), 125.11 (CH), 122.13 (CH), 43.82 (2CH$_3$), -13.52 (CH$_3$).

Elemental analysis, calcd. (%) for C$_{25}$H$_{22}$N$_2$OPtS: C 50.58; H, 3.74; found C, 50.47, H 3.68.

Pt-3:
To a solution of Pt-1 (40 mg, 0.067 mmol) in 8 mL of acetone were added with vigorous stirring 0.34 mL of DMSO and 0.67 mL of aqueous 0.1 M HCl (0.067 mmol). After 8 h the solution was concentrated to a small volume then extracted with CH₂Cl₂, dried with Na₂SO₄, and concentrated to a small volume. The residue was then treated with pentane to form a precipitate which was filtered, washed with pentane, and vacuum-pumped to give the analytical sample Pt-3 (29 mg, 70%) as a yellow solid.

$^1$H NMR (400 MHz CD₂Cl₂) δ 10.17 (1 H, s, $^3J_{Pt-H}$=50 Hz, H¹), 9.64 (1 H, d, $J$=6.0 Hz, H⁶), 9.13 (1 H, d, $J$=8.3 Hz, H¹²), 8.46 (1 H, d, $J$=9.0 Hz, H³), 7.91 - 8.07 (4 H, m, H⁵,6,4',9), 7.77 - 7.89 (2H, AB, $J$=8.5 Hz, H⁷,8), 7.53 - 7.67 (2 H, m, H¹⁰,11), 7.43 (1 H, t, $J$=6.0 Hz, H⁵), 3.62 (6 H, s, $^3J_{Pt-H}$=24 Hz, HDMSO).

Elemental analysis, calcd. (%) for C₂₄H₁₉ClN₂OPtS: C, 46.95; H, 3.12; found C 46.78, H 3.01.

Pt-4:

To a solution of Pt-3 (14.6 mg, 0.024 mmol) in CH₂Cl₂ (5 mL) was added 6.2 mg of PPh₃ (0.024 mmol). The stirred solution was kept under a nitrogen atmosphere. After 2 h the mixture was concentrated to small volume and treated with pentane to form a precipitate. The solid was filtered off, washed with pentane, and vacuum-pumped to give the analytical sample Pt-4 as a yellow solid (19 mg, 98%) that was crystallized with slow diffusion of pentane into DCM solution.

$^1$H NMR (400 MHz CD₂Cl₂) δ 9.86 (1 H, m, H⁶), 8.52 (1 H, d, $J$=8.3 Hz, H³), 8.35 (1 H, s, $^3J_{Pt-H}$=56 Hz, H¹), 8.01 - 8.08 (1 H, m, H⁵), 7.89 (1 H, d, $J$=9 Hz), 7.74 - 7.81 (6 H, m), 7.71 (1 H, d, $J$=8.3 Hz, H¹²), 7.66 (1 H, d, $J$=8.78 Hz), 7.53 - 7.60 (2 H, m), 7.45 - 7.52 (1 H, m), 7.36 - 7.43
(1 H, m), 7.31 (1 H, ddd, J=8.06, 6.94, 0.98 Hz, H$^3$), 7.23 - 7.29 (3 H, m), 7.11 - 7.20 (6 H, m), 6.40 (1 H, ddd, J=8.41, 7.01, 1.40 Hz, H$^1$)

$^{13}$C NMR (101 MHz, CD$_2$Cl$_2$) $\delta$ 163.27 (CH), 148.5 (C), 145.05 (C), 142.30 (CH), 140.12 (CH), 135.32 – 135.87 (6CH), 133.0 (C), 130.97 (CH), 130.96 (CH), 129.91 (C), 129.53 (C), 129.29 (C), 128.94 (CH), 128.79 (CH), 128.60 (C), 128.53 (C), 128.41 (C), 127.7 – 128.14 (9CH), 127.36 (CH), 126.56 (C), 126.35 (CH), 126.09 (C), 126.03 (CH), 125.44 (CH), 125.21 (C), 124.74 (CH), 122.14 (CH).

$^{31}$P NMR (162 MHz, CD$_2$Cl$_2$) $\delta$ 22.70 ($J_{\text{Pt-P}}$ = 4301.5 Hz).

Elemental analysis, calcd. (%) for C$_{40}$H$_{28}$ClN$_2$PPt: C, 60.19; H, 3.54; found C 60.03, H 3.45.

Pt-2:

To a solution of cis-(DMSO)$_2$PtMe$_2$ (20 mg, 0.05 mmol) in acetone (5 mL) was added 21.3 mg of H$_6$-bpy 63 (0.05 mmol). The stirred solution was heated to 50° C and kept under a nitrogen atmosphere. After 5 h the mixture was cooled to room temperature, concentrated to small volume, and treated with pentane to form a precipitate. The solid was filtered off, washed with pentane, and vacuum-pumped to give the analytical sample Pt-2 (31 mg, 90%) as an orange solid.

$^1$H NMR (400 MHz CD$_2$Cl$_2$) $\delta$ 9.48 – 9.57 (1 H, m, H$^6$), 8.36 – 8.41 (1 H, m), 8.10 (1 H, s, $^3J_{\text{Pt-H}}$=62.5 Hz), 7.98 (2 H, s), 7.80 – 7.96 (7 H, m), 7.72 (1 H, dd, J=8.1, 1.40 Hz), 7.61 – 7.67 (1 H, m), 7.24 (1 H, ddd, J=7.4, 5.6, 1.5 Hz), 7.13 (1 H, ddd, J=8, 6.9, 1.1 Hz), 6.63 (1 H, ddd, J=8.5, 6.9, 1.4 Hz), 2.99 (3 H, s, $^3J_{\text{Pt-H}}$=18.2 Hz), 2.89 (3 H, s, $^3J_{\text{Pt-H}}$=18.2 Hz), -0.38 (3 H, s, $^2J_{\text{Pt-H}}$=83 Hz).

$^{13}$C NMR (101 MHz, CD$_2$Cl$_2$) $\delta$ 162.18 (C), 148.49 (CH), 150.80 (CH), 145.68 (C), 140.90 (C), 138.69 (CH), 138.41 (CH), 133.56 (C), 131.73 (C), 131.70 (C), 130.04 (C), 129.63 (CH), 128.80 (CH), 128.44 (CH), 128.42 (C), 128.23 (C), 128.16 (CH), 128.01 (CH), 127.80 (CH), 127.56
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Elemental analysis, calcd. (%) for C₃₃H₂₆N₂OPtS: C, 57.13; H, 3.78; found C 57.05, H 3.72.

Pt-5:

To a solution of Pt-2 (5 mg, 7.2 μmol) in CH₂Cl₂ (2 mL) was added 3 mg of 18-crown-6-HBF₄.3H₂O (8 μmol, 10% excess). After 2 h the mixture was concentrated to small volume and treated with Et₂O to form a precipitate. The solid was filtered off, washed with Et₂O, and vacuum pumped to give the analytical sample Pt-5 (5.2 mg, 92%) as a bright-orange solid.

¹H NMR (400 MHz CD₂Cl₂) δ 13.58 (1 H, br, NH), 9.87 (1 H, d, J=5.5 Hz, H⁶⁻), 9.00 (1 H, s, ³JPt-H=65.4 Hz, H¹), 8.79 (1 H, d, J=7.8 Hz, H³⁻), 8.52 (2 H, s), 8.21 - 8.33 (2 H, m), 8.06 - 8.17 (2 H, m), 7.95 - 8.05 (2 H, m), 7.88 (1 H, d, J=7.5 Hz, H¹¹⁻), 7.59 - 7.70 (2 H, m, H⁸⁻¹⁶⁻), 7.29 (1 H, m, H¹⁴⁻), 6.87 (1 H, m, H¹⁵⁻), 3.16 (3 H, s, ³JPt-H=21 Hz), 3.06 (3 H, s, ³JPt-H=21 Hz, H_DMSO), -0.21 (3 H, s, ³JPt-H=82 Hz, H_Me-Pt)

¹³C NMR (101 MHz, CD₂Cl₂) δ 152.03(CH), 146.98 (CH), 140.99 (C), 140.22 (CH), 136.03 (C), 135.53 (CH), 134.1 (C), 134.14 (C), 133.01 (C), 132.18 (C), 131.70 (C), 129.94 (CH), 129.11 (CH), 128.88 (CH), 128.31 (C), 128.15 (CH), 128.01 (CH), 127.92 (CH), 127.25 (CH), 127.20 (C), 127.11 (CH), 126.75 (C), 126.71 (CH), 126.23 (CH), 126.15 (C), 126.04 (CH), 125.88 (C), 123.59 (C), 123.43 (CH), 120.03 (CH), 43.76 (CH₃), 43.73 (CH₃), -13.81 (CH₃).
Appendices
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<tr>
<td></td>
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<td>wR2 = 0.0460</td>
<td>wR2 = 0.1743</td>
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<td><strong>R indices (all data)</strong></td>
<td>0.0504</td>
<td>R1 = 0.0238</td>
<td>R1 = 0.0776</td>
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<tr>
<td></td>
<td></td>
<td>wR2 = 0.0466</td>
<td>wR2 = 0.1813</td>
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<tr>
<td><strong>Largest diff peak and hole (e Å(^{-3}))</strong></td>
<td>1.598 and -1.416</td>
<td>1.459 and -0.956</td>
<td>3.367 and -2.754</td>
</tr>
<tr>
<td></td>
<td>62</td>
<td>64</td>
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<tr>
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<tr>
<td>Empirical Formula</td>
<td>C_{22}H_{14}N_{2}</td>
<td>C_{34}H_{20}N_{4}</td>
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<tr>
<td>CCDC Number</td>
<td>927001</td>
<td>870779</td>
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<td>Formula Weight</td>
<td>306.35</td>
<td>484.54</td>
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<tr>
<td>Temperature (K)</td>
<td>100(2)</td>
<td>120(2)</td>
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</tr>
<tr>
<td>Wavelength (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
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</tr>
<tr>
<td>Crystal system</td>
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<td>Monoclinic</td>
<td></td>
</tr>
<tr>
<td>Space Group</td>
<td>P2_{1}2_{1}2_{1}</td>
<td>C2/c</td>
<td></td>
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<tr>
<td>a (Å)</td>
<td>4.7136(2)</td>
<td>12.388(2)</td>
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<tr>
<td>b (Å)</td>
<td>13.0891(9)</td>
<td>8.2910(10)</td>
<td></td>
</tr>
<tr>
<td>c (Å)</td>
<td>23.6221(10)</td>
<td>21.536(3)</td>
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<tr>
<td>α (Å)</td>
<td>90</td>
<td>90.00</td>
<td></td>
</tr>
<tr>
<td>β (Å)</td>
<td>90</td>
<td>95.660(10)</td>
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</tr>
<tr>
<td>γ (Å)</td>
<td>90</td>
<td>90.00</td>
<td></td>
</tr>
<tr>
<td>Volume (Å³)</td>
<td>1457.41(13)</td>
<td>2201.2(5)</td>
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<tr>
<td>Z</td>
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<tr>
<td>Color</td>
<td>yellow</td>
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<tr>
<td>ρ_{calculated} (g.cm(^{-3}))</td>
<td>1.396</td>
<td>1.462</td>
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<tr>
<td>Absorption coefficient (mm(^{-1}))</td>
<td>0.083</td>
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<td>F(000)</td>
<td>640.0</td>
<td>1008</td>
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<td>Crystal size (mm)</td>
<td>0.342<em>0.124</em>0.118</td>
<td>0.24<em>0.106</em>0.018</td>
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<td>θ range for data collection (°)</td>
<td>3.02 to 26.99</td>
<td>2.96 to 27.00</td>
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<tr>
<td>Tmin</td>
<td>0.988</td>
<td>0.989</td>
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<td>Tmax</td>
<td>0.990</td>
<td>0.998</td>
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<tr>
<td>Limiting indices</td>
<td>-5 ≤ h ≤ 6</td>
<td>-13 ≤ h ≤ 15</td>
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<tr>
<td></td>
<td>-16 ≤ k ≤ 14</td>
<td>-10 ≤ k ≤ 10</td>
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</tr>
<tr>
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<td>-30 ≤ l≤ 28</td>
<td>-22 ≤ l≤ 27</td>
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<td>Data completeness</td>
<td>99.7% (θ = 26.99°)</td>
<td>99% (θ = 27.00°)</td>
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<tr>
<td>Reflections collected</td>
<td>10719</td>
<td>7866</td>
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<tr>
<td>Reflections unique</td>
<td>3149 [R(int) = 0.0731]</td>
<td>2389 [R(int) = 0.1064]</td>
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<td>2389 / 0 / 173</td>
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<td>Goodness-of-fit on F²</td>
<td>0.807</td>
<td>1.104</td>
<td></td>
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<td>Final R indices [I&gt;2 σ (I)]</td>
<td>R1 = 0.0439, wR2 = 0.0765</td>
<td>R1 = 0.0854, wR2 = 0.3130</td>
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<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0902, wR2 = 0.0857</td>
<td>R1 = 0.2047, wR2 = 0.3369</td>
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<tr>
<td>Largest diff peak and hole (e Å(^{-3}))</td>
<td>0.195 and -0.194</td>
<td>0.429 and -0.339</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Re-3</td>
<td>Re-4</td>
<td></td>
</tr>
<tr>
<td>----------------------</td>
<td>----------------------------------------------------------------------</td>
<td>----------------------------------------------------------------------</td>
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<tr>
<td><strong>Empirical Formula</strong></td>
<td>C$<em>{32}$H$</em>{23}$BCl$<em>{4}$F$</em>{4}$N$<em>{3}$O$</em>{3}$Re</td>
<td>C$<em>{36.50}$H$</em>{23}$Cl$<em>{5}$F$</em>{6}$N$<em>{3}$O$</em>{3}$PRe</td>
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<tr>
<td><strong>CCDC number</strong></td>
<td>939180</td>
<td>942143</td>
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<tr>
<td><strong>Formula Weight</strong></td>
<td>912.34</td>
<td>991.12</td>
<td></td>
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<tr>
<td><strong>Temperature (K)</strong></td>
<td>140(2)</td>
<td>140(2)</td>
<td></td>
</tr>
<tr>
<td><strong>Wavelength (Å)</strong></td>
<td>0.71073</td>
<td>0.71073</td>
<td></td>
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<tr>
<td><strong>Crystal system</strong></td>
<td>Monoclinic</td>
<td>Orthorhombic</td>
<td></td>
</tr>
<tr>
<td><strong>Space Group</strong></td>
<td>$P_2_1/n$</td>
<td>$Fdd2$</td>
<td></td>
</tr>
<tr>
<td><strong>a (Å)</strong></td>
<td>10.8540(2)</td>
<td>22.7551(3)</td>
<td></td>
</tr>
<tr>
<td><strong>b (Å)</strong></td>
<td>24.7778(3)</td>
<td>54.8820(10)</td>
<td></td>
</tr>
<tr>
<td><strong>c (Å)</strong></td>
<td>13.4316(2)</td>
<td>11.6412(2)</td>
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<tr>
<td><strong>$\beta$ (Å)</strong></td>
<td>90</td>
<td>90.00</td>
<td></td>
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<tr>
<td><strong>$\gamma$ (Å)</strong></td>
<td>110.589(2)</td>
<td>90</td>
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</tr>
<tr>
<td><strong>Volume (Å$^3$)</strong></td>
<td>3381.54(9)</td>
<td>14538.1(4)</td>
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<tr>
<td><strong>Z</strong></td>
<td>4</td>
<td>16</td>
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<tr>
<td><strong>Color</strong></td>
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<td>yellow</td>
<td></td>
</tr>
<tr>
<td><strong>$\rho_{\text{calculated}}$ (g.cm$^{-3}$)</strong></td>
<td>1.792</td>
<td>1.811</td>
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<tr>
<td><strong>Absorption coefficient (mm$^{-1}$)</strong></td>
<td>3.970</td>
<td>3.681</td>
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<td><strong>F(000)</strong></td>
<td>1776</td>
<td>7744</td>
<td></td>
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<tr>
<td><strong>Crystal size (mm)</strong></td>
<td>0.323 * 0.216 * 0.149</td>
<td>0.191 * 0.169 * 0.067</td>
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<tr>
<td><strong>$\theta$ range for data collection (°)</strong></td>
<td>2.59 to 27.00</td>
<td>2.70 to 27.5</td>
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<tr>
<td><strong>Tmin</strong></td>
<td>0.35246</td>
<td>0.62986</td>
<td></td>
</tr>
<tr>
<td><strong>Tmax</strong></td>
<td>0.82193</td>
<td>0.81351</td>
<td></td>
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<tr>
<td><strong>Limiting indices</strong></td>
<td>-11 $\leq$ h $\leq$ 13</td>
<td>-29 $\leq$ h $\leq$ 25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-31 $\leq$ k $\leq$ 31</td>
<td>-70 $\leq$ k $\leq$ 69</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-17 $\leq$ l $\leq$ 11</td>
<td>-14 $\leq$ l $\leq$ 14</td>
<td></td>
</tr>
<tr>
<td><strong>Data completeness</strong></td>
<td>99.8% ($\theta = 27.00°$)</td>
<td>99.9% ($\theta = 27.00°$)</td>
<td></td>
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<tr>
<td><strong>Reflections collected</strong></td>
<td>23796</td>
<td>28698</td>
<td></td>
</tr>
<tr>
<td><strong>Reflections unique</strong></td>
<td>7355 [R(int) = 0.0351]</td>
<td>7488 [R(int) = 0.0335]</td>
<td></td>
</tr>
<tr>
<td><strong>Data / restraints / parameters</strong></td>
<td>7355 / 0 / 433</td>
<td>7488 / 1 / 469</td>
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</tr>
<tr>
<td><strong>Goodness-of-fit on $F^2$</strong></td>
<td>1.044</td>
<td>0.937</td>
<td></td>
</tr>
<tr>
<td><strong>Final $R$ indices [$F &gt; 2 \sigma (F)]$</strong></td>
<td>R1 = 0.0249, wR2 = 0.0616</td>
<td>R1 = 0.0320, wR2 = 0.0775</td>
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<tr>
<td><strong>$R$ indices (all data)</strong></td>
<td>R1 = 0.0386, wR2 = 0.0647</td>
<td>R1 = 0.0373, wR2 = 0.0790</td>
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</tr>
<tr>
<td><strong>Largest diff peak and hole (e Å$^{-3}$)</strong></td>
<td>1.036 and -0.619</td>
<td>1.465 and -0.940</td>
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</tr>
<tr>
<td></td>
<td>Re-5</td>
<td>Re-7</td>
<td>Re-8</td>
</tr>
<tr>
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<td>----------------------------------------</td>
<td>----------------------------------------</td>
<td>----------------------------------------</td>
</tr>
<tr>
<td>Empirical Formula</td>
<td>C₆₇H₄⁰Cl₂N₄O₇Re₂</td>
<td>C₄₁H₂₃Cl₄N₄O₆Re₂</td>
<td>C₄₃H₂₆Cl₈N₄O₆Re₂</td>
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<td>875291</td>
<td>875062</td>
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<td>1180.83</td>
<td>1350.68</td>
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<tr>
<td>Temperature (K)</td>
<td>140(2)</td>
<td>120(2)</td>
<td>120(2)</td>
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<tr>
<td>Wavelength (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space Group</td>
<td>P21/c</td>
<td>P21/n</td>
<td>P21/c</td>
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<td>a (Å)</td>
<td>15.6700(2)</td>
<td>9.62980(10)</td>
<td>12.8050(4)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>16.5072(3)</td>
<td>29.8192(3)</td>
<td>10.0663(3)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>21.2401(4)</td>
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<td>34.5747(9)</td>
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<td>α (Å)</td>
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<td>90.00</td>
<td>90</td>
</tr>
<tr>
<td>β (Å)</td>
<td>96.244(2)</td>
<td>104.4380(10)</td>
<td>95.046(3)</td>
</tr>
<tr>
<td>γ (Å)</td>
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<td>90.00</td>
<td>90</td>
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<tr>
<td>Volume (Å³)</td>
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<td>3785.98(8)</td>
<td>4439.4(2)</td>
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<tr>
<td>Z</td>
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<td>4</td>
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</tr>
<tr>
<td>Color</td>
<td>yellow</td>
<td>yellow</td>
<td>yellow</td>
</tr>
<tr>
<td>ρcalculated (g.cm⁻³)</td>
<td>1.771</td>
<td>2.072</td>
<td>2.021</td>
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<tr>
<td>Absorption coefficient (mm⁻¹)</td>
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<td>6.727</td>
<td>5.984</td>
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<tr>
<td>F(000)</td>
<td>2840</td>
<td>2248</td>
<td>2584</td>
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<td>Crystal size (mm)</td>
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<td>0.141 * 0.096 * 0.090</td>
<td>0.171 * 0.144 * 0.090</td>
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<tr>
<td>θ range for data collection (°)</td>
<td>2.62 to 27.00</td>
<td>2.57 to 27.5</td>
<td>2.58 to 27.00</td>
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<td>Tmin</td>
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<td>0.65246</td>
<td>0.94755</td>
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<tr>
<td>Tmax</td>
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<td>0.92193</td>
<td>0.49759</td>
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<tr>
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<td>-12 ≤ h ≤ 12</td>
<td>-16 ≤ h ≤ 16</td>
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<tr>
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<td>-21 ≤ k ≤ 21</td>
<td>-12 ≤ k ≤ 38</td>
<td>-12 ≤ k ≤ 12</td>
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<tr>
<td></td>
<td>-27 ≤ l ≤ 27</td>
<td>-17 ≤ l ≤ 17</td>
<td>-43 ≤ l ≤ 44</td>
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<tr>
<td>Data completeness</td>
<td>99.8% (θ = 27.00°)</td>
<td>99.9% (θ = 27.00°)</td>
<td>99.8% (θ = 27.00°)</td>
</tr>
<tr>
<td>Reflections collected</td>
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<td>34893</td>
<td>33377</td>
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<tr>
<td>Reflections unique</td>
<td>11893 [R(int) = 0.0734]</td>
<td>8266 [R(int) = 0.0428]</td>
<td>9663 [R(int) = 0.1446]</td>
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<td>11893 / 0 / 729</td>
<td>8266 / 0 / 514</td>
<td>9663 / 0 / 568</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>0.868</td>
<td>0.794</td>
<td>0.870</td>
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<td>Final R indices [I&gt;2σ(I)]</td>
<td>R₁ = 0.0381, wR₂ = 0.0697</td>
<td>R₁ = 0.0222, wR₂ = 0.0394</td>
<td>R₁ = 0.0597, wR₂ = 0.1243</td>
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<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.0803, wR₂ = 0.0749</td>
<td>R₁ = 0.0366, wR₂ = 0.0413</td>
<td>R₁ = 0.1397, wR₂ = 0.1403</td>
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<tr>
<td>Largest diff peak and hole (e Å⁻³)</td>
<td>2.006 and -1.098</td>
<td>0.876 and -0.467</td>
<td>3.086 and -2.660</td>
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<tr>
<td><strong>Empirical Formula</strong></td>
<td>Pt-4</td>
<td></td>
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<tr>
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<tr>
<td></td>
<td>C₄₀H₂₈ClN₂P₃Pt</td>
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<td><strong>Formula Weight</strong></td>
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<td><strong>Temperature (K)</strong></td>
<td>120(2)</td>
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<td></td>
</tr>
<tr>
<td><strong>Wavelenght (Å)</strong></td>
<td>0.71073</td>
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<td><strong>Crystal system</strong></td>
<td>Triclinic</td>
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<tr>
<td><strong>Space Group</strong></td>
<td>P-1</td>
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<tr>
<td><strong>a (Å)</strong></td>
<td>9.3961(2)</td>
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<tr>
<td><strong>b (Å)</strong></td>
<td>10.3378(2)</td>
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<td></td>
</tr>
<tr>
<td><strong>c (Å)</strong></td>
<td>15.9069(3)</td>
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<tr>
<td><strong>α (Å)</strong></td>
<td>91.674(2)</td>
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<td></td>
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<tr>
<td><strong>β (Å)</strong></td>
<td>103.563(2)</td>
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<tr>
<td><strong>γ (Å)</strong></td>
<td>90.529(2)</td>
<td></td>
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</tr>
<tr>
<td><strong>Volume (Å³)</strong></td>
<td>1501.18(5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Z</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td><strong>Color</strong></td>
<td>yellow</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>ρ(calculated)</strong></td>
<td>1.766</td>
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</tr>
<tr>
<td><strong>Absorption coefficient (mm⁻¹)</strong></td>
<td>4.850</td>
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<td><strong>F(000)</strong></td>
<td>784</td>
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<tr>
<td><strong>Crystal size (mm)</strong></td>
<td>0.283<em>0.236</em>0.149</td>
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<tr>
<td><strong>θ range for data collection (º)</strong></td>
<td>2.64 to 27.0</td>
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</tr>
<tr>
<td><strong>Tmin</strong></td>
<td>0.264</td>
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<tr>
<td><strong>Tmax</strong></td>
<td>0.485</td>
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</table>
| **Limiting indices**  | -12 ≤ h ≤ 12  
                         | -13 ≤ k ≤ 13  
                         | -20 ≤ l ≤ 20 |
| **Data completeness** | 99.9% (θ = 27.00º) |
| **Refractions collected** | 19078 |
| **Refractions unique** | 6528  
                         | [R(int) = 0.0302]  
                         | 6528 / 0 / 406 |
| **Goodness-of-fit on F²** | 0.989 |
| **Final R indices [I>2 σ (I)]** | R1 = 0.0202,  
                          wR2 = 0.0460 |
| **R indices (all data)** | R1 = 0.0238,  
                          wR2 = 0.0466 |
| **Largest diff peak and hole (e Å⁻³)** | 1.459 and -0.956 |
ORTEP diagrams with ellipsoids at 50% probability.

Pt-4

Re-5

Re-3

Re-4
Résumé

La chiralité (propriété des objets et des molécules de ne pas être superposables à leur image spéculaire) concerne divers domaines de la chimie, de la biologie et de la physique. Dans ce travail de thèse, nous avons tout d'abord étudié un aspect fondamental de la chiralité visant à déterminer la différence d'énergie due à la violation de la parité entre les deux énantiomères d'une molécule chirale.

En 1956, les deux théoriciens chinois Lee et Yang ont découvert que les particules élémentaires (électrons, protons ...) sont intrinsèquement chirales à cause de la force faible existant entre les particules élémentaires (l'une des quatre forces fondamentales) et qui brise la symétrie gauche-droite! En 1957, cette dissymétrie a été vérifiée expérimentalement par Wu et ses collaborateurs sur la désintégration β du $^{60}$Co d'où l'émission de particules β a été jugée plus favorisée dans le sens opposé à celui du spin nucléaire (Figure 1), soit plus d'électrons sont émis dans la direction opposée au champ magnétique, montrant ainsi expérimentalement que la parité est violée au niveau des interactions faibles.

La violation de la parité a également été observée au niveau atomique en mesurant une petite rotation optique d'une vapeur de Bismuth, ou en observant des transitions très interdites du Césium. Depuis ces découvertes, les scientifiques ont pensé que les courants neutres faibles responsables de la violation de parité dans les atomes sont bien sûr également opérationnels dans les molécules et par conséquent une légère différence d'énergie pourrait exister entre les deux énantiomères en raison de la force faible qui casse la symétrie gauche-droite (Figure 2)! Cette brisure de symétrie dans un miroir est appelée violation de la parité (PV) ou non conservation de la parité (PNC) et n'a jamais été clairement observée expérimentalement dans les molécules chirales jusqu'à maintenant.

*Figure 1: Principe de l'expérience de Mme Wu*

*Figure 2: Le miroir brisé: deux énantiomères ne sont pas de vrais énantiomères...*
Letokhov avait remarqué en 1975 qu'il devait exister une différence entre les niveaux d'énergie des molécules gauches et droites en raison des interactions faibles et des courants chargés qui peuvent conduire à des effets observables ou à un petit changement des énergies d'absorption dans le spectre moléculaire. Il rechercha ensuite le splitting $\Delta v$ par spectroscopie d'absorption laser sous-Doppler dans le spectre de CHFCIBr racémique et il a proposé le protocole expérimental envisagé à la Figure 3.

En raison de sa simplicité, le bromochlorofluorométhane (CHFCIBr) a été pendant longtemps considéré comme la molécule de choix pour la recherche des effets de violation de parité au niveau moléculaire. En effet, le groupe de Christian Chardonnet (LPL, Villetaneuse) a essayé de mesurer une différence de PV entre les énantiomères gauche et droit de CHFCIBr en 1997, puis ils ont répété cette expérience en 2002 avec des échantillons ayant des excès énantiomériques ($ee$') plus élevés, en utilisant un laser à CO$_2$ et de la spectroscopie infra-rouge (IR) à ultra-haute résolution. Les grandes valeurs expérimentales obtenues en comparaison avec leurs calculs théoriques attendus pour $\Delta E_{PV}$ ont révélé l'existence de grandes erreurs expérimentales dues aux gaz résiduels incontrôlables présents dans les cellules d'absorption qui induisent des collisions entre les molécules, en provoquant des changements des fréquences de transition. Pour contourner ce problème, le LPL a décidé de développer un dispositif expérimental adapté à la spectroscopie des molécules chirales pour une nouvelle expérience de mesure de PV basée sur la spectroscopie en jet moléculaire supersonique et en utilisant la technique de franges de Ramsey à deux photons. En s'appuyant sur des calculs théoriques effectués par P. Schwerdtfeger et ses collègues, ils ont limité le choix aux composés contenant un élément lourd (en tant que ligands ou centres chiraux) car le $\Delta E_{PV}$ est proportionnel à $Z^n$ ($n \approx 5$; $Z =$ numéro atomique).

En bref, la molécule chirale idéale pour cette expérience devrait satisfaire aux paramètres suivants:

1. Afficher une grande différence de fréquence vibrationnelle PV ($\Delta E_{PV}$) d'une bande fondamentale intense de préférence dans la plage de fonctionnement du laser à CO$_2$ (850 à 1120 cm$^{-1}$).
2. Être disponible avec un $ee$ élevé ou, idéalement, sous forme énantiopure.
3. Ne pas être trop grosse car la sensibilité de l’expérience sera largement déterminée par la fonction de partition des molécules.

4. Permettre la production de l’expansion supersonique (se sublimer sans décomposition de l’état solide à l’état gazeux).

5. Être disponible à l’échelle de plusieurs grammes.

Crassous et ses collègues ont synthétisé différents complexes oxorhénium chiraux avec des $\Delta E_{PV}$ théoriques de l’ordre de $10^2$ mHz, mais malheureusement, soit ces complexes étaient encombrants et difficiles à sublimer, soit ils se décomposaient au cours de la sublimation. Nous avons donc décidé de synthétiser un oxorhénium chiral dérivé d’un précurseur disponible dans le commerce, le méthyl trioxorhenium (MTO) qui a la capacité de se sublimer à 40 °C sous 0,01 mbar et de former ainsi facilement un jet moléculaire supersonique qui constitue une étape majeure pour l’objectif visé.

Nos molécules cibles (+)- et (-)-28 ont été synthétisées par la réaction du MTO avec le mercaptopropan-2-ol l’éantiopur (ligands (-)- et (+)-31) respectivement dans le dichlorométhane anhydre à température ambiante pendant 3-5 heures avec un rendement quantitatif comme indiqué sur le Schéma 1.

Les spectres expérimentaux de dichroïsme circulaire vibrationnel (VCD) des énantiomères de 28 montrent une relation image-miroir (Figure 4). Ils présentent une forte bande active en VCD à 1012 cm$^{-1}$ (facteur de dissymétrie $\Delta \varepsilon / \varepsilon = 1.5 \times 10^4$) qui correspond à la bande d’élongation symétrique Re=O. La présence de cette bande indique l’environnement chiral autour de l’atome de rhénium, bien que le rhénium lui-même n’est pas un centre stéréogène.
Ce complexe commence à se sublimer après chauffage à 40 °C sous la ligne à vide, et les calculs théoriques prévoient des différences de fréquence vibrationnelle due à PV dans la gamme du sous-Hz (1-3 x 10² mHz). Malheureusement, 28 se décompose pendant la formation du jet moléculaire supersonique. Par la suite, le complexe énantiopur d’oxorhénium ((+)- et (-)-33) a été préparé à partir de MTO et du 2-mercaptocyclohexanol 36 énantiopur ((-)- et (+)-36) respectivement, voir Schéma 2); il a montré une bonne stabilité sous argon/vide et a la capacité à se sublimer sous la ligne à vide à 40-60 °C.

Les spectres expérimentaux de VCD de (+)- et (-)-33 montrent également une relation image-miroir (Figure 5). Ils présentent une forte bande d’absorption active en VCD correspondant à l’élongation de la liaison Re=O symétrique qui s’étend à ~1025 cm⁻¹ avec Δe/e = 6.9x10⁻⁵. En effet, la présence du ligand énantiopur fournit un environnement chiral autour de l’atome de rhénium, bien que le rhénium lui-même n’est pas un centre stéréogénique.
Les calculs théoriques de $\Delta E_{PV}$ de 33 indiquent une différence supérieure à 100 mHz. En outre, les caractéristiques intrinsèques de ce complexe en ce qui concerne sa stabilité raisonnable, la capacité à se sublimer sur la ligne sous vide à 40-60°C, et l'existence de l'élongation de la liaison Re=O qui est compatible avec le laser à CO$_2$ dans la région IR, nous espérons pouvoir préparer dans les mois à venir un jet moléculaire supersonique de 33 pour l'étude de la spectroscopie IR.

La préparation des complexes chiraux n’a pas été limitée à des dérivés oxorhénium, mais nous nous sommes aussi intéressés à la synthèse de molécules comportant un carbone asymétrique coordonné à un métal lourd et possédant une bande d'élongation de liaison C-F. Nous avons d'abord examiné l’addition oxydante d'alcanes halogénés de précursors de Pt, et le complexe Pt(IV) 40 a été préparé en mélangant [PtMe$_2$(bpy)] avec un excès d'halothane dans l'acétoné anhydre à la température ambiante pendant 24 heures (Schéma 3).

De la même manière, nous avons pu synthétiser le complexe de Pt (IV) 41 (Schéma 4). L'intérêt majeur de ce composé est le carbone asymétrique coordonné au métal lourd et l’existence de la bande d'élongation de liaison C-F sur le carbone asymétrique et qui est compatible avec le laser à CO$_2$ utilisé lors des tentatives de mesures de PV.
Le complexe 41 montre une bonne stabilité thermique, mais malheureusement il ne se sublime pas, donc nous n'avons pas pu l'étudier dans le jet moléculaire supersonique. Toutefois, à l'avenir, nous sommes intéressés par l'étude de l'ablation laser (en anglais Pulse Laser Deposition, PLD) de ce complexe au lieu de chauffer l'échantillon, pour produire le jet moléculaire et étudier sa spectroscopie.

Un autre type de complexe chiral est le Ru(tmhd)$_3$ [tmhd = 2,2,6,6-tétraméthylheptane-3,5-dionate], un complexe de symétrie $D_3$ neutre avec un Ru$^{3+}$ et trois dérivés de type acétyle-acétonate comme ligands (Figure 6). Le Ruthénium est un centre stéréogène où la chiralité est celle des complexes OC-6 (octaédriques) possédant trois substituants bis-chélates (complexes ($\Delta$) et ($\Lambda$)).
Pour étudier la compatibilité de ce complexe avec le dispositif expérimental utilisé pour mesurer la différence de PV, le spectre IR a été enregistré. Différentes bandes IR intenses ont été observées entre 1130 et 1610 cm\(^{-1}\) qui ne coïncident pas avec la bande de laser à CO\(_2\) autour de 1000 cm\(^{-1}\). Cependant, la future utilisation de diodes laser à cascade quantique (en anglais Quantum Cascade Lasers, QCL) pourrait nous permettre d'examiner les différents domaines de longueur d'onde. En parallèle, nous essayerons de moduler le système pour obtenir une molécule plus appropriée. Le dédoublement énantiomérique de Ru(tmh)\(_3\) a ensuite été étudié. Malheureusement, la séparation des deux énantiomères par HPLC sur les différentes phases stationnaires chiraux a échoué jusqu'à présent. Cela est dû à la faible polarité du composé. Nous envisagerons dans le futur proche la préparation de dérivés chiraux qui devraient être plus polaires et donc plus faciles à dédoubler. En outre, la spectroscopie sur un jet moléculaire supersonique sera étudiée.

Parallèlement à la chiralité fondamentale et à la violation de parité dans les molécules chiraux, nous nous sommes intéressés à la synthèse d'hélicènes qui possèdent des propriétés chiroptiques (dichroïsme circulaire électronique et pouvoir rotatoire) très élevées. Les carbo- ou hétéro[n]hélicènes sont des molécules aromatiques ou hétéroaromatiques orthocondensées (n = nombre de cycles fusionnés) qui adoptent une forme hélicoïdale en raison de l'encombrement stérique entre les cycles terminaux. Ils sont caractérisés par des fonctionnalités intéressantes comme la conjugaaison \(\pi\), la chiralité intrinsèque, une capacité à s'auto-assembler, etc... A partir de \(n \geq 5\), la répulsion stérique entre les cycles terminaux rend les hélicènes configurationnellement stables. Ils peuvent s'enrouler dans des directions opposées, gauche ou droite. Sur la base de la règle d'hélicité proposée par Cahn, Ingold et Prelog en 1966, une hélice gauche (en sens inverse des aiguilles d'une montre lorsqu'on avance le long de l'hélice) est désignée «moins» et notée par \(M\) alors qu'une droite est désignée «plus» et notée \(P\) (Figure 7).

![M-helicity](image1.png) ![P-helicity](image2.png)

Figure 7

Depuis la synthèse et le dédoublement du carbo[6]hélicène (également nommé hexahélicène) par Newman dans les années 1950, beaucoup de travaux ont été effectués sur des hélicènes avec un squelette composé soit uniquement d'atomes de carbone ou contenant des hétéroatomes. Dans ce dernier cas, les azahelicenes ont un intérêt croissant en raison de la présence d'un atome d'azote qui a la possibilité de présenter une chimie de coordination très intéressante, ainsi qu'une bonne réactivité vis-à-vis du pH, de l'alkylation, et des réactifs d'oxydation. L'implication de la paire libre de l'azote dans une de ces réactions, que ce soit la coordination, la
protonation/déprotonation, ou la méthylation peut avoir un impact particulier sur les propriétés chiroptiques de la molécule d’hélicène. En raison de ces caractéristiques intrinsèques, nous nous sommes intéressés à la synthèse d’une nouvelle classe d’hélicènes portant une fonctionnalité de type 2,2’-bipyridine qui a été désigné comme le "ligand le plus largement utilisé " en raison de sa chimie de coordination exceptionnelle. En outre, la présence de différentes propriétés caractéristiques dans la molécule (la chiralité, la capacité de coordination, et le système π étendu) peut donner lieu à des complexes organométalliques ou de coordination chiraux inédits et de possédant de fortes propriétés chiroptiques.


La coordination de type chélate \( N^N' \) des hélicènes portant des unités 2,2'-bipyridines a été examinée avec les complexes tricarboxyl de rhénium(I) \( d^6 \), de formule générale \( \text{fac-}[\text{Re}(CO)_3(N^N')X]^+ \) dans laquelle les complexes analogues avec \( N^N' = 1,10\)-phénanthroline, 2,2'-bipyridine, etc ... et \( X = \) ligands monodentés tels que les halogénures pour \( n = 0 \), et les pyridines, les phosphines, ou les isocyanates pour \( n = 1 \) ont été largement étudiés et continuent à attirer beaucoup d'attention depuis que leurs propriétés de luminescence ont été étudiées en 1974 par Wrighton et Morse. Les avantages de l'utilisation de complexes de Re(I) sur les autres métaux de transition \( d^6 \) sont les suivants:

- Facilité de préparation
- Excitation et d'émission (généralement phosphorescence) dans l'UV-visible
- Grands déplacements de Stokes
- Longues durées de vie de luminescence
- Facilité de modulation des couleurs d'émission
- Résistance au photoblanchiment
- Un fort couplage spin-orbite dû au métal lourd

Par conséquent, nous nous sommes intéressés à l’étude de l'impact de la complexation du Re(I) sur les propriétés photophysiques et chiroptique de hélicènes.

Schéma 5

Pour étudier leurs propriétés d’émission, les complexes ont été excités dans leurs bandes de basse énergie (MLCT), et leurs spectres d'émission ont été enregistrés dans le dichlorométhane désoxygoné à 298 K et dans le verre EPA à 77 K (EPA = diéthyléther / isopentane / éthanol 2:2:1 v/v). À 298 K, tous les complexes Re(I) diimine tricarbonyles montrent des spectres d'émission larges et similaires qui sont attribués à l’émission de 3MLCT (phosphorescence) et ils sont caractérisés par un faible rendement quantique et une durée de vie en ns. À l'inverse, les ligands libres montrent une émission de fluorescence bleue à température ambiante avec une durée de vie dans l'échelle ns et des rendements quantiques relativement élevés. A basse température, l'émission de fluorescence des ligands libres est accompagnée par la phosphorescence verte à longue durée de vie que l'on attribue à l'état triplet (peuplé par croisement inter-système ISC) à la fois en raison du grand décalage de Stokes et en raison de leur très longue durée de vie. D'autre part, à 77K, la similitude frappante de l'émission hautement structurée pour les complexes de rhénium(I) avec le ligand ne laisse aucun doute que ces émissions structurées sont attribués à de la phosphorescence localisée sur les ligands (émission de type 3LL).

Les complexes énantiopurs chiraux sur le rhénium sont encore rares. Les complexes de rhénium énantiopurs ont été préparés et leurs propriétés chirioptiques étudiées. Les spectres de dichroïsme circulaire électronique (ECD) affichent des valeurs image-miroir pour les énantiomères (+) et (-) aux erreurs expérimentales près. Les spectres ECD de (P,CRe)(+)-Re-5 and (P,ARe)(+)-Re-6 de la Figure 8 ont des bandes de ECD similaires à celles du ligand libre, mais avec une légère augmentation des valeurs de Δε de (+)-Re-5, et une diminution dans le cas de (+)-Re-6. À λ > 300 nm, les deux complexes montrent un décalage fort dans le rouge avec une diminution de Δε par rapport au ligand libre accompagné de bandes plus faibles entre 380-450 nm qui sont liées au caractère MLCT.
D'autre part, les spectres ECD images miroirs de ($M,A_{Re}^{Re},A_{Re}^{P}$)-(-)- et ($P,C_{Re}^{Re},C_{Re}^{C}$)-(+) Re-7 (Figure 9) montrent plusieurs bandes d'intensités moyennes où l'on observe une grande diminution de $\Delta\varepsilon$ du ECD par rapport au ligand libre. Cela s'explique probablement par les réponses opposées et qui se compensent entre les deux centres Re asymétriques et l'hélicène chiral.

Les 2,2'-bipyridines agissent le plus souvent comme ligands chélatés $N^N$, mais récemment, un nouveau comportement de coordination appelé cyclométallation de type "roll-over" a été publié dans la littérature et est caractérisé par un comportement de type chélate $N^C$, suite à l'activation C-H du fragment N-C(H). Lors de l'étude de ce comportement, il a été constaté qu'un centre

Figure 8

![Graphique d'ECD](image8.png)

Figure 9

![Graphique d'ECD](image9.png)
métallique riche en électrons ainsi que des 2,2'-bipyridines substituées en position 6 sont indispensables pour que la cyclométallation de type "roll-over" ait lieu.

Ainsi, nous avons étudié la réactivité de hélicènes-bipyridines avec (DMSO)₂PtMe₂ (riche en électrons) jusqu’à la formation de complexes cyclometalés (Schéma 6).

Schéma 6
La particularité des complexes cyclometalatés "roll-over" découle de la présence de l’azote non coordonné. Tirant parti de sa capacité de coordination à un autre métal de transition ou de répondre aux variations de pH par protonation/déprotonation, il est envisageable de régler la photophysique ainsi que les propriétés chiroptiques des espèces cyclometalatés. La réaction du complexe Pt-2 dans le dichlorométhane (DCM) à température ambiante pendant 2 heures avec l’acide [18-couronne-6.HBF₄.H₂O] possédant des anions de faible coordination a abouti à la protonation sélective de l'azote N libre (Schéma 7).

Schéma 7
Les propriétés photophysiques des complexes Pt(II) cyclometalés (Pt-2 et Pt-5) ont été mesurées. La Figure 10 montre les spectres d'absorption de Pt-2, Pt-5, et du ligand libre 63 dans du DCM à température ambiante. Par comparaison, les bandes d'énergie les plus élevées sont attribuées aux transitions π-π* centrée sur le ligand avec un décalage vers le rouge d'environ 10 nm des λmax pour l'espèce protonée Pt-5 (en vert). Les bandes de basse énergie sont attribuées aux transitions de transfert de charge métal-ligand. Le complexe Pt-5 montre une bande MLCT à des longueurs d'onde plus élevées (380 à 510 nm) que les espèces neutres correspondantes Pt-2 (380-460 nm). Par conséquent, il semble que la protonation a un effet sur la densité électronique suggérant ainsi une extension plus efficace de la délocalisation de la charge sur le complexe.
Avec la même stratégie de synthèse et en utilisant un ligand H6-bpy énantiopur, les énantiomères non-protonés et les protonés de Pt-2 ont été préparés et leurs propriétés chiroptiques ont été étudiées. Les spectres ECD ont été enregistrés sur les solutions d'échantillons dans CH₂Cl₂. Dans tous les cas, ils affichent des valeurs image-miroirs pour les énantiomères (+) et (-) aux erreurs expérimentales près. En comparant les complexes non-protonés avec le ligand libre (Figure 11), il est clair qu'il y a peu d'effet sur les spectres de ECD, excepté un déplacement bathochrome.

La protonation de l'azote libre donnant le complexe Pt-5 a un grand impact sur les spectres de ECD (Figure 12). Dans la région 230-330 nm, le M(-)-Pt-5 présente une bande intense positive centrée à 275 nm avec une très légère diminution de Δε comparé au complexe non protoné M(-)-Pt-2. Cependant entre 330 et 430 nm, M(-)-Pt-5 présente une bande négative centrée à 343 nm avec une grande diminution en Δε, approximativement divisée par 2, comparée au complexe non protoné (-126 M⁻¹ cm⁻¹ vs. -213 M⁻¹ cm⁻¹). En outre, à λ > 430 nm, une nouvelle bande ECD large au maximum 471 nm (Δε = -35 M⁻¹ cm⁻¹) s'étendant jusqu'à 510 nm est apparue. Ce résultat
est en accord avec ce que nous avons obtenu lors de la protonation de 63 en [6]héliènium-bipyridine 75.

Le processus de protonation/déprotonation s’est révélé réversible en utilisant le Na$_2$CO$_3$ comme base et le [18-couronne-6.HBF$_4$.H$_2$O] comme acide dans l’acétone. Cette réversibilité effective a un effet direct sur leurs propriétés chiroptiques où les bandes de ECD sont modifiées de manière réversible, donnant lieu à un commutateur chiroptique réversible acido-basique (Figure 13).

Les propriétés de luminescence polarisée circulairement (CPL) des énantiomères purs M(-)/P-(-)-Pt-2 et M(-)/P-(-)-Pt-5 ont été mesurées dans une solution d’acétone de 1 mM à 295 K pour
une excitation à 447 nm pour les complexes Pt-2, et 436/441 nm pour les complexes Pt-5. Les spectres obtenus sont représentés sur la Figure 14. Ils sont caractérisés par des valeurs de $g_{\text{CPL}}$ de -1x10^{-3} et 1,1x10^{-3} respectivement pour les énantiomères $M-(\cdot)$ et $P-(\cdot)$-Pt-2 au maximum d’émission (~540 nm). Les espèces protonées $M-(\cdot)$ et $P-(\cdot)$-Pt-5 présentent des valeurs $g_{\text{CPL}}$ respectives de -2.2 x 10^{-3} et 1,8 x10^{-3} à une longueur d’onde d’émission de ~585 nm.

La CPL a également été mesurée pour les ligands libres et protonés 63 et 75 (Figure 14) où les valeurs $g_{\text{lum}}$ sont +3,4x10^{-3} et -3x10^{-3} et pour les énantiomères $P-(\cdot)/M-(\cdot)$-63 autour du maximum d’émission ($\lambda_{\text{em}} = 426$ nm), et de 3,2x10^{-3} et -2.5x10^{-3} pour les isomères $P-(\cdot)/M-(\cdot)$-75 autour du maximum d’émission ($\lambda_{\text{em}} = 568$ nm), respectivement.

Grâce à tous ces résultats, nous montrons donc que les hélicène-bipyridines sont des commutateurs chiroptiques acido-basiques multifonctionnels, avec des réponses différentes en absorption et émission polarisées circulairement.

Figure 15