A NEW CLASS OF LUMINESCENT ORGANOMETALLICS
-DIETHYNYLRHODACYCLOPENTADIENES

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A NEW CLASS OF LUMINESCENT ORGANOMETALLICS - DIETHYNYL RHODACYCLOPENTADIENES

MENG GUAN TAY

Ph.D THESIS 2010
Declaration

The work described in this thesis was carried out in the Department of Chemistry at Durham University between August 2006 and September 2009, under the supervision of Prof. Todd B. Marder. All the work is my own, unless otherwise stated, and has not been submitted previously for a degree at this or any other university.

Meng Guan Tay

Statement of Copyright

The copyright of this thesis rests with the author. No quotation from it should be published without prior consent and information derived from it should be acknowledged.
To my wife, daughter and son:
For the love, support and fun they give
Acknowledgements

On the rainy and chilly morning of 21st August 2006, my family and I first arrived in the UK at Newcastle Airport. A gentleman and two of my Malaysian seniors met us at the airport and led us to a fully furnished, nice and tidy house located in Belmont. In the first paragraph of my acknowledgements, I would like to express my most sincere thanks to this gentleman, who is my supervisor, Professor Todd B. Marder. A million thanks for his arrangements upon our arrival in Durham, and of course, for his excellent guidance, support and ideas during my entire Ph.D project.

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Our friendship never ends after this.)

Last but not least, thanks to Universiti Malaysia Sarawak (UNIMAS) for the Ph.D
scholarship. Thanks to all the people who have given their support and shared their
knowledge that I forgot to mention by name in this section. And also to all the people who read this thesis, thank for your time and comments.

Meng Guan Tay
Publications

2,5-Bis(p-R-Arylethynyl)-Rhodacyclopentadienes: Unprecedented Intense Fluorescence Denying the Presence of a Heavy Atom.


The Synthesis of Extended Arylene Ethynylene Butadiynes via the Oxidative Homocoupling of (4-ethynylphenylethynyl)arenes

The main objective in this project is to develop a greater understanding of the unusual photophysical properties of 2,5-bis(arylethynyl)rhodacyclopentadienes. Three distinct and unusual photophysical properties were found in the 2,5-bis(arylethynyl)-rhodacyclopentadienes: (i) long-lived singlet excited states, from which some of them exhibit high-intensity fluorescence with nanosecond lifetimes; (ii) slow intersystem crossing rates ($k_\Delta$ values $\approx 10^{8}$ s$^{-1}$) compared to typical luminescent organometallic complexes (with $k_\Delta$ values $\approx 10^{12}$ s$^{-1}$); and (iii) no phosphorescence was observed even at 77 K in a rigid glass. Many photophysical experiments such as e.g. low-temperature lifetime measurements, singlet oxygen sensitisation and time-resolved infrared (TRIR) have been carried out in order to investigate further and explain the unusual photophysical properties of this class of organometallic complexes.

Five different types of ligand X on 2,5-bis($p$-arylethynyl)-X-rhodacyclopentadienes [X = 4-[4-(N,N-di-n-hexylamino)phenylethynyl]phenylethynyl- (DHAPEPE-), trimethyl silyl ethynyl- (TMSE-), methyl- (Me-), $\eta^2$-benzoato- and acetylacetonato- (acac-)] have been synthesised and the photophysical properties of the complexes were investigated. The TMSE-rhodacyclopentadienes gave the highest fluorescence quantum yields compared to the other series of rhodacyclopentadienes. Extended phenylene-ethynylene ligands (i.e. DHAPEPE-) did not impart any effects on the $\lambda_{\text{max}}$ values in absorption and emission but the quantum yields were lower than those for the TMSE-rhodacyclopentadienes. $\eta^2$-Benzoato- and acac- ligands shifted the $\lambda_{\text{max}}$ values in absorption and emission to lower energy, which implies that they induce smaller energy gaps between the excited and ground states. The emissions from the $\eta^2$-benzoato-
rhodacyclopentadienes were quenched (especially for those with \( R = H \) and SMe substituents, which have quantum yields of less than 0.01).

The first example of isomeric biphenyl-rhodacyclopentadiene by-product formation was found in the synthesis of acac-rhodacyclopentadienes. The isomeric biphenyl-rhodacyclopentadiene by-product with \( R = \text{CO}_2\text{Me} \) was isolated and its molecular structure was confirmed by X-ray analysis. Its emission spectrum shows two emission bands with \( \lambda_{\text{max}} \) values of 394 and 544 nm in degassed toluene solution. The fluorescent emission at 394 nm has a quantum yield of 0.03, whereas the phosphorescent emission at 544 nm has a quantum yield of 0.05. The unusual long lifetime (237.6 \( \mu \)s) of the phosphorescence at room temperature indicates that the transition is from a ligand-centred (LC) \( \pi \rightarrow \pi^* \) transition.

In addition, the syntheses of 1,4-bis(\( p \)-R-phenyl)buta-1,3-diynes and novel 1,12-bis(\( p \)-R-phenyl)dodaca-1,3,9,11-tetraynes, which serve as the starting materials for the synthesis of the rhodacyclopentadienes, are also reported. Four novel 1,12-bis(\( p \)-R-phenyl)dodaca-1,3,9,11-tetraynes (where \( R = H, \text{SMe}, \text{CO}_2\text{Me} \) and \( \text{BMes}_2 \)) have been synthesised and characterised. The formation of homo-coupling products was a major problem which reduced the yields of the 1,3,9,11-dodacatetraynes. The 1,3,9,11-dodacatetraynes were separated from their respective homo-coupling products using column chromatography, and the yields obtained were 30 – 46\%.
### Abbreviations

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<td>Absorbance</td>
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<tr>
<td>ΔE</td>
<td>Energy gap</td>
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<tr>
<td>acac</td>
<td>Acetylacetone</td>
</tr>
<tr>
<td>EML</td>
<td>Emissive layer</td>
</tr>
<tr>
<td>Å</td>
<td>Angstrom</td>
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<tr>
<td>ETL</td>
<td>Electron transport layer</td>
</tr>
<tr>
<td>Aryl</td>
<td>Aryl</td>
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<tr>
<td>ε</td>
<td>Extinction coefficient</td>
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<tr>
<td>bpy</td>
<td>Bipyridine</td>
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<tr>
<td>EI</td>
<td>Electron impact ionisation</td>
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<td>BMes₂</td>
<td>Dimesityl boryl</td>
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<tr>
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<td>Triethylamine</td>
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<tr>
<td>BPEBs</td>
<td>1,4-Bis(phenyl ethynyl)benzenes</td>
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<tr>
<td>EM</td>
<td>Emission</td>
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<td>Electroluminescence</td>
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<td>EPEDHA</td>
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<td>Bu</td>
<td>Butyl</td>
</tr>
<tr>
<td>ES</td>
<td>Electrospray</td>
</tr>
<tr>
<td>CO₂Me</td>
<td>Carbomethoxy</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>COD</td>
<td>1,5-Cyclooctadiene</td>
</tr>
<tr>
<td>fᵥ</td>
<td>Frank-Condon factor</td>
</tr>
<tr>
<td>COE</td>
<td>Cyclooctene</td>
</tr>
<tr>
<td>GC-MS</td>
<td>Gas chromatography mass spectroscopy</td>
</tr>
<tr>
<td>DHAPEPE</td>
<td>4-[4-(N,N-di-n-hexyl amino)phenylethynyl</td>
</tr>
<tr>
<td>HTL</td>
<td>Hole transport layer</td>
</tr>
<tr>
<td>Hex</td>
<td>Hexyl</td>
</tr>
<tr>
<td>DCCI</td>
<td>N,N'-dicyclohexyl carbodiimide</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>DMAP</td>
<td>4-(N,N-dimethyl amino)pyridine</td>
</tr>
<tr>
<td>HPLC</td>
<td>High performance liquid chromatography</td>
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<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
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<tr>
<td>IC</td>
<td>Internal conversion</td>
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<tr>
<td>DBAs</td>
<td>Dehydrobenzo annulenes</td>
</tr>
<tr>
<td>ISC</td>
<td>Intersystem crossing</td>
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</table>
\[ iPr = \text{Isopropyl} \quad 3\text{O}_2, \text{O}_2(3\Sigma) = \text{Triplet oxygen} \]

\[ [\text{Ir(ppy)}_3] = \text{Tris(2-phenylpyridine) iridium} \quad 1\text{O}_2 = \text{Singlet oxygen} \]

\[ k_{\text{IC}} = \text{Rate constant of internal conversion} \quad \text{OLEDs} = \text{Organic light emitting diodes} \]

\[ k_f = \text{Rate constant of fluorescence} \quad \text{OAc} = \text{Acetate} \]

\[ k_{\Delta} = \text{Rate constant of intersystem crossing} \quad [\text{Pt(bpy)}_3]^{2+} = \text{Tris(bipyridine) platinum}^{(II)} \text{ dication} \]

\[ \text{LUMO} = \text{Lowest unoccupied molecular orbital} \quad \text{PtOEP} = 2,3,7,8,12,13,17,18-\text{octaethyl}-21\text{H},23\text{H}-\text{porphine platinum}^{(II)} \]

\[ \text{LCDs} = \text{Liquid crystal displays} \quad \text{Ph} = \text{Phenyl} \]

\[ \text{LC} = \text{Ligand-centred} \quad \text{phen} = 1,10-\text{phenanthroline} \]

\[ \text{LDA} = \text{Lithium diisopropylamide} \quad \text{“P-olefin ligand”} = \]

\[ \tau = \text{Lifetime} \quad \text{PMe}_3 = \text{Trimethylphosphine} \]

\[ \text{MLCT} = \text{Metal-to-ligand charge transfer} \quad \text{PPh}_3 = \text{Triphenylphosphine} \]

\[ \text{MALDI} = \text{Matrix-assisted laser desorption ionisation} \]

\[ \text{Me} = \text{Methyl} \quad \Phi = \text{Quantum yield} \]

\[ \text{MC} = \text{Metal-centred} \quad \Phi_{\Delta} = \text{Quantum yield of intersystem crossing} \]

\[ \text{NBS} = \text{N-bromosuccinimide} \quad [\text{Rh(phen)}_3]^{3+} = \text{Tris(1,10-phenanthroline) rhodium}^{(III)} \text{ trication} \]

\[ \text{NMe}_2 = \text{Dimethylamino} \]

\[ \text{OMe} = \text{Methoxy} \quad [\text{Rh(bpy)}_3]^{3+} = \text{Tris(bipyridine) rhodium}^{(III)} \text{ trication} \]
\[[\text{Ru(bpy)}_3]^{2+}\] = Tris(bipyridine) ruthenium\(^{II}\) dication

TRIR = Time-resolved infrared

R.T. = Room temperature

SOC = Spin-orbit coupling

T = Time

TBAF = Tetra-\(n\)-butyl ammonium fluoride

SMe = Methylthio

ToF = Time of flight

SiMe\(_3\) = Trimethylsilyl

TMSA = Trimethylsilyl acetylene

ToF = Time of flight

THF = Tetrahydrofuran

VR = Vibrational relaxation

NMR Abbreviations

<table>
<thead>
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<th>Description</th>
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<tr>
<td>br</td>
<td>Broad</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>d</td>
<td>Doublet</td>
</tr>
<tr>
<td>q</td>
<td>Quartet</td>
</tr>
<tr>
<td>dd</td>
<td>Doublet of doublets</td>
</tr>
<tr>
<td>quint</td>
<td>Quintet</td>
</tr>
<tr>
<td>dt</td>
<td>Doublet of triplets</td>
</tr>
<tr>
<td>s</td>
<td>Singlet</td>
</tr>
<tr>
<td>J</td>
<td>Coupling constant</td>
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<td>t</td>
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Chapter 1

Introduction
1.1 Molecular photophysics

1.1.1 General terms in photophysical transitions

Luminescence is a process whereby a compound in an excited electronic state returns to its ground state by emission of light. Luminescence can be divided into several different categories depending on how the excited state is formed. Two major processes of interest are: photoluminescence (PL), in which the excited state is formed by absorption of light; and electroluminescence (EL), in which the excitation occurs when an electric field is applied to the material.

A modified Jabłoński diagram which illustrates the photophysical processes in the ground and excited states of a molecule is shown in Figure 1.1 below.

![Photophysical transitions](image)

**Figure 1.1:** Photophysical transitions between electronic states in a single molecule.
The straight arrows in Figure 1.1 represent various possible radiative transitions, whereas the wavy arrows show the non-radiative transitions between electronic or vibrational states. The singlet ground state is labelled as $S_0$, and the first, second and higher electronic excited singlet states are represented by $S_1$, $S_2$ and $S_n$, respectively, with $n = 3, 4, 5$ and so on. A molecule exhibits a singlet state when there is no net electronic spin associated with the state (all of the spins are paired). The triplet states are labelled as $T_1$ and $T_2$, where ‘$T$’ indicates that there are three possibilities of spin orientation of two unpaired electrons (Figure 1.2). The spin multiplicity formula $2S + 1$ gives the number of the states which can arise, where the ‘$S$’ is the total spin quantum number. In the case where all electrons of a molecule are spin-paired, $S = 0$ (because there is no net electronic spin associated with the state), and the spin multiplicity = 1, which represents the singlet state. In contrast, when the molecule has two unpaired spins, $S = 1$, it has to be the spin multiplicity = 3, which implies the triplet state.\(^\text{1}\)

![Diagram of electron orientation](image_url)

**Figure 1.2:** General diagram of the electron orientation in the ground ($S_0$), singlet ($S_1$) and triplet ($T_1$) excited states of a molecule for HOMO-LUMO transition.

When a photon is absorbed, the molecule can be excited from the ground state to an energetically higher lying singlet excited state with two spin-paired electrons (Figure 1.2). If the molecule is excited to the second singlet excited state ($S_0 \rightarrow S_2$), it rapidly
relaxes to the lowest vibrational level of \( S_2 \) via vibrational relaxation (VR). Internal conversion (IC) occurs when the molecule releases excess energy from the second singlet excited state to the first singlet excited state \( (S_2 \rightarrow S_1) \). These processes occur very quickly \( (10^{-12} \text{ s} \text{ or less}) \) and are generally complete before the emission occurs.\(^2\)

Fluorescence results if the molecule returns back to the ground state from the lowest singlet excited state \( (S_1 \rightarrow S_0) \) by emission of a photon, and fluorescence lifetimes are typically ca. \( 10^{-9} \) to \( 10^{-7} \text{ s} \). Kasha’s rule states that the emission generally occurs from the lowest excited state to the ground state.\(^3\) The efficiency of an emission process is measured as the quantum yield, \( \Phi \), which is defined as the ratio of photons emitted to photons absorbed of a sample.

Under certain conditions, the molecule in the singlet excited state may undergo a non-radiative process, known as intersystem crossing (ISC), to a triplet state \( (S_1 \rightarrow T_1) \), in which the molecule has two electrons with parallel spin (Figure 1.2). However, in some cases, ISC from higher lying singlet states to higher lying triplet states \( (S_n \rightarrow T_n \text{, where, } n = 2, 3, 4 \text{ and higher}) \) could also be possible. Similarly, the molecule at the higher vibrational energy levels of \( T_1 \) state can release the excess energy via VR to the lowest vibrational energy level of \( T_1 \) state. Phosphorescence results if the molecule returns back to the ground state from the lowest \( T_1 \) state \( (T_1 \rightarrow S_0) \). The rate constants for phosphorescence are several orders of magnitude smaller \( (10^6 \text{ to } 10^9 \text{ s}^{-1}) \) than those for fluorescence due to the fact that the transition from \( T_1 \) to \( S_0 \) is spin-forbidden.\(^2\) As \( T_1 \) is often lower in energy than \( S_1 \), phosphorescence generally occurs at lower frequency relative to fluorescence.\(^2\)
1.1.2 Non-radiative decay transitions in an excited molecule

Non-radiative decay such as ISC and IC from an excited state to the ground state can significantly reduce the quantum yield of a luminescence process. Typically, non-radiative processes depend on several factors such as the nature of the molecular structure, in particular its molecular rigidity, and the energy gap ($\Delta E$) between the excited states ($S_1$ or $T_1$) and $S_0$.

In general, the more rigid a molecule, the higher is its luminescence efficiency. For example, the $\Phi_f$ of the trans- (compound a) and cis (compound b) stilbenes are 0.05 and 0.00, respectively. However, the $\Phi_f$ of a structurally rigid derivative (compound c) is 1.00 (Figure 1.3).

![Figure 1.3: Influence of rigidity on the $\Phi_f$ in stilbenes.][1]

The non-radiative decay rate constant of an excited molecule can also be estimated by the energy gap law, which expresses the exponential relationship between the non-radiative rate constant of internal conversion ($k_{IC}$) and the energy gap ($\Delta E$) between the two states (Eq 1.1).[4, 5]

![Figure 1.3: Influence of rigidity on the $\Phi_f$ in stilbenes.][1]
\[ k_{IC} \sim 10^{13} \exp (-\alpha \Delta E) \quad (1.1) \]

where \( \alpha \) is a proportionality constant and the ‘\( \exp (-\alpha \Delta E) \)’ term is defined as the Frank-Condon factor \( (f_v) \), which can determine the overlap between the potential energy curves of two states and the rate of transitions between them. In principle, the overlap between two states is inversely proportional to the \( \Delta E \) of the two states; the smaller the \( \Delta E \), the greater the overlap, consequently, the faster the transitions (i.e. non-radiative decay) between two states. Therefore, Eq. 1.1 can also be written in the form of Eq. 1.2:\(^4\)

\[ k_{IC} \sim 10^{13} f_v \quad (1.2) \]

For a \( \pi \)-conjugated and rigid organic molecule, if \( \Delta E \) is less than 209 kJ/mol (ca. 2 eV), \( k_{IC} \) is about \( 10^8 \) s\(^{-1}\) or higher, and in this case, the non-radiative process becomes the dominant process, leading to a lower fluorescence quantum yield \( (\Phi_i) \).\(^4\) For example, the \( \Delta E \) of \( S_1 \) to \( S_0 \) for pentacene is about \(~209\) kJ/mol and the quantum yield of IC \( (\Phi_{IC}) \) is about 0.75. This is also the reason that non-radiative decay of triplet states occurs very efficiently in aromatic hydrocarbon molecules as the \( T_1 \) state is often lower in energy than the \( S_1 \) state and \( k_{IC} \) becomes dominant.\(^6\)

Furthermore, the largest Frank-Condon factors are usually found in high frequency vibrations.\(^4\) For example, the C-H stretching motion is the highest frequency vibration in an organic molecule; thus, the loss of vibrational energy is expected to be fastest through the C-H vibration mode. Many researchers have studied and calculated the isotope effect by replacing the hydrogen (H) atoms with deuterium (D), which has a lower C-D
vibrational energy (~2200 cm\(^{-1}\)). Robinson and Frosch\(^7\) stated that changing benzene to benzene-d\(_6\) can increase \(\Phi_P\) because there is a large deuterium effect in the benzene case, which can cause the phosphorescence to be more favourable than the non-radiative transition. Another example is naphthalene, which shows an increase in phosphorescence lifetime and quantum yield from ~2 to ~20 sec and from 0.05 to ~0.80, respectively, upon substitution of C-H for C-D.\(^4\)

In general, ISC is always a spin forbidden process. However, ISC in organic molecules can still occur even when a heavy atom such as bromine or iodine is incorporated into the molecule. The probability of ISC increases with increasing atomic number due to greater spin orbit coupling (SOC) effect of the heavy atom.\(^8\) In this context, it is important to note that the rate constant of the ISC from \(S_1\) to \(T_1\) \((k_\Delta)\) and the phosphorescence quantum yield \((\Phi_P)\) are expected to increase but the \(\Phi_F\) should decrease. The typical example for demonstrating the heavy atom effect on \(k_\Delta\), \(\Phi_F\) and \(\Phi_P\) is substituting naphthalene with different halogens as shown in Table 1.1.\(^4\) The SOC constants of the respective elements are shown in the last column.\(^9\)
Table 1.1: Summarised data of $k_\Delta$, $\Phi_F$ and $\Phi_P$ of naphthalene and its halo derivatives,\(^4\) and the SOC constant of the respective element.\(^9\)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$k_\Delta$</th>
<th>$\Phi_F$</th>
<th>$\Phi_P$</th>
<th>SOC constant (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>$10^6$</td>
<td>0.55</td>
<td>0.05</td>
<td>H = 0.24</td>
</tr>
<tr>
<td>1-Fluoronaphthalene</td>
<td>$10^6$</td>
<td>0.84</td>
<td>0.06</td>
<td>F = 269</td>
</tr>
<tr>
<td>1-Chloronaphthalene</td>
<td>$10^8$</td>
<td>0.06</td>
<td>0.54</td>
<td>Cl = 587</td>
</tr>
<tr>
<td>1-Bromonaphthalene</td>
<td>$10^9$</td>
<td>0.002</td>
<td>0.55</td>
<td>Br = 2460</td>
</tr>
<tr>
<td>1-Iodonaphthalene</td>
<td>$10^{10}$</td>
<td>0.0</td>
<td>0.70</td>
<td>I = 5069</td>
</tr>
</tbody>
</table>

Note: Data for rigid solution at 77 K. Rate constants are approximate.

From Table 1.1, the effect of a fluorine (F) substituent on $k_\Delta$ and $\Phi_P$ is negligible in 1-fluoronaphthalene; however, its $\Phi_F$ is higher than that of naphthalene. This is due to the fact that the vibrational frequency of a C-H bond is much higher than that of the C-F bond, thus energy loss is more efficient via the C-H bond than via the C-F bond. On the other hand, chloro (Cl), bromo (Br) and iodo (I) substituted naphthalenes show a decrease in $\Phi_F$, but increase $k_\Delta$ and $\Phi_P$, indicating that the SOC of the heavy atom can significantly facilitate ISC, and thus form the triplet excited state.\(^4\)

The heavy atom effect is also present in transition metal compounds, and as a result, many organometallic complexes such as $[\text{Ir(ppy)}_3]^{10, 11}$, $[\text{Ru(bpy)}_3]^{2+}^{12, 13}$ and $2,3,7,8,12,13,17,18$-octaethyl-21H,23H-porphine platinum$^{(II)}$ (PtOEP)$^{14, 15}$ are well known phosphorescent organometallic complexes with fairly high SOC constants for the $2^{\text{nd}}$ and $3^{\text{rd}}$ row transition metals (e.g. SOC constant for Ru = 1042 cm\(^{-1}\), Ir = 3909 and Pt
Therefore, fluorescence is usually not observed in organometallic complexes.

Apart from the heavy atom effect, ISC in organic molecules still can occur if the transitions involved can generate a spin momentum change such as an \( n \rightarrow \pi^* \) transition (Figure 1.4.a, ‘n’ means nonbonding orbital). As illustrated in Figure 1.4.a, a \( \pi \) electron ‘jumps’ from one \( p \) orbital (e.g. \( p_x \) orbital) to another \( p \) orbital (e.g. \( p_y \) orbital) on the oxygen atom. The \( p_x \rightarrow p_y \) orbital jump is a one-centre jump, involving a change in angular momentum, which is similar to a SOC situation, and since the total spin has to be preserved, a spin flip creating a triplet state is allowed. Consequently, the angular momentum change during the \( n \rightarrow \pi^* \) transition leads to a situation in which the formation of a singlet state is forbidden. In Figure 1.4.b, a \( \pi \rightarrow \pi^* \) transition in ethylene is shown. The \( \pi \) electron on the carbon atom cannot find a low-energy orbital in the molecular plane to ‘jump’ into in order to facilitate a change in angular momentum. Therefore, a one-centre jump spin interaction is not present in the ethylene case, and consequently, no spin flip can occur to form the triplet excited state.

\[
\begin{align*}
\text{one centre jump} & \\
\begin{array}{c}
\text{n(\(H\)) \(\pi^*\) ( )} \\
\rightarrow \\
\text{n(\(H\)) \(\pi^*\) ( )}
\end{array}
& \quad \text{‘allowed’}
\end{align*}
\]

\[
\begin{align*}
\text{b} & \\
\begin{array}{c}
\text{\(\pi(\(C\)) \(\pi^*\) ( )} \\
\rightarrow \\
\text{\(\pi(\(C\)) \(\pi^*\) ( )}
\end{array}
& \quad \text{‘forbidden’}
\end{align*}
\]

Figure 1.4: Spin-flip cases in (a) formaldehyde and (b) ethylene, respectively.
Besides the $n \rightarrow \pi^*$ transition, $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ transitions are also known as spin-flip allowed transitions.\textsuperscript{4, 8, 16} For example, the triplet excited states of the thiophene trimer (Figure 1.5) arise from a nearly pure $\pi \rightarrow \sigma^*$ transition.\textsuperscript{16}

![Figure 1.5: The structure of thiophene trimer.\textsuperscript{16}](image)

### 1.1.3 External quenching of excited states

Besides intramolecular processes, the efficiency of fluorescence and phosphorescence can be reduced by external quenching processes. In the presence of external quenchers (e.g. oxygen and halides), the excitation energy in a molecule can be lost through energy transfer and electron transfer processes. There are many mechanisms to describe the quenching processes, but in general, they can be categorised into three mechanisms, (i) ‘trivial’, (ii) collisional quenching, and (iii) Coulombic interaction.

‘Trivial’ is when the donor ($D$) emits fluorescence and the acceptor ($A$) absorbs the fluorescence (Eq. 1.3 and 1.4).\textsuperscript{17}

\[
D^* \rightarrow D + h\nu \quad (1.3)
\]

\[
h\nu + A \rightarrow A^* \quad (1.4)
\]

$A$ does not influence the emission ability of $D$, but it reduces the amount of observed photons emitted from $D$, as a result the recorded $\Phi_F$ will be less than the real one. Three factors determine how the recorded $\Phi_F$ is affected, (i) the concentration of $A$, (ii) the extinction coefficient of $A$, and (iii) the overlap of the emission spectrum of $D^*$ with the
absorption spectrum of \( A \). \( \Phi_F \) can be decreased dramatically when each of these three factors is maximised.

The second quenching mechanism is called collisional quenching, where the excitation energy of \( D^* \) is lost when it comes into physical contact with \( A \) in solution. (Eq. 1.5 and Figure 1.6). \(^4\)

\[
D^* + A \rightarrow D + A^* \tag{1.5}
\]

![Figure 1.6: Energy transfer by collisional quenching. \(^4\)](image)

In this mechanism, the electron in the lowest unoccupied molecular orbital (LUMO) of \( D^* \) ‘jumps’ to the LUMO of the ground state \( A \), and at the same time, an electron in the highest occupied molecular orbital (HOMO) in \( A \) ‘jumps’ to the HOMO of \( D^* \). As a result, the excited state of \( D \) has been quenched.

The principle of this quenching mechanism can be applied to determine the quantum yield of triplet state formation, \( \Phi_A \), of a molecule via a singlet oxygen sensitisation experiment. \(^{18,19}\) Figure 1.7 shows how the singlet oxygen (\({^1}O_2\)) is formed when a ground state molecular oxygen physically contacts with a triplet state molecule. By knowing the percentage of \( ^1O_2 \) formation from the weak emission spectrum of \( ^1O_2 \) around 1270 nm (depending on the solvent used\(^{18}\)), the \( \Phi_{TSC} \) of a molecule can be determined.
The third quenching mechanism is Coulombic interaction or dipole-dipole interaction between D and A. The principle of this quenching is depicted in Figure 1.8. The main distinction between the collisional quenching and the Coulombic interaction is that in the latter, physical contact is not necessary. Förster\textsuperscript{20, 21} proposed that the magnitude of interaction is dependent on the magnitude of two dipoles (\(\mu_D\) and \(\mu_A\)) and the distance between D and A (\(R_{DA}\)), which can be represented by Eq 1.6:

\[
\text{Interaction energy} \propto \frac{\mu_D \mu_A}{R_{DA}^3} \quad (1.6)
\]

Based on Eq. 1.6, a significant interaction energy can be caused by the large dipole moment of D (\(\mu_D\)) and A (\(\mu_A\)) and the small separation between D and A.\textsuperscript{20, 21}
Interaction between an excited molecule and a solvent molecule in a polar solvent is a typical quenching example via Coulombic interaction. In general, emission shifts to a lower energy region in polar solvents because of the strong dipole moment interaction between the excited molecules with the polar solvent molecules, which can stabilise the S₁ excited state and result in a red shift in the emission. However, due to the strong dipole moment interactions, the excitation energy can be lost from the excited molecules to solvent molecules thereby reducing the Φ. The reduction of Φ in polar solvent can be explained by Eq 1.6; a higher Φ is observed in a non-polar solvent, e.g. hexane, compared to a polar solvent because the dipole moment of non-polar solvent, μₐ, is close to zero, hence, the interaction energy is very small.

1.2 Applications of luminescent materials

1.2.1 Organic light emitting diodes

The main applications for luminescent materials are in display technologies such as organic light emitting diodes (OLEDs) and biological labelling agents. Compared to other display technologies such as plasma displays and liquid crystal displays (LCDs), OLEDs have unique properties. In addition to being brighter and having longer operational lifetimes, OLEDs can be manufactured in a portable, roll-up form with conformable displays, which display the images on windows, panels, building walls and so on. This unique property is due to the fact that OLED materials can be deposited on a wide range of substrates, ranging from glass and silicon, which are rigid substrates, to incorporation into polymers, which are highly flexible substrates. OLEDs
are thus believed to have greater potential in the application of high performance flat panel displays.\textsuperscript{28, 29} A simple general structure of an OLED device is shown in Figure 1.9, which consists of three layers, namely cathode, organic layer and anode. When a potential is applied across the device, the organic material is oxidised, forming hole carriers at the anode because its electrons are ejected from the HOMO of the organic material. At the same time, the material near the cathode is reduced, forming electron carriers when an electron is injected into the LUMO of the organic material. The holes and electrons will recombine leading to the emission of light, termed electroluminescence.

\begin{figure}[h]
\centering
\includegraphics[width=0.7\textwidth]{OLED_diagram.png}
\caption{Schematic diagram showing how an OLED device emits light.}
\end{figure}

However, the simple structure OLED device in Figure 1.9 is often inefficient. The organic material needs to satisfy a number of criteria in order to have a high probability for hole and electron carrier recombination within the layer. Therefore, multilayer OLEDs are designed, and each layer is optimised for its particular role (Figure 1.10). The selection of material for each layer is based on the HOMO-LUMO energy gap as well as
their electron and hole transport properties in order to achieve highly efficient light emission from the device.\textsuperscript{29,30}

Simple fluorescent organic compounds were employed in the EML materials in the early stages of OLED technology.\textsuperscript{31} However, in recent times, organometallic complexes have been employed in the OLED devices due to the fact that device efficiency can be improved by up to a factor of four after electron/hole recombination in the emissive layer, according to spin statistics.\textsuperscript{32} This is due to the strong SOC of heavy atoms such as 2\textsuperscript{nd} and 3\textsuperscript{rd} row transition metals, which can lead to highly emissive triplet states, and consequently increases the electroluminescence efficiency by up to four times higher than the simple fluorescent organic compounds which are typically singlet state emitters.\textsuperscript{32}

1.2.2 Biological labelling and imaging

In biological labelling applications, fluorescent probes enable researchers to observe and detect specific components in bio-molecular assemblies. They have become key research tools for non-invasive diagnostics and for biological imaging. Therefore, the design of an ideal practical probe has become a growing interest. An ideal practical
probe, which is suitable for living cells and is able to be observed by spectroscopic techniques, should be able to fulfil several criteria. The probe should be non-toxic, cell-permeable, emitting in the visible region, having a large Stokes shift to minimise re-absorption by other molecules and a long-lived emission that can allow time-resolved methods to be employed.\textsuperscript{33} The output of a fluorescent probe depends on the extinction coefficient ($\varepsilon$) of the absorption and the $\Phi$ of the emission. In principle, the higher $\Phi$ and $\varepsilon$, the better the fluorescent probe is.

The performance of a fluorescent dye is also dependent on certain external factors such as solvent polarity, the presence and concentration of quenchers, and the pH of the aqueous medium. As discussed in section 1.1, polar solvents can cause the emission wavelength of a fluorescent dye to shift to lower energy regions and result in lower $\Phi$ than less polar solvents.

In biological cases, proteins are found to be the quenchers due to the charge-transfer interaction between the amino acid and the fluorescent dyes. For example, the fluorescence of (\(\alpha\)-N-L-alanine)-7-nitro-benz-2-oxa-1,3-diazole (NBDA) is quenched when it binds to immunoglobulins, which is because of the hydrogen bond formation between the proton donor groups in immunoglobulins with the nitro or oxadiazole oxygens in NBDA.\textsuperscript{34}

An example of how the pH of the aqueous medium affects the emission efficiency of the fluorescent dye is shown in Figure 1.11. The conversion of the prototropic 3'- and 6'-hydroxyl groups of fluorescein to acetate esters can make the colour change from colourless and nonfluorescent (compound d) to highly fluorescent (di-anionic fluorescein, compound g).\textsuperscript{35}
Similar to OLED applications, utilisation of fluorescent organic compounds also has several limitations for biological imaging, sensing or labelling applications. Some of the limitations include short fluorescence lifetimes and small Stokes shifts. In order to solve these problems, various metal complexes such as lanthanide (Ln) coordination complexes containing chelating ligands, rhenium and iridium-containing diimine complexes, which display intensive and long-lived luminescence, have been developed. For example, Lo et al. synthesised a series of luminescent Re(I) isothiocyanate polypyridine complexes (Figure 1.12) to label human serum albumin. The labelled bio-conjugate exhibited an intensive and long-lived yellow emission band in the polyacrylamide gel electrophoresis study. Importantly, this band was not observed when an isothiocyanate-free Re(I) complex was used, which indicates that the yellow band is associated with the Re-labelled protein.

Figure 1.11: Ionisation equilibrium of fluorescein. 

![Chemical structures](image.png)
Long-lived luminescent Ln complexes with chelating ligands have been developed to be localised within living cells by luminescence microscopy.\textsuperscript{27, 33, 40, 41} The function of chelate ligands are (i) to protect the luminescent Ln centre from quenching by water molecules; and (ii) to allow energy transfer to the Ln centre.\textsuperscript{36} Parker and Pal\textsuperscript{33} reported a luminescent europium (Eu) complex (Figure 1.13), where upon changing the pH, the emission maxima shifts. Importantly, the lifetime and emission intensity of this Eu complex were not affected when the pH was changed. The cellular uptake profile (using mouse skin fibroblasts) of the Eu complex was also reported. Two emission maxima were observed at wavelengths of 570 nm (red, from Eu emission) and 450 nm (green, from azathiaxanthone fluorescence) indicating that the complex was localised in the cell nucleus.\textsuperscript{33}
Besides being used for displays and labelling purposes as discussed above, luminescent materials are also promising for use in other applications such as photocatalysts for CO₂ reduction,⁴²,⁴³ as singlet oxygen sensitisers⁴⁴,⁴⁵ and for sensor applications.⁴⁶,⁴⁷

1.3 Photophysical properties of luminescent organometallics

The photophysical properties of a molecule are mainly dependent on the nature of molecular orbitals, which correspond to the electronic ground state and the lowest excited state.⁴⁸ Specifically, the excitations in organometallic complexes that will be discussed here are (i) ligand-centred (LC) \( \pi \rightarrow \pi^* \) transitions, (ii) metal-centred (MC) \( d \rightarrow d^* \) transitions and (iii) metal-to-ligand charge transfer (MLCT) \( d \rightarrow \pi^* \) transitions (Figure 1.14).

**Figure 1.14:** The three types of electronic transitions that are discussed in this section.

LC \( \pi \rightarrow \pi^* \) transitions are typically found originating from the \( \pi \)-conjugated organic ligands of a metal complex. The HOMO and LUMO are the respective \( \pi \) and \( \pi^* \) orbitals of the organic ligands. As a simple example, in the ground state, the electron configuration is \( \pi^2 \) (Figure 1.15.a). Upon excitation, one electron is promoted from the \( \pi \)
orbital to the $\pi^*$ orbital and thus giving the electron configuration of $\pi^1 \pi^{*1}$, which can be a singlet (Figure 1.15.b) or triplet (Figure 1.15.c) excited state. Since formation of a singlet excited state is a spin allowed process, it corresponds to a strong absorption band with a large extinction coefficient. However, triplet excited state formation is a spin forbidden process, and it is therefore associated with a small extinction coefficient for absorption.

![LUMO and HOMO orbitals with singlet and triplet excited states](image)

**Figure 1.15:** (a) Ground state, (b) singlet excited states and (c) triplet excited state of $\pi$-conjugated organic ligands in a transition metal complex.\(^{48}\)

MC d $\rightarrow$ d* absorptions involve the transition between d-orbitals in a metal. **Figure 1.16** shows the d-orbitals splitting diagram of a transition metal complex with octahedral geometry and with a d\(^6\) configuration. The $\Delta E$ value between $t_{2g}$ and $e_g$ orbitals is influenced by the ligands attached to the metal. Based on ligand field theory, strong field ligands such as CO, CN\(^-\) and ppy\(^-\) split the orbitals greater than weak field ligands such as Br\(^-\), S\(^{2-}\), SCN\(^-\), etc.\(^{49}\)
Figure 1.16: Splitting of d-orbitals in a transition metal complex with octahedral geometry (with strong field ligands, large $\Delta E$ value).  

Upon excitation, the electron configuration can change: $t_{2g}^6 \rightarrow t_{2g}^5 e_g^1$ and $t_{2g}^6 \rightarrow t_{2g}^4 e_g^2$ etc; and as a result, the excited states have longer metal-ligand bond lengths than the ground state because of the occupation of the anti-bonding $e_g$ $\sigma^*$-orbitals. Increasing the metal-ligand bond length can increase the overlap between low-lying vibrational wavefunctions of the excited state with the high-energy vibrational wavefunctions of the ground state. An increase of Frank-Condon factor and non-radiative process rate is the result, and emission is quenched.

MLCT transition refers to the transition from a metal d-orbital to a low-lying $\pi^*$ orbital at the ligand. The transition usually occurs at low energy if the metal ion has a low oxidation number, whereby its d-orbitals are high in energy. In addition, this transition is also represented by a weaker absorption band compared to the LC absorption band in a spectrum.
1.3.1 Tris(bipyridine) ruthenium$^{(II)}$ dication, $[\text{Ru(bpy)}_3]^{2+}$

The discovery of the photophysical properties of tris(bipyridine) ruthenium$^{(II)}$ dication, $[\text{Ru(bpy)}_3]^{2+}$ (Figure 1.17) was an important landmark in modern organometallic photochemistry.$^{22,50}$ This complex has been extensively studied and has played a key role in understanding the photophysics, photochemistry, electroluminescence, and electron and energy transfer mechanisms in organometallic complexes.$^{12}$ The HOMO of the $d^6$ configuration $[\text{Ru(bpy)}_3]^{2+}$ complex arises from the $t_{2g}$ orbitals of the Ru centre, whereas the LUMO arises from the $\pi^*$ of the bpy ligands.$^{12,13}$

![Structure of $[\text{Ru(bpy)}_3]^{2+}$](image)

**Figure 1.17**: Structure of $[\text{Ru(bpy)}_3]^{2+}$.

Five electronic transitions are observed in the absorption spectrum of $[\text{Ru(bpy)}_3]^{2+}$ at 185, 285, 240, 344 (shoulder) and 450 nm (Figure 1.18).$^{12}$ The absorption bands at 185 and 285 nm are due to the LC $\pi \rightarrow \pi^*$ transitions,$^{12,51}$ while the other two bands at 240 and 450 nm are believed to be the MLCT $d \rightarrow \pi^*$ transitions. The shoulder at 344 nm may be the MC $\pi_{\text{metal}} \rightarrow \sigma^*_{\text{metal}}$ (or $d \rightarrow d^*$) transition.$^{12}$
Figure 1.18: Absorption spectrum of [Ru(bpy)$_3$]$^{2+}$ (Diagram taken from reference 12).

Apart from the above mentioned transitions, Klassen and Crosby observed a shoulder at 550 nm when they recorded the absorption spectrum at 77 K in a rigid ethanol-methanol glass. The authors assigned this absorption feature to the spin-forbidden $^3$MLCT transition with $\varepsilon \sim 600$ M$^{-1}$ cm$^{-1}$. The initial excited state species that is produced from the absorption of a photon is generally a singlet state, but because of the extremely fast ISC process that occurs in [Ru(bpy)$_3$]$^{2+}$, the singlet state lifetime is only $\leq 10$ ps$^{51}$ and all the singlet states ‘cross over’ to the triplet excited state.$^{53, 54}$ However, by using femtosecond fluorescence spectroscopic technology, Cannizzo et al. were able to determine the lifetime of fluorescence, which is 15 ± 10 fs at the emission $\lambda_{\text{max}}$ of 520 nm.$^{55}$ This indicates that the fluorescence in organometallic complexes is very hard to observe due to the present of strong SOC from the metal that generates the extremely fast ISC process. At room temperature, the triplet state $\lambda_{\text{max}}$ emission occurs at 626 nm with a lifetime of 0.9 µs and a quantum yield of 0.062 in argon-purged acetonitrile.$^{56}$ The
lifetime and Φ of the triplet state emission is temperature dependent; the higher the temperature, the lower the Φ and the shorter the lifetime. For example, the emission lifetime at 77 K was reported to be about 5 µs with a Φ of 0.40. A summary of the excited state decay of [Ru( bpy)₃]²⁺ at room temperature is shown in Figure 1.19.

![Figure 1.19: Proposed model of the excited state decay in [Ru(bpy)₃]²⁺ at room temperature.](image)

Tuning the emission colour, lifetime and Φ of [Ru(bpy)₃]²⁺ via modification of the ligands has been attempted over the past few decades. Unfortunately, ligand modification in [Ru(bpy)₃]²⁺ to tune the emission colour has proven relatively ineffective, and the emission wavelengths are limited to the orange-red spectral region. For example, changing the ligand bpy to 1,10-phenanthroline (phen) to form [Ru(phen)₃]²⁺ (Figure 1.20), which has higher degree of rigidity than the bpy framework, does not improve the Φ. At room temperature, the lifetime and Φ (in ethanol) of [Ru(phen)₃]²⁺ are 340 ns and 0.023, respectively, whereas the lifetime and Φ (in ethanol) of
[Ru(bpy)$_3$]$^{2+}$ are 870 ns and 0.075, respectively. The emission wavelength of [Ru(phen)$_3$]$^{2+}$ also shifted to higher energy (587 nm) compared to [Ru(bpy)$_3$]$^{2+}$.\textsuperscript{58}

![Structure of [Ru(phen)$_3$]$^{2+}$](image)

**Figure 1.20:** Structure of [Ru(phen)$_3$]$^{2+}$.

1.3.2 Tri(2-phenylpyridine) iridium, [Ir(ppy)$_3$]

Another remarkable luminescent organometallic, which has been extensively studied since the year 2000, is [Ir(ppy)$_3$] (Figure 1.21). Two isomers are found for [Ir(ppy)$_3$], the facial isomer, $fac$-[Ir(ppy)$_3$], (Figure 1.21.a) and meridional isomer, $mer$-[Ir(ppy)$_3$] (Figure 1.21.b). The photophysical properties of the $fac$-[Ir(ppy)$_3$] isomer were initially reported by Watts and co-workers\textsuperscript{10} in 1985 and were then applied in OLED devices by Baldo et al.\textsuperscript{11} in 2000.

![Cyclometallated Ir$^{(III)}$ complex](image)

**Figure 1.21:** Cyclometallated Ir$^{(III)}$ complex; (a) $fac$- and (b) $mer$-[Ir(ppy)$_3$].
[Ir(ppy)₃] and its derivatives are still the most promising materials for OLED technology because (i) they have high Φ for phosphorescence and relatively short phosphorescence lifetimes, (ii) they are thermally stable, and (iii) the emission colour can be tuned efficiently by changing the ligands.⁵⁹ Based on TD-DFT theoretical calculations (with B3LYP functional) from Hay in 2002, the HOMO of fac-[Ir(ppy)₃] consists of a mixture of phenyl-π from the ppy ligands and d-orbitals from the Ir centre, whereas the LUMO has contributions mainly from the pyridyl π-orbitals in the ppy ligand.⁶⁰ Similar to [Ru(bpy)₃]²⁺, fac-[Ir(ppy)₃] also shows MLCT character in the lowest energy excited state.¹⁰ Upon absorption of a photon, an electronic transition occurs from the 5d orbital on the Ir centre to the pyridyl π*-orbitals of the ppy ligand to form a singlet excited MLCT state. Then, with an extremely fast ISC rate that is promoted by the strong SOC from Ir, the initial singlet excited state converts to a triplet excited MLCT state within 100 fs.⁶¹ However, based on the results from femtosecond timescale experiments carried out by Hedley and co-workers, the authors claimed that the ISC timescale is actually < 100 fs. The diagram to illustrate the excited state timescale in fac-[Ir(ppy)₃] is shown in Figure 1.22.⁶²
Figure 1.22: Proposed model of the excited state processes that occur in \textit{fac-}\[\text{Ir(ppy)}_3\].\textsuperscript{52}

The non-radiative relaxation to the lowest vibrational level of the triplet excited state in \textit{fac-}\[\text{Ir(ppy)}_3\] is through an IC process known as intramolecular vibrational energy redistribution (IVR), which involves energy transfer from hot vibrational modes to the lower frequency modes.\textsuperscript{62} The authors found that about 86\% of the non-radiative relaxation within the sub-states is IVR with a timescale of 200 fs and the rest (14\%) is a vibrational cooling process such as transferring energy to the solvent molecules.\textsuperscript{62} At room temperature, the phosphorescence lifetime for \textit{fac-}\[\text{Ir(ppy)}_3\] in a degassed toluene solution is about 1.1 \(\mu\)s and \(\Phi_P = 0.73\) with \(\lambda_{\text{max}}\) (emission) occurring at 509 nm.\textsuperscript{63, 64} However, in air-saturated toluene solution, the phosphorescence lifetime is 23 ns and \(\Phi_P\) is only 0.01 to 0.02 at room temperature.\textsuperscript{64} This indicates that triplet oxygen quenching can significantly affect the phosphorescence efficiency of \textit{fac-}\[\text{Ir(ppy)}_3\].

Since the photophysical properties of \[\text{Ir(ppy)}_3\] have been extensively studied, many modifications to the ligand have been carried out in order to tune the emission colour as well as to improve the efficiency of phosphorescence. According to You and Park, the
phosphorescence efficiency of [Ir(ppy)$_3$] analogues can be improved by several approaches, which include: (i) isomer control, (ii) substituents on the ligands, (iii) rigidity control, (iv) de-stabilizing a thermal accessible non-emissive state.$^{59}$

As already mentioned, there are two isomers in the cyclometallated Ir$^{III}$ complex, namely fac-[Ir(ppy)$_3$] (Figure 1.21.a) and mer-[Ir(ppy)$_3$] (Figure 1.21.b). The mer-isomer can be synthesised at a lower temperature (about $<$150 °C) than the fac-isomer, which requires $>$200 °C.$^{59}$ Although the mer-isomer is easier to synthesise compared to the fac-isomer, the $\Phi_P$ of the mer-isomer is lower than that of the fac-isomer. This is because of the self-quenching which occurs in the excited state of the mer-isomer due to the bond dissociation in forming the fac-isomer, and the longer trans Ir-C bond length, which is caused by the strong trans-influence of the mutually trans C-bound ligands in the mer-isomer.

Many researchers have tuned the emission colour by introducing electron donating and electron withdrawing substituents on the ligands of [Ir(ppy)$_3$]. If an electron withdrawing group is located on the pyridyl ring of the ppy ligand (where the LUMO is located), the emission wavelength is shifted to lower energy because the electron withdrawing substituent stabilises the LUMO and reduces the HOMO-LUMO gap. This is why many Ir$^{III}$ complexes with electron withdrawing substituents on the pyridyl moiety are known to exhibit yellow, orange and red emission.$^{65-67}$ In contrast, blue-shifted emission is observed if an electron withdrawing substituent is introduced at the phenyl moiety of ppy (where the HOMO is located). The common example is replacing hydrogen (H) atoms by electron withdrawing fluorine (F) atoms on the phenyl ring of the ppy ligands.$^{64, 68-70}$
Ono et al. have used different degrees of rigidity in the phenylpyridine (ppy) ligand framework to enhance the phosphorescence efficiency of their Ir complexes (Figure 1.23). The carbazole substituted Ir complex (complex b) was found to have a higher $\Phi_P$ compared to the other two.\(^{71}\)

![Figure 1.23: Ir(III) complexes with different rigidity of the substituted ppy ligand.\(^{71}\)](image-url)

The Ir(ppy)$_3$ analogue complexes have a high energy MC $d \rightarrow d^*$ transitions,\(^{72}\) which are known as non-emissive transitions. However, because a blue emissive organometallic molecule requires a large energy gap between excited and ground states, the corresponding high-lying excited state can approach the MC $d \rightarrow d^*$ state. A non-radiative transition can result when the excited state energy transfers to the MC $d \rightarrow d^*$ transition state and hence reduces $\Phi$. Nazeeruddin et al. employed basic ligand field theory to tune the emission colours of [Ir(ppy)$_2$X$_2$]$^-$ salts, where $X = \text{CN}^-$, NCS$^-$ and NCO$^-$, to avoid the MC $d \rightarrow d^*$ transition.\(^{73}\) Based on the frontier molecular orbital (MO) diagram in Figure 1.24, the $t_{2g}$ orbitals in [Ir(ppy)$_2$(CN)$_2$]$^-$ complex were stabilised by the strong field ligand (CN$^-$), leading to a larger energy gap between the $t_{2g}$ orbital and the $\pi_{ppy}^*$ orbital without changing the energy level of the $\pi_{ppy}^*$ orbital. Consequently, the [Ir(ppy)$_2$(CN)$_2$]$^-$ complex gives a blue-shifted emission spectrum.
1.3.3 Luminescent rhodium complexes

The luminescent properties of rhodium (Rh) complexes also have received considerable attention. So far, three general classes of Rh complexes have been investigated for their luminescent properties: (i) amino complexes and substituted derivatives, (ii) multiply bridged dirhodium complexes, and (iii) polypyridine and related complexes. Similarly to Ru complexes, the photophysical properties of cyclometallated Rh complexes that contain pyridine ligands such as [Rh(bpy)$_3$]$^{3+}$ (Figure 1.25.a) and [Rh(phen)$_3$]$^{3+}$ (Figure 1.25.b) have been widely studied.
The photophysical behaviour of \([\text{Rh(bpy)}_3]^{3+}\) is very different from that of \([\text{Ru(bpy)}_3]^{2+}\). The various high intensity bands that are observed below 350 nm in the absorption spectrum of \([\text{Rh(bpy)}_3]^{3+}\) are generally assigned to the \(1\text{LC }\pi \rightarrow \pi^*\) transitions in the bpy ligands, and no MLCT transition band was found in the spectrum.\(^{75}\) At room temperature, \([\text{Rh(bpy)}_3]^{3+}\) is non-emissive in fluid solution. The emission from \([\text{Rh(bpy)}_3]^{3+}\) at 448 nm with a lifetime of 2.2 ms was only observed at low temperature (77 K) in a rigid glass. The long-lived millisecond lifetime suggests that the emission belongs to the \(3\text{LC }\pi \rightarrow \pi^*\) excited state.\(^{75-77}\) However, Yersin and co-workers\(^{75}\) found that there is little mixing of MC d \(\rightarrow\) d* character with the lowest triplet states, and this phenomenon is even more obvious in the \([\text{Pt(bpy)}_3]^{2+}\) case. In view of this, the authors claimed that \([\text{Pt(bpy)}_3]^{2+}\) is the intermediate situation in between \([\text{Ru(bpy)}_3]^{2+}\) and \([\text{Rh(bpy)}_3]^{3+}\), and a comparison of spectroscopic properties for the bpy ligand, \([\text{Rh(bpy)}_3]^{3+}\), \([\text{Pt(bpy)}_3]^{2+}\) and \([\text{Ru(bpy)}_3]^{2+}\) is shown in Table 1.2.\(^{75}\)
Table 1.2: Summary of the comparison of spectroscopic properties for bpy and its complexes.\textsuperscript{75}

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lowest triplet transition (cm\textsuperscript{-1})</th>
<th>Emission lifetime ((\mu)s)</th>
<th>Characterisation of the electronic transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>bpy</td>
<td>23504</td>
<td>4000000\textsuperscript{a}</td>
<td>(^3)LC ((\pi \rightarrow \pi^*))</td>
</tr>
<tr>
<td>[Rh(bpy)\textsubscript{3}]\textsuperscript{3+}</td>
<td>22757</td>
<td>2200\textsuperscript{b}</td>
<td>(^3)LC ((\pi \rightarrow \pi^<em>)) + small MC (d (\rightarrow) d</em>) contribution</td>
</tr>
<tr>
<td>[Pt(bpy)\textsubscript{3}]\textsuperscript{2+}</td>
<td>21237</td>
<td>50\textsuperscript{a}</td>
<td>(^3)LC ((\pi \rightarrow \pi^*)) + small MLCT contribution</td>
</tr>
<tr>
<td>[Ru(bpy)\textsubscript{3}]\textsuperscript{2+}</td>
<td>17684</td>
<td>5.0\textsuperscript{c}</td>
<td>(^3)MLCT (d (\rightarrow) (\pi^*))</td>
</tr>
</tbody>
</table>

\textsuperscript{a}At 1.3 K, data from reference 77.  
\textsuperscript{b}At 77 K, data from reference 76.  
\textsuperscript{c}At 77 K, data from reference 12.

On the other hand, the photophysical properties of [Rh(phen)\textsubscript{3}]\textsuperscript{3+} are similar to [Rh(bpy)\textsubscript{3}]\textsuperscript{3+}.\textsuperscript{78} The absorption bands in [Rh(phen)\textsubscript{3}]\textsuperscript{3+} are also assigned to the LC \(\pi \rightarrow \pi^*\) transition, and similarly, the emission band also belongs to the \(^3\)LC \(\pi \rightarrow \pi^*\) excited state.\textsuperscript{78, 79} Interestingly, the [Rh(phen)\textsubscript{3}]\textsuperscript{3+} complex is a typical example wherein the emission is similar to that of the free ligand in terms of energy and structure.\textsuperscript{78} However, the shorter lifetime of [Rh(phen)\textsubscript{3}]\textsuperscript{3+} (48 ms) compared to that of the free ligand (1.52 s) suggests that the Rh is involved in the transitions.\textsuperscript{78} A broad, structureless and weak emission, which is assigned to phosphorescence from the triplet MC d \(\rightarrow\) d* state, has been observed at about 578 nm in MeCN solution at room temperature. This proves that there is very little metal character in the lowest triplet states, which is similar to [Rh(bpy)\textsubscript{3}]\textsuperscript{3+}.\textsuperscript{76, 79, 80} On the other hand, Indelli et al. found that the efficiency of ISC to the \(^3\)LC \(\pi \rightarrow \pi^*\) state in [Rh(phen)\textsubscript{3}]\textsuperscript{3+} is 100%, even at room temperature.\textsuperscript{79}
Compared to \( \text{fac-[Ir(ppy)\textsubscript{3}]} \), reports on the photophysical properties of \( \text{fac-[Rh(ppy)\textsubscript{3}]} \) (Figure 1.26) are very limited. Only Colombo et al., in 1994, compared the photophysical properties of \( \text{fac-[Rh(ppy)\textsubscript{3}]} \) and \( \text{fac-[Ir(ppy)\textsubscript{3}]} \).\textsuperscript{81}

\[ \text{Figure 1.26: Structure of \text{fac-[Rh(ppy)\textsubscript{3}].} } \]

The absorption spectra of \( \text{fac-[Ir(ppy)\textsubscript{3}]} \) and \( \text{fac-[Rh(ppy)\textsubscript{3}]} \) are nearly identical. The only difference found is a weak broad band in the \( \text{fac-[Ir(ppy)\textsubscript{3}]} \) spectrum at about 454 nm which corresponds to the spin-forbidden triplet excited state MLCT transition. The reason why this band is observed in the \( \text{fac-[Ir(ppy)\textsubscript{3}]} \) but not in the \( \text{fac-[Rh(ppy)\textsubscript{3}]} \) absorption spectrum is because the SOC constant of Ir (SOC for Ir = 3909 cm\textsuperscript{-1}) is larger than that of Rh (SOC for Rh = 1259 cm\textsuperscript{-1}). The larger the SOC constant, the more intense the corresponding \( ^3\text{MLCT} \) bands are. The other two high intensity bands in the higher energy region belong to the spin-allowed \( ^1\text{LC} \pi \rightarrow \pi^* \) transition from the ppy ligands and the \( ^1\text{MLCT} \text{d} \rightarrow \pi^* \) transition, respectively.\textsuperscript{81}

The emission spectra of \( \text{fac-[Ir(ppy)\textsubscript{3}]} \) and \( \text{fac-[Rh(ppy)\textsubscript{3}]} \) are different. At room temperature, \( \text{fac-[Rh(ppy)\textsubscript{3}]} \) shows a structured emission band, with the structure becoming finer as the temperature is lowered to 9 K, whereas, the \( \text{fac-[Ir(ppy)\textsubscript{3}]} \) emission spectrum consists of a broad, asymmetric band at room temperature. The structured
emission band in \( \text{fac-[Rh(ppy)₃]} \) is assigned to the triplet \( \pi \rightarrow \pi^* \) transition. The emission lifetime of \( \text{fac-[Rh(ppy)₃]} \) at 77 K was determined to be 45 \( \mu \)s, which was considered a short-lived emission for a triplet \( \pi \rightarrow \pi^* \) transition of a \( \text{Rh}^{3+} \) complex. This is due to the fact that there is considerable mixing of MLCT character into the transition.\(^{81}\)

1.4 Photophysical properties of main group heterocycle analogues, EC₄

[\text{Ru(bpy)₃}^{2+}] and [\text{Ir(ppy)₃}] have a metallacyclopentadiene motif (Figure 1.27). Metallacyclopentadienes consist of a five-membered ring system containing a metal atom, for example, in Figure 1.27, (a) metal 2,2’-biphenyl complex,\(^{82}\) (b) metal bipyridine complex e.g. [\text{Ru(bpy)₃}]^{2+},\(^{12}\) (c) metal 2-phenylpyridine complex e.g. [\text{Ir(ppy)₃}],\(^{11}\) and (d) metal diimine complex.\(^{83,84}\) Among the metallacyclopentadienes in Figure 1.27, the photophysical properties of those with bipyridine ligands have been extensively studied over last few decades. However, complexes of type e, which are structurally-related to the rhodacyclopentadienes that we synthesised in this work, are the best known as an intermediate in metal catalysed [2+2+2] cycloaddition (or cyclotrimerisation) reactions of alkynes, but there are no comprehensive reports on their photophysical properties.
Interestingly, the photophysical properties of the main group heterocyclic analogues (EC₄, E = Si, P and S), which are structurally-related to e-type complexes in Figure 1.27 have been widely investigated. Therefore, due to the structural similarity of EC₄ to rhodacyclopentadienes (RhC₄), the synthesis and photophysical properties of siloles (Figure 1.28.a), phospholes (Figure 1.28.b) and thiophenes (Figure 1.28.c) are discussed in this section.

1.4.1 Siloles

The synthetic methodology for preparing siloles (1-silacyclopentadienes) was first reported in 1959.⁸⁵⁻⁸⁷ As shown in Figure 1.29, siloles possess low-lying LUMO levels, which have contributions from the σ* orbital of the SiR₂ moiety as well as the π* orbital from the butadiene moiety, forming a σ*-π* conjugation interaction.⁸⁶⁻⁸⁸ The orbital
interaction between silicon and butadiene occurs effectively because of the fixed perpendicular arrangement of the plane of the SiR₂ moiety to the plane of butadiene moiety.\textsuperscript{89}

![Frontier orbital diagram of silole](image)

**Figure 1.29:** Frontier orbital diagram of silole.\textsuperscript{88}

A series of blue silole emitters are shown in **Figure 1.30** and were reported by Tang et al. in 2001.\textsuperscript{90} All of the siloles shown in **Figure 1.30** exhibit two absorption bands at about 250 and 360 nm, which are assigned to the \( \pi \rightarrow \pi^* \) transition of the phenyl groups and the silacyclopentadiene ring, respectively. Changing the methyl group to a phenyl group at the R and R’ substituents on the silicon atom can slightly shift the absorption \( \lambda_{\text{max}} \) value to lower energy. In other words, the electronic properties on the siloles can be tuned by the electronegativity of the R and R’ substituents on the silicon atom. This result is consistent with the findings of Tamao et al., who noted that the more electronegative the R and R’ substituents are, the lower the energy of the absorption maxima is.\textsuperscript{91}
The siloles in Figure 1.30 show only one peak in their emission spectra. Similar to the absorption, a red-shift is observed in the emission if methyl is changed to phenyl at the R and R’ substituents. The methyl-substituted compound (Figure 1.30.a) emits at about 470 nm, whereas the phenyl one (Figure 1.30.d) shows a 35 nm red-shift and emits at about 505 nm.\(^{\text{90}}\)

In 2004, Pagenkopf et al.\(^{\text{92}}\) reported a series of donor-acceptor \(\pi\)-conjugated siloles (Figure 1.31) by adapting the synthetic methodology from Tamao and co-workers.\(^{\text{88, 89, 93}}\) Pagenkopf et al. found that by increasing the degree of electron delocalisation between the donor (D) and acceptor (A), the absorption \(\lambda_{\text{max}}\) can shift from 429 nm for the parent silole (D & A = H) to 496 nm for the most polar silole (D = -NMe_2; A = -NO_2). In fact, they also found that the consequences of varying the D and A groups are also observed in the photoluminescence spectra. Interestingly, the silole with D = OMe and A = NO_2 was the one to display the lowest energy emission wavelength at 649 nm rather than the most polar one.\(^{\text{92}}\)
1.4.2 Phospholes

The synthetic methodology for preparing phospholes was also reported in the same year as siloles.\textsuperscript{94} Due to the fact that phospholes are not aromatic,\textsuperscript{87} they promote delocalisation of the endocyclic $\pi$-system along the conjugated chain. At the same time, the phosphorus atom becomes versatile in terms of its reactivity. Calculations at the HF/6-31 + G*/B3LYP/6-31 + G* level show that the LUMO energy level of the parent phosphole is very close to that of the silole (LUMO: silole, 1.39 eV; phosphole, 1.50 eV), which is known as a highly electron-deficient heterocycle.\textsuperscript{95} In other words, the interaction between the $\pi^*$ orbitals from the butadiene moiety and the low-lying $\sigma^*$ orbital from the P-R moiety in the phosphole are very similar to those of the silole as shown in Figure 1.29.

The absorption $\lambda_{\text{max}}$ of a phosphole is dependent on the hydrogen bond donor ability (HBDA) of the solvent to the lone pair of electrons on the phosphorus atom.\textsuperscript{95} The absorption and emission $\lambda_{\text{max}}$ values of a phosphole recorded in different solvents are shown in Table 1.3. The HBDA influence on the emission $\lambda_{\text{max}}$ is negligible. In the
absorption spectra, there is a bathochromic shift upon increasing the HBDA of the solvent.\textsuperscript{95} For this reason, absorption and emission spectra of the phospholes should be recorded in the non-hydrogen-bonding solvent, THF.

Table 1.3: Influence of the solvent on the absorption and emission $\lambda_{\text{max}}$ of phosphole.\textsuperscript{95}

<table>
<thead>
<tr>
<th>Solvents</th>
<th>$\lambda_{\text{max}}$ ABS</th>
<th>$\lambda_{\text{max}}$ EM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahydrofuran (THF)</td>
<td>390</td>
<td>463</td>
</tr>
<tr>
<td>Dichloromethane (DCM)</td>
<td>374</td>
<td>463</td>
</tr>
<tr>
<td>Chloroform (CHCl$_3$)</td>
<td>372</td>
<td>463</td>
</tr>
<tr>
<td>Ethanol (EtOH)</td>
<td>364</td>
<td>466</td>
</tr>
</tbody>
</table>

Similarly to siloles, the band in the phosphole’s absorption spectrum is attributed to the $\pi \rightarrow \pi^*$ transition, which is due to the extended $\pi$-conjugated system of the phosphole. The $\lambda_{\text{max}}$ value of the absorption and emission are greatly influenced by the 2,5-substituents of the phosphole ring. For example, replacing the phenyl groups (Figure 1.32.a) with either 2-pyridyl (Figure 1.32.b) or 2-thienyl (Figure 1.32.c) rings shifts the absorption $\lambda_{\text{max}}$ from 354 nm to 390 and 412 nm, respectively.\textsuperscript{87} This is due to the charge transfer from the 2-thienyl or 2-pyridyl substituents to the highly electron-deficient heterocycle ring of the phosphole. Calculations (Table 1.4) indicate that the 2-thienyl substituent stabilises the LUMO but also destabilises the HOMO; as a result, the HOMO-
LUMO gap decreases causing a red-shift in its absorption spectrum compared to the 2,5-diphenyl analogue.\textsuperscript{95}

![Figure 1.32: The structures of (a) 2,5-diphenylphosphole, (b) 2,5-di-2-pyridylphosphole, and (c) 2,5-di-2-thienylphosphole.](image)

Table 1.4: Calculated energy levels (eV) of the HOMO and LUMO of phospholes at the HF/6-31 + G*/B3LYP/6-31 + G* level.\textsuperscript{95}

<table>
<thead>
<tr>
<th></th>
<th>R = phenyl</th>
<th>R = 2-pyridyl</th>
<th>R = 2-thienyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>LUMO</td>
<td>1.24</td>
<td>0.97</td>
<td>0.96</td>
</tr>
<tr>
<td>HOMO</td>
<td>-7.36</td>
<td>-7.49</td>
<td>-7.17</td>
</tr>
<tr>
<td>HOMO-LUMO gap</td>
<td>8.60</td>
<td>8.46</td>
<td>8.13</td>
</tr>
</tbody>
</table>

Réau and co-workers also studied the effect of a combination of thienyl and pyridyl substituents on the absorption and emission spectra of a phosphole (Figure 1.33). It was found that both the absorption and emission shifted to lower energy ($\lambda_{\text{max}}$: ABS, 427 nm; EM, 570 nm) compared to either thienyl ($\lambda_{\text{max}}$: ABS, 412 nm; EM, 501 nm) or pyridyl ($\lambda_{\text{max}}$: ABS, 390 nm; EM, 463 nm) individual substituents.\textsuperscript{96}
The Réau group prepared a series of polarised $P^{\delta^+}=Y^{\delta^-}$ phospholes ($Y = \text{Se}, \text{S}, \text{and O}$) in order to observe the effect on the photophysical properties of phospholes (Figure 1.34). Synthetically, 2,5-bis(2-thienyl)phosphole was treated with selenium, sulfur and bis(trimethylsilyl)peroxide, respectively, to give polarised $P^{\delta^+}=Y^{\delta^-}$ phospholes in very high yields (> 90%). For the $Y = \text{Se}, \text{S}$ and $\text{O}$ derivatives, a bathochromic shift of $\lambda_{\text{max}}$ ABS $= 11 - 22$ nm, and $\lambda_{\text{max}}$ EM $= 46 - 55$ nm was observed with respect to the 2,5-bis(2-thienyl)phosphole.\textsuperscript{96} Increasing the electronegativity of $Y$ leads to an increase in the bathochromic shift.

Very recently, the synthesis and photophysical properties of a series of 2,5-bis($p$-X-arylethynyl)phospholes, where $X = \text{H}$ (a), NO$_2$ (b) and NMe$_2$ (c) in Figure 1.35, have been reported by Matano et al.\textsuperscript{97} The $\lambda_{\text{max}}$ value of both absorption and emission were bathochromically shifted to lower energy from $X = \text{NO}_2$ to NMe$_2$, because the NMe$_2$
substituent has a greater effect on the π-conjugative push-pull interaction when compared to the NO₂ substituent. The absorption maxima are assigned to the $\pi \rightarrow \pi^*$ transition of the π-conjugated system of the 2,5-bis(p-X-arylethynyl)phospholes. The $\lambda_{\text{max}}$ values for fluorescence were found at 449 nm for $X = \text{H}$, 499 nm for $X = \text{NO}_2$ and 518 nm for $X = \text{NMe}_2$, with $\Phi_f$ of 0.10, 0.09 and 0.13, respectively.

\[ R_3\text{Si} \quad 1) \text{Ti(OPr)}_2 \text{Cl} \quad 2) \text{Pd} \quad 3) \text{PhPCl}_2 \]

1) Ti(OPr)$_2$Cl, 2) Pd, 3) PhPCl$_2$

\[ \text{CuI, Et}_3\text{N, nBu}_3\text{NF} \]

THF, R.T., 4-12 h

Figure 1.35: Synthetic route to 2,5-bis(p-X-arylethynyl)phospholes.\textsuperscript{97}

1.4.3 Thiophenes

As a π-conjugated system, thiophenes show interesting electronic and luminescent properties.\textsuperscript{98-101} In 2007, Marder et al.\textsuperscript{101} reported the photophysical properties of a series of 2,5-bis(phenylethynyl)thiophenes (BPETs) (Figure 1.36). Compounds with substituents at the para-position of the phenyl ring ranging from the strong electron withdrawing group, NO$_2$, to the strong electron donating group, NMe$_2$, were prepared in good yields using standard Sonogashira coupling reactions.
Both electron withdrawing and electron donating substituents at the \textit{para}-position of the phenyl ring cause a bathochromic shift compared to the parent (R = H) compound. The greatest red-shift was observed with the strongest electron withdrawing and electron donating substituents in the series, from 350 nm for the parent to 386 nm (R = NMe$_2$) and 387 nm (R = NO$_2$) in the absorption spectra, and from 382 nm for the parent to 434 nm (R = NMe$_2$) and 435 nm (R = NO$_2$) in the emission spectra. The reason for this is due to the fact that electron donating groups raise the HOMO more than the LUMO, while electron withdrawing groups stabilise the LUMO more than the HOMO and, as a result, both significantly reduce the HOMO-LUMO gap. Lower emission quantum yields of BPETs were observed compared to the 1,4-bis(arylethynyl)benzene (BPEB) and 9,10-bis(arylethynyl)anthracene (BPEA) analogues, because the excited singlet state in BPETs undergoes relatively rapid ISC to the non-emissive (at room temperature) triplet excited state, T$_1$. The presence of sulfur as the heteroatom in the BPETs is believed to facilitate the ISC.

\textbf{Figure 1.36:} Synthesis of BPETs.$^{101}$
1.5 Rhodacyclopentadienes: the chemistry and photophysical properties

The main group heterocycles (EC₄) are able to exhibit interesting luminescent properties with the \( \pi \rightarrow \pi^* \) transitions. Similar to those transition metal analogues such as \([\text{Ir}(ppy)_3]\), their emission colours can also be tuned either by attaching a different ligand at the centre atom (E) or using different electron withdrawing and electron donating substituents at the \textit{para}-position of the phenyl rings. However, unlike the transition metal analogues, the EC₄ analogues could not phosphorescence because the E atom does not offer a highly efficiency SOC like the 2\textsuperscript{nd} and 3\textsuperscript{rd} row transition metals do. Therefore, it is very interesting to investigate the photophysical properties of the e-type metallacyclopentadiene in Figure 1.27, which is structurally-related to the EC₄ analogues. So far until now, only one publication was found to report briefly about the luminescent properties of the e-type metallacyclopentadiene called rhodacyclopentadiene from Marder and Rourke et al.\textsuperscript{102}

The first rhodacyclopentadiene was reported by Mague and Wilkinson in 1968 when they synthesised \([\text{RhCl(SbPh}_3)_2\text{C}_4\text{(CF}_3)_4]\) by reaction of \([\text{RhCl(SbPh}_3)_3]\) with two equivalents of \text{CF}_3-\equiv\text{C-}\text{CF}_3 (Figure 1.37). The rhodacyclopentadiene’s identity was then confirmed by X-ray crystallography a year later.\textsuperscript{103, 104}

![Figure 1.37: Synthesis of the five coordinate rhodacyclopentadiene complex, \([\text{RhCl(SbPh}_3)_2\text{C}_4\text{(CF}_3)_4]\).\textsuperscript{103, 104}](image-url)
Two years later, Mague reported a rhodacyclopentadiene complex (Figure 1.38).[^105] [RhCl(CO)(AsMe₃)₂] reacted CF₃-C≡C-CF₃ to give an initial complex, [RhCl(CO)(AsMe₃)₂C₄(CF₃)₄], then, the CO group was removed in refluxing wet benzene to form [RhCl(H₂O)(AsMe₃)₂C₄(CF₃)₄]. The structure of the product was confirmed by X-ray crystallography in 1973.[^106] Mague noted that the C₂-C₃ bond length is significantly longer than C₁-C₂ and C₃-C₄ bond lengths in the heterocycle ring, resembling a cis-1,3-butadienylene moiety.[^105][^106]

![Figure 1.38: Preparation of an octahedral rhodacyclopentadiene with a coordinated water molecule.][^105]

In 1972, Müller and co-workers reacted [RhCl(PPh₃)₃] with 2,2’-bis(arylethynyl)biphenyl to form a rhodacyclopentadiene complex (Figure 1.39.a) and a valence isomeric cyclobutadienylrhodium complex (Figure 1.39.b).[^107] Then, adding one equivalent of alkyne to the rhodacyclopentadiene complex led to the formation of a triphenylene derivative (Figure 1.39.c).[^107]
Figure 1.39: Reaction of $[\text{RhClL}_3]$ with a di-alkyne compound to form rhodacyclopentadiene and cyclobutadienylrhodium complexes.$^{107}$

In 2001, Marder and Rourke et al.$^{102}$ developed a high yield, one-pot, regiospecific synthesis of a luminescent rhodacyclopentadiene from two equivalents of 1,4-bis($p$-tolyl)buta-1,3-diyne with $[\text{Rh}(\text{C}≡\text{C-SiMe}_3)(\text{PMe}_3)_4]$. The chemistry of rhodacyclopentadienes in the Marder group was developed further when Ward$^{108}$ synthesised a series of six-coordinate rhodacyclopentadienes with different $\sigma$-donor ligands attached to the rhodium centre; the synthesis with $\text{Me}_2\text{SiC}≡\text{C}$- (TMSE) as the $\sigma$-donor ligand is shown in Figure 1.40.
Figure 1.40: The synthesis of rhodacyclopentadiene complexes with TMSE- as the \( \sigma \)-donor ligand.\textsuperscript{108}

All of the rhodacyclopentadienes in Figure 1.40 have been characterised using spectroscopic techniques and several structures have been confirmed by X-ray crystallography. Besides Ward, van Leeuwen\textsuperscript{109} in the Marder group also synthesised a series of rhodacyclopentadienes with 4-[4-(\( N,N \)-di-\( n \)-hexylamino)phenylethynyl]phenylethynyl- (-C\( \equiv \)C-C\(_6\)H\(_4\)-C\( \equiv \)C-C\(_6\)H\(_4\)-p-NHex\(_2\)) as the alkynyl ligand in order to investigate the effect of a long conjugated carbon chain on the photophysical properties of rhodacyclopentadienes.

The mechanism of rhodacyclopentadiene formation was also studied by Ward.\textsuperscript{108} He found that the intermediate \( \pi \)-complexes formed very quickly when one equivalent of diarylbutadiyne was added to the [RhMe(PMe\(_3\)]\(_4\)] in THF. The formation of the intermediate \( \pi \)-complex is represented in Step 1 – 3 in Figure 1.41.
In order to form the metallacycle ring, one equivalent of PMe$_3$ must dissociate from the intermediate π-complex before it can bind the second butadiyne (Step 4) and form a bis(π-complex) (Step 5). The bis(π-complex) then undergoes a reductive coupling (Step 6) to form a five-membered metallacycle ring. The remaining vacant site at the rhodium centre is then filled by the PMe$_3$ which dissociated in Step 4, giving the six-coordinate rhodacyclopentadiene. Step 2 and 4 are reversible processes, where the concentration of PMe$_3$ is the key to facilitate the reaction to move forward. Therefore, removal of PMe$_3$ during the reaction is necessary.
1.5.1 The photophysical properties

The photophysical properties of the rhodacyclopentadienes have also been studied by Ward\textsuperscript{108} and van Leeuvan.\textsuperscript{109} Photophysical data of the TMSE-rhodacyclopentadienes are listed in Table 1.5, and their absorption and emission spectra are shown in Figure 1.42.

**Table 1.5:** Summary of photophysical data for the TMSE-2,5-bis(p-R-arylethynyl)-rhodacyclopentadienes (see Figure 1.40) in toluene solution at room temperature.\textsuperscript{108}

<table>
<thead>
<tr>
<th>R group</th>
<th>$\lambda_{\text{max}}$ ABS (nm)</th>
<th>$\varepsilon$ (mol$^{-1}$cm$^{-1}$dm$^3$)</th>
<th>$\lambda_{\text{max}}$ EM (nm)</th>
<th>Stokes shift (cm$^{-1}$)</th>
<th>$\Phi$</th>
<th>$\tau$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>453</td>
<td>26000</td>
<td>496</td>
<td>1910</td>
<td>0.15</td>
<td>0.87</td>
</tr>
<tr>
<td>SMe</td>
<td>468</td>
<td>35000</td>
<td>515</td>
<td>1950</td>
<td>0.10</td>
<td>0.71</td>
</tr>
<tr>
<td>CO$_2$Me</td>
<td>485</td>
<td>21000</td>
<td>536</td>
<td>1960</td>
<td>0.16</td>
<td>0.98</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>517</td>
<td>22000</td>
<td>590</td>
<td>2390</td>
<td>0.18</td>
<td>1.21</td>
</tr>
</tbody>
</table>

The bathochromic shift of $\lambda_{\text{max}}$ for both absorption and emission are dependent on the electron withdrawing and electron donating substituents at the para-position of the phenyl ring. However, electron withdrawing substituents have a greater effect on the bathochromic shift than electron donating substituents. The stronger the electron-withdrawing group, the greater the bathochromic shift.\textsuperscript{108}
Comparing the emission lifetimes of the rhodacyclopentadienes to the lifetimes of [Ru(bpy)$_3$]$_{2}^{2+}$, [Ir(ppy)$_3$] and [Rh(bpy)$_3$]$_{3}^{3+}$ analogues, we note that the rhodacyclopentadienes have the shortest lifetimes. The single decay component lifetimes in the nanosecond range indicate that the emissions occur purely from the singlet excited state. Fluorescence is rarely observed in organometallics with 4d/5d transition metal centres, because the singlet excited states are too short-lived, due to the strong SOC of the metal that can facilitate ISC to form the triplet excited states. As mentioned in section...
1.3.1, the singlet lifetime of $[\text{Ru(bpy)}_3]^{2+}$ is only $\leq 10 \text{ ps}$, but the singlet lifetimes of rhodacyclopentadienes are on the nanosecond timescale, which is a long-lived singlet emission lifetime and absolutely unexpected for organometallic complexes. Indeed, these unusual results for the rhodacyclopentadienes have become a driving force for this project to investigate further their photophysical behaviour.
1.6 Objectives

The main objective of this project was to explore as well as to understand the photophysical behaviour of the rhodacyclopentadienes. Many photophysical experiments such as time-resolved infrared (TRIR) measurements were carried out in order to understand the structure-properties relationship of the rhodacyclopentadienes.

This project also aimed to develop synthetic methodology for the preparation of novel rhodacyclopentadienes. For example, we have developed new synthetic methodology for the preparation of η²-benzoato- (Figure 1.43.a) and acetylacetonato- (acac-) (Figure 1.43.b) rhodacyclopentadienes. The reason for using η²-benzoato- and acac- ligands is to increase the Rh participation in the excited state by destabilising the Rh d-orbitals since the η²-benzoato- and acac- ligands are strong σ- and π- donors. These two series of rhodacyclopentadienes have been spectroscopically characterised and their photophysical data were collected and discussed in detail in Chapter 3.

Figure 1.43: Rhodacyclopentadienes with (a) η²-benzoato-, and (b) acac- ligands.
References:


Chapter 2

The synthesis and characterisation of butadiynes and 1,3,9,11-dodecatraynes
2.1 Introduction

2.1.1 Introduction to butadiynes

Butadiynes and 1,3,9,11-dodecatetraynes served as the important starting materials for the synthesis of the rhodacyclopentadienes (Figure 1.40 and 1.41). Therefore, this chapter will discuss the chemistry, syntheses and characterisations of the butadiynes and novel 1,3,9,11-dodecatetraynes.

Butadiynes contain the -C≡C-C≡- moiety and they are present in a variety of natural products. Many of these have been studied with regard to their biological activities.\(^1,2\) For example, the butadiyne-containing natural products shown in Figure 2.1 have been examined with regard to their anti-bacterial activities (Figure 2.1.a and Figure 2.1.b) by Gibbons et al. in 2004,\(^3,4\) and their anti-cancer properties (Figure 2.1.c) by Kim and co-workers in 1989.\(^2\)

![Figure 2.1: Butadiyne containing natural products.\(^2-4\)](image)

In addition, butadiyne derivatives can be highly toxic. For example, cicutoxin, which is shown in Figure 2.2, is a highly poisonous butadiyne that can be found in water hemlock
(Cicuta virosa). Cicutoxin can cause nausea, emesis and abdominal pain in humans and subsequently lead to death.  

**Figure 2.2:** Cicutoxin.  

Several researchers are also interested in the electronic properties, liquid crystal phase behaviour\textsuperscript{6-8} and non-linear optical properties\textsuperscript{9-11} of rigid-rod conjugated butadiynes. However, information in the literature regarding the photophysical properties of butadiynes remains rare. In 2003, Kang and co-workers reported the luminescent properties of a butadiyne, which is shown in **Figure 2.3.a.\textsuperscript{12}** Its absorption $\lambda_{\text{max}}$ value is 356 nm, which is attributed to the $\pi \rightarrow \pi^*$ transition, whereas its emission $\lambda_{\text{max}}$ value is 405 nm, with a fluorescence quantum yield of 0.31 at room temperature. Interestingly, a weak phosphorescent emission ($\lambda_{\text{max}} = 561$ nm) was also observed at 77 K with a lifetime of 550 $\mu$s. On the other hand, the authors also reported the luminescence properties of the tolan-based compound for comparison purposes (**Figure 2.3.b**). They found that increasing the number of C\equiv C bonds in the structure causes a red-shift of the $\lambda_{\text{max}}$ values in both absorption and emission.  

**Figure 2.3:** Luminescent $\pi$-conjugated organic compounds.  

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Ward investigated the photophysical properties of some 1,4-bis(p-R-phenyl)-1,3-butadiynes (Figure 2.4) in his Ph.D. studies. His findings were consistent with Kang et al., in which both absorption and emission $\lambda_{\text{max}}$ values of extended, conjugated butadiynes where $R = 3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3\text{C}≡\text{C}$ (Figure 2.4.a) and 4-($n$-Hex)$_2\text{N-C}_6\text{H}_4\text{C}≡\text{C}$ (Figure 2.4.b) are shifted to lower energy compared to their shorter analogues. In addition, Ward also found that the extended conjugated butadiynes have higher quantum yields than their shorter analogues. 

![Figure 2.4: π-conjugated butadiynes synthesised by Ward.](image)

2.1.2 Coupling chemistry in butadiyne synthesis

Oxidative homo-couplings of terminal alkynes have been known since 1869, when Glaser homo-coupled two equivalents of phenylacetylene to produce a butadiyne in the presence of EtOH, NH$_4$OH, CuCl and oxygen (Figure 2.5).
Since that time, this coupling chemistry has been extensively developed due to its ability to form a new carbon-carbon bond by the coupling of two sp-hybridised carbons. In 1959, Eglinton and Galbraith reported an oxidative homo-coupling reaction using Cu(II) as the oxidising agent to produce butadiynes in the presence of water and oxygen. The reaction worked well with water-soluble ethynyl compounds such as HC≡CMe₂OH, but for water-insoluble compounds, the reactions were very slow and required excess Cu(II). Then, in 1962, Hay found that most Cu(II) salts (except Cu(II) carboxylates) are ineffective in the coupling reactions. Indeed, Hay noticed that Cu(I) salts can perform much better than Cu(II) salts, and he suggested that the use of CuCl and the bidentate amine ligand, \( N,N,N',N' \)-tetramethylethylenediamine, is best for homo-coupling compared to the other two conditions [(i) Cu(OAc)₂ + pyridine and (ii) CuCl + pyridine] in his study.

Catalytic systems based on palladium and copper have been developed, which can help to complete the reaction in a shorter time. For example, Liu and Burton reported the synthesis of symmetrical butadiynes via oxidative homo-coupling of two alkynes with iodine as the oxidising agent in the presence of \([\text{PdCl}_2(\text{PPh}_3)_2]\) (1.3 mol%) and CuI (5 mol%) in diisopropyl amine, obtaining good to excellent yields of the products.

Haley and co-workers studied the catalytic function of Cu(II), Cu(I) and Pd complexes with mono- and bidentate phosphine ligands in the ring closure of 14- and 15-membered ring containing dehydrobenzoannulenes (DBAs) (Figure 2.6). The authors found that the
yield of 14-membered ring DBA was better using Pd and CuI co-catalysts rather than Cu catalysts, whereas 15-membered gave the opposite result. This is because the smaller ring compound is formed via the cis-Pd-bis(acetylide) intermediate (Pathway I, Figure 2.6), whereas the larger ring is formed via a dimeric Cu(I) acetylide intermediate (Pathway II, Figure 2.6).

<table>
<thead>
<tr>
<th>A yield %</th>
<th>Catalyst</th>
<th>B yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>Cu(OAc)$_2$</td>
<td>80</td>
</tr>
<tr>
<td>35</td>
<td>CuCl</td>
<td>76</td>
</tr>
<tr>
<td>67</td>
<td>[(PPh$_3$)$_2$PdCl$_2$], CuI</td>
<td>24</td>
</tr>
<tr>
<td>76</td>
<td>[(dppe)PdCl$_2$], CuI</td>
<td>12</td>
</tr>
</tbody>
</table>

**Figure 2.6:** Comparison of Cu and Pd catalysts in the ring closure of DBAs.\(^{19}\)
In the development of cross-coupling reactions, Cadiot and Chodkiewicz cross-coupled a haloalkyne with terminal alkyne to produce an unsymmetrical butadiyne in the presence of Cu(I) in a basic solution (e.g. aqueous $n$-butylamine). Reducing agents such as hydroxylamine hydrochloride were added to the reaction to prevent the Cu(I) being oxidised to Cu(II). The chemistry of the Cadiot-Chodkiewicz coupling can be represented by the two equations below:

\[
\text{RC}≡\text{CH} + \text{Cu}^+ \rightarrow \text{RC}≡\text{C-Cu} + \text{H}^+ \text{(fast)} \quad (1)
\]

\[
\text{RC}≡\text{C-Cu} + \text{XC}≡\text{CR'} \rightarrow \text{RC}≡\text{C-C≡CR'} + \text{CuX} \quad (2)
\]

where $X = \text{Br}; \ R, R' = \text{aryl, allyl}$

The nature of the R group in the ethynyl compounds can directly affect the product yields from the reaction. For example, terminal alkynes that bear electron withdrawing groups give higher yields than those with electron donating groups, because the ethynyl hydrogen is more acidic for electron withdrawing groups than electron donating groups. As a result, the reaction in Eq. 1 is faster in the electron withdrawing group case. Unlike the R group in the terminal alkynes, the R’ group in the haloalkyne only has a small effect on the reaction. This is due to the fact that the halogen (normally Br) in the haloalkyne is highly reactive towards the Cu(I) acetylide (Eq. 2). In addition, Eglinton and McCrae also recommended that bromoalkynes are the best choice compared to the other haloalkynes. They stated that chloroalkynes are not reactive, while, iodoalkynes are excessively reactive.
In order to reduce the possibility of homo-coupling occurring in the reaction, it is important to maintain the reaction under the following conditions: (i) \( \text{Cu}^+ \) must be kept in low concentration (ca. 1 - 2 mol%), because \( \text{Cu}^+ \) can also homo-couple haloalkynes to produce a symmetrical butadiyne as shown in Eq. 3; (ii) the bromoalkyne needs to be added to the reaction slowly; (iii) a reducing agent must be used; and (iv) the reaction must be kept free of oxidants such as oxygen.

\[
2R'C=\text{CBr} + 2\text{Cu}^+ \rightarrow R'C=\text{C}=\text{C}R' + 2\text{Br}^- + 2\text{Cu}^{2+} \quad (3)
\]

### 2.1.3 Palladium (Pd) catalysed cross-coupling reactions

The use of Pd as a catalyst is one of the most remarkable developments in C-C coupling chemistry. In general, most of the Pd-catalysed cross-coupling reactions can be represented by the equation shown in **Figure 2.7**:

\[
\begin{array}{c}
\text{R}^1\text{-M} + \text{R}^2\text{-X} \\
\xrightarrow{\text{cat. PdL}_n\text{ additive}\text{ solvent}} \\
\text{R}^1\text{-R}^2 + \text{M}\text{-X}
\end{array}
\]

\( \text{cat.} = \text{catalyst} \quad \text{R}^2 = \text{aryl, alkyl, vinyl} \)
\( \text{L} = \text{ligand, e.g. PPh}_3 \quad \text{X} = \text{halide, e.g. Br and I} \)
\( \text{R}^1 = \text{aryl, alkyl, vinyl} \quad \text{M} = \text{B, Zn, Sn} \)

**Figure 2.7:** General equation for Pd-catalysed cross-coupling reactions.$^{22}$

The ‘M’ in **Figure 2.7** can be various elements, the most well known being B, Zn and Sn, as reported by Suzuki-Miyaura,$^{23-26}$ Negishi,$^{25, 27, 28}$ and Stille,$^{29, 30}$ respectively.

The general catalytic cycle for Pd-catalysed cross-coupling is shown in **Figure 2.8**. It involves three major steps, namely oxidative addition, transmetallation and reductive
elimination. Oxidative addition involves the reaction of \( R^2-X \) with the Pd metal centre to form an \( R^2-Pd-X \) species, in which the oxidation state of Pd increases from 0 to +2. Transmetallation is a step in which two metals exchange their ligands. In a cross-coupling reaction, \( R^1-M \) exchanges its \( R^1 \) group with the X ligand from \( R^2-Pd-X \) to form \( R^2-Pd-R^1 \) and CuX. Lastly, in the reductive elimination step, \( R^2-Pd-R^1 \) eliminates \( R^1-R^2 \) as the cross-coupling product, with the Pd returning to the 0 oxidation state and then being available to repeat the catalytic cycle.

![Diagram of the catalytic cycle](image)

**Figure 2.8:** General catalytic cycle for Pd-catalysed reaction.

### 2.1.3.1 Sonogashira cross-coupling reaction

The Pd/Cu based catalytic system in cross-coupling chemistry was initiated by Sonogashira and co-workers,\(^{31}\) who used \([\text{PdCl}_2(\text{PPh}_3)_2]\), CuI and \( \text{Et}_3\text{N} \) to synthesise alkynyl-arenes. The main difference between Sonogashira cross-coupling and other cross-coupling reactions (e.g. Suzuki-Miyaura coupling and Stille coupling) is that the
R\textsuperscript{1}-M species in the Sonogashira reaction is formed in-situ, whereas in the other cross-coupling reactions, it has to be pre-formed. As illustrated in the catalytic cycle proposed by Sonogashira et al.\textsuperscript{31} (Figure 2.9), two important components are involved in the cross-coupling reaction, namely (i) the reductive initiation step in which Pd\textsuperscript{(II)} is reduced to Pd\textsuperscript{(0)}, and (ii) the main catalytic cycle involving oxidative addition, transmetallation and reductive elimination to give the cross-coupled product.

Cu\textsuperscript{(I)} plays an important role in the initiation reductive step and the transmetallation step. In the reductive initiation step, Cu\textsuperscript{(I)} exchanges its acetylide (C≡C-R) ligand with [PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}] to give the [Pd(C≡C-R)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}] species. Then, [Pd(C≡C-R)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}] undergoes reductive elimination to give a [Pd\textsuperscript{(0)}(PPh\textsubscript{3})\textsubscript{2}] species as the active catalyst in the catalytic cycle and a butadiyne as the by-product from the reaction. Indeed, Marder and co-workers found that under conditions where an oxidant (e.g. air or oxygen) is present, this reductive initiation step can be repeated in a catalytic cycle to produce significant amounts of butadiyne and that the re-oxidation of Pd\textsuperscript{(0)} to Pd\textsuperscript{(II)} is faster than oxidative addition of aryl halide under standard Sonogashira conditions.\textsuperscript{32, 33} This finding is also consistent to the result from Liu and Burton, who used I\textsubscript{2} as the oxidising agent to homo-couple two terminal alkynes with catalytic amounts of [PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}] and CuI.\textsuperscript{18}
Lin, Marder and Fairlamb et al.\textsuperscript{33} have performed DFT (B3LYP) and CCSD(T) calculations to explain the alkyne homo-coupling reactions (\textbf{Eq. 4 – 6}) from the view of reaction energy ($\Delta E$) and free energy ($\Delta G$) (Table 2.1). They concluded that \textbf{Eq. (4)} is slightly endothermic, i.e., thermodynamically unfavourable. \textbf{Eq. (5)} shows that, in the presence of oxidant (e.g. O$_2$), the homo-coupling reactions are favourable due to the energetically favourable formation of water.
\[ 2 \text{RC}≡\text{CH} \rightarrow \text{RC}≡\text{C}≡\text{CR} + \text{H}_2 \]  \quad (4)

\[ 2 \text{RC}≡\text{CH} + \frac{1}{2}\text{O}_2 \rightarrow \text{RC}≡\text{C}≡\text{CR} + \text{H}_2\text{O} \]  \quad (5)

\[ \text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} \]  \quad (6)

**Table 2.1:** Reaction energies and free energies (kcal mol\(^{-1}\)) for Eq. (4) – (6), calculated using two different theoretical methods.\(^{33}\)

<table>
<thead>
<tr>
<th></th>
<th>(\Delta E_1(4))</th>
<th>(\Delta G_1(4))</th>
<th>(\Delta E_2(5))</th>
<th>(\Delta G_2(5))</th>
<th>(\Delta E_3(6))</th>
<th>(\Delta G_3(6))</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP R = Me</td>
<td>0.9</td>
<td>-0.8</td>
<td>-57.9</td>
<td>-51.3</td>
<td>-58.3</td>
<td>-50.6</td>
</tr>
<tr>
<td>B3LYP R = Ph</td>
<td>-1.2</td>
<td>-1.3</td>
<td>-60.0</td>
<td>-51.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCSD(T) R = Me</td>
<td>3.7</td>
<td></td>
<td>-56.4</td>
<td>-60.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As illustrated in **Figure 2.9**, the \([\text{Pd}^{(0)}(\text{PPh}_3)_2]\) species acts as a reagent in the oxidative addition step with aryl halide, forming an Ar-Pd-X intermediate. The halide can significantly influence the rate of reaction. In fact, Fitton and Rick\(^{34}\) found that the reaction rates are ArI > ArBr >> ArCl.

Marder and Lin et al.\(^{35}\) used DFT calculations to study the effect of the halide group on the oxidative addition step, and found that the choice of monophosphine vs. bisphosphine Pd pathways changes as a function of the nature of ArX (**Figure 2.10**).
The authors found that ArCl prefers the monophosphine pathway, and that TS_{C-D} is calculated to have a significantly higher energy than intermediate B, meaning that the oxidative addition of ArCl is generally very slow. For ArBr, the reaction also prefers the monophosphine pathway, but the calculations show that TS_{C-D} has a similar stability to that of B. In the ArI case, the calculations still indicate that the monophosphine one is the preferable pathway, but the energy profile shows that the barrier for the bisphosphine pathway is very close to that of the monophosphine pathway. Therefore, it is believed that the two pathways may exist simultaneously in the ArI case.

In the transmetallation step, the amine, which is often the solvent used in the reaction, deprotonates the acetylene to generate a Cu(I) acetylide and an ammonium salt. Then, the Cu(I)-acetylide undergoes transmetallation with Ar-Pd-X to yield CuX and Ar-Pd-(C≡CR). Ar-Pd-(C≡CR) undergoes reductive elimination to give Ar-C≡CR as the product, and regenerates Pd(0). Different substituents in the para-position of the phenyl ring can strongly affect the rate of the reaction. Generally, electron withdrawing groups such as C≡N, NO₂, CO₂Me lead to much faster reactions than electron donating groups.
such as Me, OMe and SME. Fitton\textsuperscript{34} explained that this is due to the fact that electron withdrawing substituents lower the energies of the Ar-X antibonding orbitals, consequently causing a more facile oxidative addition.

2.1.3.2 C(sp)-C(sp) Pd-catalysed cross-coupling in unsymmetrical butadiynes synthesis

The main problem of synthesising unsymmetrical butadiynes by Pd-catalysed cross-coupling is the formation of homo-coupling products,\textsuperscript{36} which can potentially reduce the isolated yield of unsymmetrical butadiyne. Figure 2.11 shows a schematic diagram to explain how the homo-coupling products can be formed in an unsymmetrical butadiyne synthesis reaction.\textsuperscript{37} The key step, namely reductive elimination, is very important, as it leads to the desired cross-coupling product $R^1\text{-C≡C-Pd≡C-R}^2$, through Path A. However, the $R^1\text{-C≡C-Pd≡C-R}^2$ species also can undergo a transmetallation process with Cu(I)-acetylides present in the reaction system to form the homo-coupling products via Paths B and C. In this case, if transmetallations are faster than reductive elimination, there will be more homo-coupling products are formed.
In order to eliminate homo-coupling product formation in the unsymmetrical butadiyne synthesis, many alternative ligands such as bulky ligands and \( \pi \)-acid ligands, which can facilitate the reductive elimination process, have been developed and investigated. In 2008, Lei et al. reported a new phosphine containing an electron-deficient olefin, hence forth refined to as the “P-olefin ligand” (Figure 2.12), which gave promising results in promoting reductive elimination process and produced high yields of cross-coupling products in most cases.37

![Figure 2.11: Proposed pathways for Pd-catalyzed C(sp)-C(sp) coupling.](image)

The group also compared their method to other palladium catalysts and ligands (Table 2.2) by using the reaction of bromoethynylbenzene and 2-methylbut-3-yn-2ol as the model reaction.
Table 2.2: Comparing Lei’s method to other Pd-catalysed methods for the cross-coupling of BrC≡CPh with HC≡C-(CH₃)₂OH.³⁷

![Chemical structure diagram]

<table>
<thead>
<tr>
<th>entry</th>
<th>Pd (2 mol %)</th>
<th>ligand</th>
<th>yield (%)</th>
<th>Selectivity (cross-/homo-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>none</td>
<td>8</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>[PdCl₂(PPh₃)₂]</td>
<td>none</td>
<td>42</td>
<td>69:31</td>
</tr>
<tr>
<td>3</td>
<td>[Pd(dba)₂]</td>
<td>none</td>
<td>69</td>
<td>83:17</td>
</tr>
<tr>
<td>4</td>
<td>[Pd(dba)₂]</td>
<td>P-olefin</td>
<td>90</td>
<td>91:9</td>
</tr>
</tbody>
</table>

Based on the results in Table 2.2, it is noticeable that [Pd(dba)₂] worked better than [PhCl₂(PPh₃)₂] in the cross-coupling reaction. Addition of the P-olefin ligand, increased both the selectivity by 8% (entries 3 and 4), and the isolated yield of the desired product by 21%.

Alami and Ferri pointed out that the use of amines can affect the cross-coupling reaction to synthesise unsymmetrical butadiynes.⁴¹ In the cross-coupling conditions shown in Table 2.3, Et₂NH, Et₃N, iPr₂NH and iPr₂NH-THF gave very poor yields of the cross-coupling product. However, in the case where pyrrolidine was used, the reaction was completed in shorter time, and produced higher yield of cross-coupling product (yield = 95%) compared to the other amines.⁴¹
Table 2.3: Comparing cross-coupling product yields in different amines.

```
R=C_5H_11 + R' = (CH_2)_2OH
```

<table>
<thead>
<tr>
<th>entry</th>
<th>amine</th>
<th>Time</th>
<th>Cross-coupling product yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Et_3N</td>
<td>24 h</td>
<td>20</td>
</tr>
<tr>
<td>2.</td>
<td>Et_2NH</td>
<td>7 h</td>
<td>35</td>
</tr>
<tr>
<td>3.</td>
<td>BuNH_2</td>
<td>6 h</td>
<td>54</td>
</tr>
<tr>
<td>4.</td>
<td>iPr_2NH</td>
<td>3 h</td>
<td>25</td>
</tr>
<tr>
<td>5.</td>
<td>piperidine</td>
<td>2 h</td>
<td>79</td>
</tr>
<tr>
<td>6.</td>
<td>pyrrolidine</td>
<td>15 min</td>
<td>95</td>
</tr>
</tbody>
</table>

2.1.4 Miscellaneous methods to synthesise unsymmetrical butadiynes

Alternatively, rather than using cross-coupling based synthetic routes, unsymmetrical butadiynes can also be synthesised by converting a carbonyl moiety to an alkyne. For example, Tykwinski et al.\textsuperscript{42} reported this method using starting materials such as aryl- or vinyl-aldehydes, carboxylic acids or acid chlorides to form alkynyl alcohols which were oxidised to ketones and then converted to 1,1-dibromo-olefins (Figure 2.13.c). The 1,1-dibromo-olefin was then reacted with butyllithium to produce a carbene/carbenoid intermediate, followed by rearrangement to afford a unsymmetrical butadiyne in good yield (Figure 2.13).
On the other hand, Wong et al. prepared terminal butadiynes (Figure 2.14) via the cross-coupling of alkynes with \textit{cis}-1,2-dichloroethylene, and HCl elimination from the resulting compound with lithium diisopropylamide (LDA) gave the terminal butadiyne.\textsuperscript{43} This method is the same as that used by Marder et al.\textsuperscript{44} for the syntheses of ferrocenyl butadiynes, which was based on the earlier report of Kende and Smith.\textsuperscript{45}

\textbf{Figure 2.14:} Synthesis of a terminal butadiyne.\textsuperscript{43}
Compared to internal butadiynes, the terminal butadiynes were often reported to be unstable; however, the ferrocenyl terminal butadiyne, which was reported by Marder et al.,\textsuperscript{44} was shown to be stable. Bryce and co-workers\textsuperscript{46} have also reported an alternative synthesis of terminal arylbutadiynes and have shown these to be stable; several have been characterised by crystallography.

2.1.5 Outline of the synthetic routes to butadiynes and 1,3,9,11-dodecatetraynes

In this project, cross-coupling and oxidative homo-coupling reactions were used to synthesise all of the required butadiynes and 1,3,9,11-dodecatetraynes. Two types of diarylbutadiynes were synthesised, namely the simple 1,4-bis(p-R-phenyl)buta-1,3-diynes and extended phenyl ethynylene butadiynes.

The synthetic route to the simple diarylbutadiynes is shown in Figure 2.15. In general, the synthesis of the butadiynes involves three steps namely: i) the cross-coupling of an aryl halide with trimethylysilylacetylene (TMSA) to give a (trimethylysilylethynyl)arene using a Sonogashira reaction; ii) its deprotection by removal of the trimethylsilyl (SiMe\textsubscript{3}) group to form an ethynyl-arene; and iii) the oxidative homo-coupling of the ethynyl-arene to produce the corresponding butadiyne.

![Synthetic route to simple diarylbutadiyne.](image)

**Figure 2.15:** Synthetic route to simple diarylbutadiyne.
Similar to that of the simple butadiynes, the synthesis of the extended bis(arylethynyl)diarylbutadiynes (Figure 2.16) begins with a Sonogashira cross-coupling reaction of 1-bromo-4-iodobenzene with 2-methylbut-3-yn-2-ol to give 4-(4-bromophenyl)-2-methylbut-3-yn-2-ol. Then, the resulting product was cross-coupled with TMSA using the Sonogashira reaction to produce 4-(4-trimethylsilylethynylphenyl)-2-methylbut-3-yn-2-ol. The protecting group, 2-methyl-2-ol [-C(CH₃)₂OH], was then removed to produce 4-(ethynylphenylethynyl)trimethylsilane. This compound was cross-coupled with the appropriate aryl halide to form (trimethylsilylethynylphenylethynyl)arenes, followed by removal the trimethylsilyl protecting group to give (ethynylphenylethynyl)arenes, which were homo-coupled to form the extended bis(arylethynyl)diarylbutadiynes.

\[
\begin{align*}
\text{Br} & \quad \text{I} & \quad \text{H} & \quad \text{Me}_3\text{Si} & \quad \text{OH} \\
\text{Sonogashira reaction} & \quad & \text{Br} & \quad \text{H} & \quad \text{Me}_3\text{Si} & \quad \text{OH} \\
\text{Me}_3\text{Si} & \quad \text{H} & \quad \text{I} & \quad \text{Me}_3\text{Si} & \quad \text{OH} \\
\text{Sonogashira reaction} & \quad & \text{Me}_3\text{Si} & \quad \text{H} & \quad \text{Me}_3\text{Si} & \quad \text{OH} \\
\text{Sonogashira reaction} & \quad & \text{Me}_3\text{Si} & \quad \text{H} & \quad \text{Me}_3\text{Si} & \quad \text{OH} \\
\text{Desilylation} & \quad & \text{Me}_3\text{Si} & \quad \text{H} & \quad \text{Me}_3\text{Si} & \quad \text{OH} \\
\text{Oxidative homo-coupling} & \quad & \text{Me}_3\text{Si} & \quad \text{H} & \quad \text{Me}_3\text{Si} & \quad \text{OH} \\
\end{align*}
\]

**Figure 2.16:** Synthetic route to the extended bis(arylethynyl)diarylbutadiynes.
For the synthesis of the 1,3,9,11-dodecatetraynes (Figure 2.17), ethynyl arenes were cross-coupled with 1,8-dibromocta-1,7-diyne to produce the desired product.

\[ \text{Cross-coupling reaction} \]

Figure 2.17: Synthetic route to 1,3,9,11-dodecatetraynes.

Very recently, two structurally-related 1,3,8,10-undecatetraynes (Figure 2.18) have been reported by Manato and co-workers\(^{47}\) in the course of their study on the luminescent properties of 2,5-bis(arylethynyl)phospholes. The starting material, hepta-1,6-diyne, was iodinated using \(n\)BuLi and I\(_2\) in THF to produce the 1,7-diiodohepta-1,6-diyne in 87% yield. Then, the resulting compound was further cross-coupled with H-C≡C-SiR\(_3\) (where, \(R = \text{Me and } i\text{Pr}\)) using CuI in piperidine, give 1,11-bis(trialkylsilyl)undeca-1,3,8,10-tetraynes in yields of 86% for \(R = \text{Me}\) and 76% for \(R = i\text{Pr}\).\(^{47}\)

Figure 2.18: Synthetic route to 1,11-bis(trialkylsilyl)undeca-1,3,8,10-tetraynes.\(^{47}\)
2.2 Results and discussion

2.2.1 Synthesis of 1,4-bis(p-R-phenyl)buta-1,3-diynes

The first step of the butadiyne synthesis is shown in Figure 2.19; (trimethylsilylthynyl) arenes were prepared from the reaction of aryl halides with TMSA using standard Sonogashira cross-coupling conditions, and the yields of (trimethylsilylthynyl) arenes are shown in Table 2.4.

\[
\text{R}^+X + H\text{SiMe}_3 \xrightarrow{\text{Cul, [PdCl}_2(\text{PPh}_3)_2]} \text{R-SiMe}_3
\]

For the electron donating substituted aryl halides in which X = Br, such as compounds 5 and 7, the reactions were heated at 60 °C and monitored by GC-MS. The reaction to produce 5 was complete in 15 h, but the reaction for 7 took about 72 h to finish. The yield

<table>
<thead>
<tr>
<th>Compound</th>
<th>R Group</th>
<th>X</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-CO\textsubscript{2}Me</td>
<td>I</td>
<td>99</td>
</tr>
<tr>
<td>2</td>
<td>-CF\textsubscript{3}</td>
<td>Br</td>
<td>29</td>
</tr>
<tr>
<td>3</td>
<td>-C≡N</td>
<td>Br</td>
<td>62</td>
</tr>
<tr>
<td>4</td>
<td>-NO\textsubscript{2}</td>
<td>Br</td>
<td>87</td>
</tr>
<tr>
<td>5</td>
<td>-Me</td>
<td>Br</td>
<td>83</td>
</tr>
<tr>
<td>6</td>
<td>-OMe</td>
<td>I</td>
<td>85</td>
</tr>
<tr>
<td>7</td>
<td>-SMe</td>
<td>Br</td>
<td>74</td>
</tr>
</tbody>
</table>

Figure 2.19: The synthesis of (trimethylsilylthynyl)arenes.
obtained for \( 2 \) was relatively low (29\%) compared to the others. This is due to the high volatility of \( 2 \), causing yield losses during the work-up process. The \(^1\)H NMR spectrum of \( 1 \) (Figure 2.20) displays a singlet at 0.24 ppm, which is assigned to the trimethylsilyl group, while two symmetric doublets in the region 7.48 – 7.97 ppm indicate that the CO\(_2\)Me group is in the para-position relative to trimethylsilylethynyl group.

![NMR spectrum of 1](image)

**Figure 2.20:** \(^1\)H NMR spectrum (300 MHz, CDCl\(_3\)) of 1.

Comparing compounds 1, 5, 6 and 7, the singlet, associated with the CH\(_3\) protons, occurs at 3.91 (CH\(_3\)O-C=O), 2.30 (CH\(_3\)), 3.58 (CH\(_3\)O) and 2.44 ppm (CH\(_3\)S), respectively.

The second step of the butadiyne preparation is shown in Figure 2.21, wherein the SiMe\(_3\) protecting group was removed using a basic solution containing sodium carbonate (Na\(_2\)CO\(_3\)) in a mixture of methanol (MeOH) and water.\(^{48}\)

![Deprotection reaction](image)

**Figure 2.21:** Deprotection of the TMS group to produce ethynyl arenes.
The deprotection reactions were complete in 4 to 5 h, and the products were extracted using dichloromethane (CH$_2$Cl$_2$). Large amounts of water were needed in order to remove residual MeOH and carbonate during the extraction. The CH$_2$Cl$_2$ layer was separated, dried over MgSO$_4$ and removed in vacuo to give the ethynyl arenes.

The fact that the SiMe$_3$ peak at 0.24 ppm has disappeared in the $^1$H NMR spectrum proves that the protecting group has been removed (Figure 2.22 for compound 8). An additional singlet was observed at 3.23 ppm which is assigned to the alkyne proton, C≡C-H. The yields obtained from this method are shown in Table 2.5. Again, the low yield obtained for 9, the compound with a CF$_3$ substituent, is due to the high volatility of this compound.

**Figure 2.22:** $^1$H NMR spectrum (200 MHz, CDCl$_3$) of 8.
Table 2.5: Yields of ethynyl arenes following deprotection.

<table>
<thead>
<tr>
<th>Compound</th>
<th>R Group</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>-CO₂Me</td>
<td>97</td>
</tr>
<tr>
<td>9</td>
<td>-CF₃</td>
<td>29</td>
</tr>
<tr>
<td>10</td>
<td>-C≡N</td>
<td>74</td>
</tr>
<tr>
<td>11</td>
<td>-NO₂</td>
<td>89</td>
</tr>
<tr>
<td>12</td>
<td>-Me</td>
<td>70</td>
</tr>
<tr>
<td>13</td>
<td>-OMe</td>
<td>74</td>
</tr>
<tr>
<td>14</td>
<td>-SMe</td>
<td>50</td>
</tr>
</tbody>
</table>

The six terminal alkynes (i.e., all except R = OMe) above were homo-coupled under Pd-catalysed oxidative homo-coupling conditions, utilising either O₂ or I₂ as oxidants, and the yields obtained are shown in Table 2.6.

Table 2.6: Yields of buta-1,3-diynes 15 - 20.

<table>
<thead>
<tr>
<th>Compound</th>
<th>R Group</th>
<th>Oxidant</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>-CO₂Me</td>
<td>I₂</td>
<td>80</td>
</tr>
<tr>
<td>16</td>
<td>-CF₃</td>
<td>O₂</td>
<td>26</td>
</tr>
<tr>
<td>17</td>
<td>-C≡N</td>
<td>I₂</td>
<td>56</td>
</tr>
<tr>
<td>18</td>
<td>-NO₂</td>
<td>I₂</td>
<td>69</td>
</tr>
<tr>
<td>19</td>
<td>-Me</td>
<td>O₂</td>
<td>61</td>
</tr>
<tr>
<td>20</td>
<td>-SMe</td>
<td>O₂</td>
<td>63</td>
</tr>
</tbody>
</table>
According to the $^1$H NMR spectrum of 15 in Figure 2.23, the disappearance of the C≡C-H singlet at 3.23 ppm shows that the homo-coupling of the two ethynyl arenes to form a butadiyne was successful.

![Figure 2.23: $^1$H NMR spectrum (300 MHz, CDCl$_3$) of 15.]

It is worth noting that the solubility of compounds 17 and 18 in CH$_2$Cl$_2$ is very poor. High purity samples of these two compounds can be obtained by recrystallisation from boiling toluene and washing with CH$_2$Cl$_2$ at room temperature.

1,4-bis($p$-methoxyphenyl)buta-1,3-diyne (21, R = OMe) was synthesised by Eglinton-Galbraith coupling using 3 equivalent of Cu(OAc)$_2$ in a mixture of MeOH and pyridine, and the reaction was heated at 70 °C for 15 min. 1.0 M hydrochloric acid (HCl) was added to the reaction mixture and the product was extracted with Et$_2$O. The solvent was removed in vacuo to give 21 as a yellow solid in 81% yield.

2.2.2 Synthesis of extended bis(arylethynyl)diarylbuta-1,3-diynes

In this project, two extended bis(arylethynyl)diarylbutadiynes were also synthesised as the starting materials for the preparation of rhodacyclopentadienes. The first two steps of
the extended bis(arylethynyl)diarylbutadiyne synthesis (preparation of 22 and 23) is shown in Figure 2.24.

\[
\begin{align*}
\text{Br} & \quad \text{I} \quad \text{OH} \quad \text{CuI} \quad \text{[PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}]} \quad \text{Et\textsubscript{3}N} \quad \text{R.T.} \\ & \quad \text{Br} \quad \text{OH} \quad \text{CuI} \quad \text{[PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}]} \quad \text{80 °C} \quad \text{Et\textsubscript{3}N} \\ & \quad \text{Me\textsubscript{3}Si} \quad \text{OH} \quad \text{80 °C} \\
\end{align*}
\]

**Figure 2.24:** Synthetic route to 23.

In the first step, 1-bromo-4-iodobenzene was cross-coupled with 2-methyl-but-3-yn-2-ol under standard Sonogashira conditions at room temperature to give 22 in 85% yield. The appearance of singlets at 2.55 ppm for OH and 1.60 ppm for CH\textsubscript{3} in the \textsuperscript{1}H NMR spectrum indicates that the –C(CH\textsubscript{3})\textsubscript{2}OH moiety is present in 22.

Compound 22 was further cross-coupled with TMSA under Sonogashira conditions at 80 °C and monitored by GC-MS until all of the starting materials had reacted to produce 23 as a beige solid. The isolated yield of 23 was 80% after purification by recrystallisation from hot hexane.

Removal of the –C(CH\textsubscript{3})\textsubscript{2}OH protecting group in 23 required reaction with 0.1 equivalent of freshly powdered NaOH in a refluxing toluene solution at 110 °C for 2 h. The reaction is an equilibrium (Figure 2.25) which requires the acetone generated to be removed by heating up to 110 °C under a stream of nitrogen gas.

\[
\begin{align*}
\text{Me\textsubscript{3}Si} & \quad \text{OH} \quad \text{NaOH, toluene, 110 °C} \quad \text{Me\textsubscript{3}Si} \\
& \quad \text{H} \quad \text{24} \\
\end{align*}
\]

**Figure 2.25:** Removal of the alcohol protecting group in basic toluene solution.
Once the reaction was complete, the black toluene solution was filtered using a sinter funnel and the toluene was removed \textit{in vacuo} to give a black-brown solid. Filtration of a hexane solution of the black-brown solid through a short silica gel pad was needed to obtain the high-purity product 24 in 78% yield.

Iodoctylbenzoate 25 in Figure 2.26 was prepared via esterification of 4-iodobenzoic acid with octan-1-ol in the presence of 4-(dimethylamino)pyridine (DMAP), \(N,N\'-\text{dicyclohexylcarbodiimede (DCCI)}\) and CH\(_2\)Cl\(_2\). The mixture was stirred overnight at room temperature and the solvent was removed \textit{in vacuo}.

\[
\begin{align*}
\text{Me}_3\text{Si} & \equiv \equiv \equiv \equiv \text{H} \quad 24 \\
\{\text{[PdCl}_2\{(\text{PPh}_3)_2\}], \text{CuI, Et}_3\text{N, R.T.}\} & \quad \rightarrow \\
\text{Me}_3\text{Si} & \equiv \equiv \equiv \equiv \text{O} \quad \text{Me}_3\text{Si} \equiv \equiv \equiv \equiv \text{O} \quad \text{OC}_9\text{H}_{17} \quad 27 \\
\text{Me}_3\text{Si} & \equiv \equiv \equiv \equiv \text{N} \quad \text{Me}_3\text{Si} \equiv \equiv \equiv \equiv \text{N} \quad \text{C}_6\text{H}_{13} \quad \text{C}_6\text{H}_{13} \quad 28
\end{align*}
\]

\textbf{Figure 2.26:} Cross-coupling reactions of 24 to give 27 and 28.

The crude product was passed through a 5 cm silica gel column, eluting with hexane. However, the hexane eluent contained the mixture of 25 and DCCI. Separation of the mixtures was carried out using Kugelrohr distillation at 120 – 130 °C, 3.1 x 10\(^{-3}\) Torr, with the impurities being distilled into the second flask leaving a yellow-brown oil in the first flask. The oil was examined by GC-MS to confirm that 25 was pure (Figure 2.27). However, there was some yield loss during the distillation process, as some of the product also distilled into the second flask, and the isolated yield of 25 was 49%.
Iododihexylaniline 26 was synthesised by reacting p-iodoaniline with excess 1-iodohexane in a weakly basic (excess Na₂CO₃) DMF solution at reflux for 40 h. One problem that occurred in the synthetic process was the formation of the monohexyl by-product, which can be seen from the ¹H NMR and GC-MS spectra (Figure 2.28).
Compound 26 was purified further by passage through a silica gel column with hexane : CH$_2$Cl$_2$ (10 : 1 v/v).

![Figure 2.28: GC-MS TIC data for 26 before further purification.](image)

Compound 24 was then cross-coupled, using standard Sonogashira conditions, with two different 1-iodo-4-R-benzenes [R = CO$_2$(n-C$_8$H$_{17}$), 25; R = N(n-C$_6$H$_{13}$)$_2$, 26] to produce 27 and 28 as shown in Figure 2.26. The yields obtained were 94 and 88%, respectively.

The TMS protecting group in 27 was removed using [n-Bu$_4$NF (TBAF) (1.0 M solution in THF) to give 29 in 67% yield after purification. This deprotection method is different from that described in Section 2.2.1, because the n-octyl ester in 27 is converted to the methyl ester if it is stirred in a basic solution of MeOH and water.$^{49}$

The removal of TMS group in 28 was carried out using the typical method described in Section 2.2.1; however, Et$_2$O was added in order to dissolve 28, which is insoluble in MeOH. The yield obtained for the terminal alkyne product 30 was 79%.
The two terminal alkyne products were each homo-coupled in the presence of oxidants, namely I\(_2\) for \(R = \text{CO}_2(n-C_8H_{17})\) and O\(_2\) for \(R = \text{N}(n-C_6H_{13})\), to produce 31 and 32, as shown in Figure 2.29.

![Figure 2.29: Synthesis of extended bis(arylethynyl)diarylbutadiynes, 31 and 32.](image)

### 2.2.3 Synthesis of 1,12-bis(\(p\)-R-phenyl)dodeca-1,3,9,11-tetraynes

The synthesis was initiated by the bromination of 1,7-octadiyne to form 1,8-dibromo-1,7-octadiyne (33, Figure 2.30) using excess \(N\)-bromosuccinimide (NBS) and Ag\(\text{NO}_3\) as the catalyst in acetone.

![Figure 2.30: Bromination of 1,7-octadiyne to produce 33.](image)

A CH\(_2\)Cl\(_2\)/H\(_2\)O extraction was used to remove the NBS and Ag\(\text{NO}_3\) residues. The presence of trace NBS can be detected in the \(^1\text{H}\) NMR spectrum by the peak at 2.76 ppm (Figure 2.31). The golden-yellow, oily product was stored in a refrigerator to avoid decomposition.
Figure 2.31: $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 33 with trace amount of NBS.

With the exception of the parent compound (R = H), all of the 1,12-bis($p$-R-phenyl)dodeca-1,3,9,11-tetraynes were prepared by cross-coupling of 1,8-dibromo-1,7-octadiyne with 2.1 equivalent of the respective ethynyl arenes using the method and conditions described by Lei et al. (Figure 2.32).$^{37}$

![Chemical structure]

Figure 2.32: Synthetic route to 35, 36 and 37 using Lei’s method.$^{37}$
To synthesise the parent compound \([R = \text{H}, \text{34(a)}]\), Cadiot-Chodkiewicz coupling was used. About two equivalents of phenyl acetylene and 1,8-dibromo-1,7-octadiyne were stirred in an aqueous \(n\)-butylamine solution in the presence of CuCl and hydroxyamine hydrochloride. The crude material contained the desired \text{34(a)}, the homocoupling product [\text{34(b)}], and a small amount of the mono-cross-coupling product [\text{34(c)}]. The crude material was further purified by recrystallisation from hot hexane to give a white solid at room temperature, which was separated by filtration, and washed with hexane again in order to remove the unwanted \text{34(b)}, and afford the pure product \text{34(a)} in 42% yield.

![Figure 2.33](image-url)

**Figure 2.33**: Three products obtained from Cadiot-Chodkiewicz coupling.

The synthesis of 1,12-bis(\(p\)-carbethoxyphenyl)dodeca-1,3,9,11-tetrayne (35) was initially attempted by using the Sonogashira cross-coupling method. Thus, 1.2 equivalents of 1,7-octadiyne was stirred with two equivalents of 4-(bromoethynyl)benzoic acid methyl ester under standard Sonogashira conditions for 40 h. The \(^1\text{H} \text{NMR}\) spectrum of the crude material (Figure 2.34) shows that the reaction was not complete although it had been stirred for 40 h.
Figure 2.34: $^1$H NMR spectrum (400 MHz, CDCl$_3$) of crude material of 35 using the standard Sonogashira cross-coupling method.

There are number of compounds present in the crude material and three of them are the homo-coupling by-product, the mono-cross-coupling product and the starting material, 4-(bromoethynyl)benzoic acid methyl ester. No desired product was observed in the $^1$H NMR spectrum. The result from Figure 2.34 implies that the Sonogashira method is not appropriate for the synthesis of 35 because the reaction was very slow. At the same time, the homo-coupling product was forming in the reaction, which will eventually reduce the yields of the desired product. In view of this, a method which can produce the cross-coupling product faster than the homo-coupling product is essential for these syntheses. By using the same conditions reported by Lei et al., the ratio of the cross-coupled product to the homo-coupled product is about 2:1 based on the $^1$H NMR spectrum.
(Figure 2.35) of the crude material. After passage through two silica gel columns, the pure product was obtained in ca. 30% yield.

**Figure 2.35:** $^1$H NMR spectrum (400 MHz, CDCl$_3$) of the crude material of 35 using Lei’s method.

Cadiot-Chodkiewicz coupling was not attempted for the synthesis of 35 because it had failed for the preparation 1,12-bis($p$-nitrophenyl)dodeca-1,3,9,11-tetrayne; after 48 h of stirring under an inert atmosphere, the starting materials still remained as the major components observed by GC-MS, which indicated that the Cadiot-Chodkiewicz coupling method was not successful.

Since 35 was obtained in reasonable yield by Lei’s method, 36 (R = BMes$_2$, where Mes = mesityl) and 37 (R = SMe) were also synthesised using similar conditions. The ratios of cross-coupled products to homo-coupled products in crude 36 and 37 were also 2:1 based on $^1$H NMR spectroscopy. By following work-up processes similar to that used for 35, tetrayne 36 was obtained in 41% yield, whereas 37 was obtained in 33% yield.

The elemental analysis result of 36 shows only 86.88% for the C% value, which is 2.89% lower than the calculated one. This is a common problem that often occurs in the
compounds containing BMes₂, which has been postulated to be due to boron carbide formation during the elemental analysis; that causes the C% to be lower than the calculated value. In order to confirm the composition of 36, the sample was submitted for accurate mass MS measurement, and the result shows that the accurate mass of 36 is 801.5075, which is 4.3 ppm different from the calculated mass of 801.5032.

For the barely soluble 1,3,9,11-dodecatetraynes with R = NO₂ and CN, the separation of the cross-coupling products from the homo-coupling products was even more difficult. Unfortunately, due to the poorly solubility of the homo- and cross-coupling products, these always eluted together product in all attempts at chromatographic separation.

### 2.2.4 Crystallographic data for 34(a) and 35

Tetrayne 34(a) was recrystallised by dissolution in hot hexane and cooling to 5 °C to produce single crystals, which were characterised by X-ray diffraction. The molecular structure of 34(a) is shown in Figure 2.36, and the crystallographic data are listed in Table 2.7. Compound 34(a) crystallises in the monoclinic space group, \( P2_1/n \). The centres of the molecules are co-incident with crystallographic inversion centres. The C=C bond lengths for C8-C7 and C9-C10 are 1.1994(12) and 1.2026(12) Å, respectively, which are typical for C=C triple bonds. However, the C8-C9 bond length of 1.3771(12) Å is much shorter than a typical single C=C bond length (1.54 Å), due to the sp hybridisation at these atoms. The C11-C12 and C12-C12’ single C-C bond lengths are about 1.5361(12) and 1.5206(17) Å, respectively.
A single crystal of \textit{35} was grown at -20 °C from a concentrated CH$_2$Cl$_2$ solution. The crystal was characterised by single-crystal X-ray diffraction and the structure is shown in Figure 2.37, and the crystallographic data are listed in Table 2.7. Compound \textit{35} crystallised in the triclinic space group, \textit{P}$\overline{1}$. Similar to \textit{34(a)}, the centres of the molecules are also co-incident with crystallographic inversion centres. The C13-C14 and C14-C14’ single C-C bond lengths are 1.535(3) and 1.509(4) Å, respectively, and the C10-C11 bond length of 1.379(2) Å is indicative of sp hybridisation. The sp$^2$-sp$^2$ C1-C7 single bond length is 1.490(2) Å. Similarly to \textit{34(a)}, the C≡C bond lengths for C9-C10 and C11-C12 are 1.200(2) and 1.199(2) Å, respectively.
**Table 2.7:** Crystallographic data for 34(a) and 35

<table>
<thead>
<tr>
<th>Compound</th>
<th><strong>34(a)</strong></th>
<th><strong>35</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{24}H_{18}</td>
<td>C_{28}H_{22}O_{4}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>306.38</td>
<td>422.46</td>
</tr>
<tr>
<td>Temperature (K)</td>
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<td>120(2)</td>
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<td>Triclinic</td>
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<tr>
<td>Space group</td>
<td>(P2_1/n)</td>
<td>(P\overline{1})</td>
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<tr>
<td>(a) (Å)</td>
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<td>5.2122(3)</td>
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<tr>
<td>(b) (Å)</td>
<td>8.3988(3)</td>
<td>9.6467(5)</td>
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<tr>
<td>(c) (Å)</td>
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<td>11.5659(5)</td>
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<td>(\alpha) (°)</td>
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<td>72.603(18)</td>
</tr>
<tr>
<td>(\beta) (°)</td>
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<td>77.652(18)</td>
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<tr>
<td>(\gamma) (°)</td>
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<td>75.178(18)</td>
</tr>
<tr>
<td>Volume (Å³)</td>
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<td>530.49(5)</td>
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<tr>
<td>(Z)</td>
<td>2</td>
<td>1</td>
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<tr>
<td>Density (calculated) (Mg/m³)</td>
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<tr>
<td>Absorption coefficient (mm⁻¹)</td>
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<td>Crystal size (mm³)</td>
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<td>(\Theta) range for data collection (°)</td>
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<tr>
<td>Independent reflections</td>
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<td>1877</td>
</tr>
<tr>
<td>Data / Restraints / Parameters</td>
<td>2550 / 0 / 145</td>
<td>1877 / 0 / 189</td>
</tr>
<tr>
<td>Final (R) indices [I &gt; 2(\sigma)(I)]</td>
<td>(R1 = 0.0437) (wR2 = 0.1220)</td>
<td>(R1 = 0.0471) (wR2 = 0.1113)</td>
</tr>
<tr>
<td>(R) indices (all data)</td>
<td>(R1 = 0.0491) (wR2 = 0.1269)</td>
<td>(R1 = 0.0678) (wR2 = 0.1227)</td>
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</tbody>
</table>
2.3 Conclusions

Seven known 1,4-bis(p-R-phenyl)buta-1,3-diyynes and two known extended phenyl ethynylene butadiynes have been synthesised using standard oxidative homo-coupling methods in the presence of the oxidants I\textsubscript{2} and O\textsubscript{2}. All of them have been purified and characterised by NMR, MS and elemental analysis.

Four novel 1,12-bis(p-R-phenyl)dodeca-1,3,9,11-tetraynes have been synthesised and characterised by NMR, IR, MS and elemental analysis. The phenyl-based compound (R = H) was synthesised via Cadiot-Chodkiewicz coupling and the yield obtained was 42%. The other three compounds, with R = CO\textsubscript{2}Me, BMes\textsubscript{2} and SMe, were synthesised using the procedures described by Lei et al.\textsuperscript{37} The ratios of cross-coupled product to homo-coupled product for these three compounds in the crude material were 2:1. The yields of pure compounds obtained varied from 30% to 46%. The solubility of the homo- and cross-coupling products plays an important role in determining the yield of the isolated cross-coupling products. For highly soluble compounds such as 36 (R = BMes\textsubscript{2}), the cross-coupling product can be separated from homo-coupling product much more easily than for insoluble compounds with R = CN and NO\textsubscript{2}. 
2.4 Experimental

2.4.1 General

All of the homo- and cross-coupling reactions namely Sonogashira, Cadiot-Chodkiewicz and Lei reactions were carried out in a fume cupboard equipped with a Schlenk vacuum line. Triethylamine, which was used for the Sonogashira and Lei reactions, was distilled from CaH\(_2\) under nitrogen. The “P-olefin ligand” was supplied by Prof. Lei’s group from the Green Catalyst Institute, Wuhan University, China. The compound 4-ethynylphenyldimesitylborane was supplied by Dr. Jonathan Collings from our group.

NMR spectra were recorded using Varian Mercury 200, Varian Unity 300, Bruker Avance 400 and Varian Inova 500 spectrometers at the following frequencies: \(^1\)H – 200, 300 and 400 MHz, \(^{13}\)C\(\{^1\)H\}\) NMR – 50.3, 100.6 MHz, \(^{19}\)F\(\{^1\)H\}\)NMR – 188, 376 MHz in CDCl\(_3\) solvent. \(^{13}\)C assignments for 33, 34(a), 35 and 37 were based on the ChemNMR C-13 Estimation from ChemDraw Ultra\(^\text{®}\) software version 7.0.1. Proton and carbon spectra were referenced to external SiMe\(_4\) via residual protons in the deuterated solvents or the solvent resonance, respectively.

Elemental analyses were performed using an Exeter Analytical CE-440 Elemental Analyser in the Department of Chemistry at Durham University. GC-MS spectra were obtained from Hewlett-Packard 6890 Series II gas chromatograph equipped with a 5973 inert mass selective detector in EI mode and a 10 m fused silica capillary column (5% cross linked phenylmethylsilicone), under the following operating conditions: injector temperature at 250 °C, detector temperature 300 °C, the oven temperature was increased
at a rate of 20 °C/min from 50 - 280 °C. Ultra high purity grade helium gas was used as the carrier.

The mass spectra of 17, 18, 20, 29, 31, 34(a), 35, 36 and 37 were obtained using an Applied Biosystem Voyager-DE STR MALDI ToF mass spectrometer. The mass spectrum of 32 was obtained by electrospray (ES) using a Thermo-Finnigan LTQ FT spectrometer operating in positive ion mode.

IR spectra for 34(a), 35, 36 and 37 were recorded as KBr discs using a Perkin Elmer Spectrum 100 series FT-IR spectrometer.

The crystallographic data collections and structure solutions were carried out by Dr. Andrei S. Batsanov, Department of Chemistry, Durham University, using a Bruker three-circle diffractometer with a CCD area detector. The structures were solved by direct methods and refined by full-matrix least squares against $F^2$ of all data, using SHELXTL software.

### 2.4.2 Preparation of trimethylsilyl (TMS) protected ethynylbenzenes

1 – Preparation of 4-[(trimethylsilyl)ethynyl]benzoic acid methyl ester$^{50-53}$

![Chemical structure]

The compounds 4-iodobenzoic acid methyl ester (9.17 g, 35.0 mmol), CuI (0.13 g, 0.70 mmol) and $[\text{PdCl}_2(\text{PPh}_3)_2]$ (0.25 g, 0.35 mmol) were added to a flask which had been evacuated and refilled 3 times with N$_2$. Dry, degassed Et$_3$N (200 mL) was added via cannula. Trimethylsilylacetylene (TMSA) (3.78 g, 38.5 mmol) was added to the rapidly stirred mixture under N$_2$. The reaction was monitored in situ by GC-MS and the solvent was removed in vacuo once the reaction was complete (ca. 3 h). The grey solid residue
was transferred to the top of a 5 cm silica gel column and eluted with hexane. The hexane eluant was evaporated in vacuo to give 1 as a beige solid. Yield: 8.03 g, 99%. \(^1\)H NMR (300 MHz, CDCl\(_3\) \(\delta\): 7.97 (d, \(J = 8\) Hz, 2H, CH\(_{\text{arom}}\)), 7.52 (d, \(J = 8\) Hz, 2H, CH\(_{\text{arom}}\)), 3.91 (s, 3H, CO\(_2\)CH\(_3\)), 0.26 (s, 9H, Si(CH\(_3\))\(_3\)). MS(EI) \(m/z\): 232 [M\(^+\)].

2 – Preparation of 4-[(trimethylsilyl)ethynyl]benzotrifluoride\(^{50,54}\)

![Structure of 4-[(trimethylsilyl)ethynyl]benzotrifluoride](image)

The compounds 4-bromobenzotrifluoride (22.50 g, 100.0 mmol), CuI (0.38 g, 2.00 mmol) and [PdCl\(_2\)(PPh\(_3\))\(_2\)] (0.70 g, 1.00 mmol) were added to a flask, which had been evacuated and refilled 3 times with N\(_2\). Dry, degassed Et\(_3\)N (450 mL) was added to the flask via cannula. TMSA (10.80 g, 110.0 mmol) was added into the rapidly stirred mixture under N\(_2\). The reaction was heated at 60 °C for 15 h and examined by GC-MS. Once complete, the solvent was removed in vacuo. The residue was transferred to the top of a 5 cm silica gel column and eluted with hexane. The hexane eluant was evaporated in vacuo to give 2 as a brown-yellow oil. Yield: 7.09 g, 29%. \(^1\)H NMR (400 MHz, CDCl\(_3\) \(\delta\): 7.55 (m, 4H, CH\(_{\text{arom}}\)), 0.26 (s, 9H, Si(CH\(_3\))\(_3\)). \(^{19}\)F\\{\(^1\)H\} NMR (188 MHz, CDCl\(_3\) \(\delta\): -63.30 (s, 3F, CF\(_3\)). MS (EI) \(m/z\): 242 [M\(^+\)].

3 – Preparation of 4-[(trimethylsilyl)ethynyl]benzonitrile\(^{51,55}\)

![Structure of 4-[(trimethylsilyl)ethynyl]benzonitrile](image)

The compounds 4-bromobenzonitrile (10.19 g, 56.0 mmol), CuI (0.21 g, 1.12 mmol) and [PdCl\(_2\)(PPh\(_3\))\(_2\)] (0.39 g, 0.56 mmol) were added to a flask, which had been evacuated...
and refilled 3 times with N$_2$. Dry, degassed Et$_3$N (250 mL) was added via cannula. TMSA (6.05 g, 61.6 mmol) was added to the rapidly stirred mixture under N$_2$. The reaction was stirred at room temperature for 4 h and monitored in situ by GC-MS and the solvent was removed in vacuo once the reaction was complete. The residue was transferred to the top of a 5 cm silica gel column and eluted with hexane. The hexane eluant was evaporated in vacuo to give 3 as a yellow solid. Yield: 6.91 g, 62%. $^1$H NMR (200 MHz, CDCl$_3$) $\delta$: 7.54 (m, 4H, CH$_{arom}$), 0.25 (s, 9H, Si(CH$_3$)$_3$). MS (EI) m/z: 199 [M$^+$].

4 – Preparation of 4-[(trimethylsilyl)ethynyl]nitrobenzene$^{55, 56}$

![Structure of 4-[(trimethylsilyl)ethynyl]nitrobenzene]

The compounds 1-iodo-4-nitrobenzene (18.68 g, 75.00 mmol), CuI (0.29 g, 1.50 mmol) and [PdCl$_2$(PPh$_3$)$_2$] (0.53 g, 0.75 mmol) were added to a flask, which had been evacuated and refilled 3 times with N$_2$. Dry, degassed Et$_3$N (350 mL) was added via cannula. TMSA (8.10 g, 82.50 mmol) was added to the rapidly stirred mixture under N$_2$. The reaction was stirred at room temperature for 4 h and monitored in situ by GC-MS and the solvent was removed in vacuo once the reaction was complete. The residue was transferred to the top of a 5 cm silica gel column and eluted with hexane. The hexane eluant was evaporated in vacuo to give 4 as a yellow solid. Yield: 14.39 g, 87%. $^1$H NMR (200 MHz, CDCl$_3$) $\delta$: 8.17 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 7.59 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 0.27 (s, 9H, Si(CH$_3$)$_3$). MS (EI) m/z: 219 [M$^+$].
5 – Preparation of 4-[(trimethylsilyl)ethynyl]toluene<sup>55-57</sup>

\[
\text{Me} \quad \text{SiMe}_3 \quad \equiv 
\]

The compounds 4-bromotoluene (15.40 g, 90.02 mmol), CuI (0.34 g, 1.80 mmol) and [PdCl\(_2\)(PPh\(_3\))\(_2\)] (0.63 g, 0.90 mmol) were added to a flask, which had been evacuated and refilled with N\(_2\) 3 times. Dry, degassed Et\(_3\)N (350 mL) was added via cannula. TMSA (9.73 g, 99.02 mmol) was added to the rapidly stirred mixture under N\(_2\). The reaction was heated to 65 - 68 °C for 15 h and then examined by GC-MS. Once complete, the solvent was removed \textit{in vacuo}. The dark grey solid residue was transferred to the top of a 5 cm silica gel column and eluted with hexane. The hexane eluant was evaporated \textit{in vacuo}, which gave 5 as a dark brown oil. Yield: 14.08 g, 83%. \(^1\)H NMR (200 MHz, CDCl\(_3\)) \(\delta\): 7.35 (d, \(J = 8\) Hz, 2H, CH\(_{\text{arom}}\)), 7.07 (d, \(J = 8\) Hz, 2H, CH\(_{\text{arom}}\)), 2.29 (s, 3H, CH\(_3\)), 0.26 (s, 9H, Si(CH\(_3\))\(_3\)). MS (EI) \(m/z\): 188 [M\(^+\)].

6 – Preparation of 4-[(trimethylsilyl)ethynyl]anisole<sup>50, 55-57</sup>

\[
\text{MeO} \quad \equiv \quad \text{SiMe}_3 
\]

The compounds 4-iodoanisole (4.91 g, 20.99 mmol), CuI (0.08 g, 0.42 mmol) and [PdCl\(_2\)(PPh\(_3\))\(_2\)] (0.15 g, 0.21 mmol) were added to a flask, which had been evacuated and refilled 3 times N\(_2\). Dry, degassed Et\(_3\)N (150 mL) was added to the flask via cannula. TMSA (2.27 g, 23.10 mmol) was added to the rapidly stirred mixture under N\(_2\). The reaction was heated to 60 – 65 °C for 15 h and monitored \textit{in situ} by GC-MS. Once completed, the solvent was removed \textit{in vacuo}. The residue was transferred to the top of a 5 cm silica gel column and eluted with hexane. The hexane eluant was evaporated \textit{in
vacuo giving 6 as a yellowish-brown oil. Yield: 3.65 g, 85%. $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.42 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 6.81 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 3.75 (s, 3H, OCH$_3$), 0.28 (s, 9H, Si(CH$_3$)$_3$). MS (EI) m/z: 204 [M$^+$.]

7 – Preparation of 4-[(trimethylsilyl)ethynyl]thioanisole$^{58, 59}$

![Diagram of 4-[(trimethylsilyl)ethynyl]thioanisole]

The compounds 4-bromothioanisole (15.01 g, 73.90 mmol), CuI (0.28 g, 1.48 mmol) and [PdCl$_2$(PPh$_3$)$_2$] (0.52 g, 0.74 mmol) were added to a flask, which had been evacuated and refilled 3 times N$_2$. Dry, degassed Et$_3$N (350 mL) was added to the flask via cannula. TMSA (7.98 g, 81.29 mmol) was added to the rapidly stirred mixture under N$_2$. The reaction was heated at 60 °C for 72 h and the solvent was removed in vacuo when the reaction completed. The residue was transferred to the top of a 5 cm silica gel column and eluted with hexane. The hexane eluant was evaporated in vacuo giving 7 as a yellowish oil. Yield: 12.06 g, 74%. $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.40 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 7.15 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 2.44 (s, 3H, SCH$_3$), 0.25 (s, 9H, Si(CH$_3$)$_3$). MS (EI) m/z: 220 [M$^+$].

2.4.3 Preparation of ethynylbenzenes

8 – 4-ethynylbenzoic acid methyl ester$^{32, 51, 52}$

![Diagram of 4-ethynylbenzoic acid methyl ester]

Compound 1 (1.63 g, 7.00 mmol) was added to a suspension of Na$_2$CO$_3$ (2.97 g, 28.00 mmol) in MeOH (175 mL) and water (50 mL) and the mixture was stirred for 4 h. Then,
water (ca. 450 mL) was added to into the reaction. The suspension was transferred to a separatory funnel and Et₂O (3 x 50 mL) was added. The organic layer was separated and dried over MgSO₄. The solvent was removed \emph{in vacuo} to give 8 as a white solid. Yield: 1.09 g, 97%. $^1$H NMR (200 MHz, CDCl₃) δ: 7.95 (d, $J = 8$ Hz, 2H, CH arom), 7.50 (d, $J = 8$ Hz, 2H, CH arom), 3.87 (s, 3H, CO₂CH₃), 3.23 (s, 1H, C≡C-H). MS (EI) m/z: 160 [M⁺].

9 – 4-ethynylbenzotrifluoride$^{32,54}$

\[
\begin{align*}
\text{F}_3\text{C} & \quad \equiv \\
\end{align*}
\]

Compound 2 (7.01 g, 28.92 mmol) was added to a suspension of Na₂CO₃ (12.26 g, 115.68 mmol) in MeOH (400 mL) and H₂O (100 mL) and the mixture was stirred for 24 h. Water (ca. 700 mL) was added into the reaction and the suspension was transferred to a separatory funnel, then, Et₂O (3 x 100 mL) was added. The organic layer was separated and dried over MgSO₄. The Et₂O solvent was removed by distillation at ambient pressure. \textbf{(CAUTION:} Terminal alkynes should not be distilled at elevated temperatures as explosions have been reported.)\textbf{)} The remaining liquid was dissolved in CH₂Cl₂ (150 mL) and filtered through a sinter. Then, most of the solvent was removed by distillation using a Vigreux column and the remainder was removed via evaporation at ambient temperature to give 9 as a light yellow oil. Yield: 1.43 g, 29%. $^1$H NMR (400 MHz, CDCl₃) δ: 7.60 (m, 4H, CH arom), 3.20 (s, 1H, C≡C-H). $^{19}$F{ $^1$H} NMR (376 MHz, CDCl₃) δ: -63.32 (s, 3F, CF₃). MS (EI) m/z: 170 [M⁺].

101
10 – 4-ethynylbenzonitrile$^{32, 51, 60}$

Compound 3 (5.01 g, 25.12 mmol) was added to a suspension of Na$_2$CO$_3$ (10.65 g, 100.48 mmol) in MeOH (350 mL) and H$_2$O (80 mL) and the mixture was stirred for 15 h. Then, water (ca. 500 mL) was added into the reaction. The suspension was transferred to separatory funnel and Et$_2$O (3 x 100 mL) was added. The organic layer was separated and dried over MgSO$_4$. The solvent was removed in vacuo to give 10 as a yellow-orange solid. Yield: 2.37 g, 74%. $^1$H NMR (200 MHz, CDCl$_3$) δ: 7.59 (m, 4H, CH$_{arom}$), 3.30 (s, 1H, C≡C-H). MS (EI) m/z: 127 [M$^+$].

11 – 4-ethynylnitrobenzene$^{32, 55}$

Compound 4 (10.01 g, 45.65 mmol) was added to a suspension of Na$_2$CO$_3$ (19.35 g, 182.60 mmol) in MeOH (400 mL) and H$_2$O (100 mL) and the mixture was stirred for 15 h. Then, water (ca. 700 mL) was added into the reaction. The suspension was transferred to separatory funnel and CH$_2$Cl$_2$ (3 x 100 mL) was added. The organic layer was separated and dried over MgSO$_4$. The solvent was removed in vacuo to give 11 as a yellow solid. Yield: 5.95 g, 89%. $^1$H NMR (200 MHz, CDCl$_3$) δ: 8.20 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 7.64 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 3.35 (s, 1H, C≡C-H). MS (EI) m/z: 147 [M$^+$].
12 – 4-ethynyltoluene\textsuperscript{32, 57, 61}

\[
\begin{array}{c}
\text{Me} \\
\text{H}
\end{array}
\begin{array}{c}
-11
\end{array}
\]

Compound 5 (10.01 g, 53.16 mmol) was added to a suspension of Na\textsubscript{2}CO\textsubscript{3} (22.54 g, 212.64 mmol) in MeOH (400 mL) and H\textsubscript{2}O (100 mL) and the mixture was stirred 15 h. Then, water (ca. 700 mL) was added into the reaction. The suspension was transferred to a separatory funnel and Et\textsubscript{2}O (3 x 100 mL) was added. The organic layer was separated and dried over MgSO\textsubscript{4}. The solvent was removed \textit{in vacuo} to give 12 as a brown oil. Yield: 4.35 g, 70%. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 7.41 (d, \(J = 8\) Hz, 2H, CH\textsubscript{arom}), 7.14 (d, \(J = 8\) Hz, 2H, CH\textsubscript{arom}), 3.05 (s, 1H, C≡C-H), 2.37 (s, 3H, CH\textsubscript{3}). MS (EI) \(m/z\): 116 [M\textsuperscript{+}].

13 – 4-ethynylanisole\textsuperscript{32, 57}

\[
\begin{array}{c}
\text{MeO} \\
\text{H}
\end{array}
\begin{array}{c}
-11
\end{array}
\]

Compound 6 (1.00 g, 4.90 mmol) was added to a suspension of Na\textsubscript{2}CO\textsubscript{3} (2.08 g, 19.6 mmol) in MeOH (150 mL) and H\textsubscript{2}O (50 mL) and the mixture was stirred for 15 h. Then, water (ca. 450 mL) was added into the reaction. The suspension was transferred to a separatory funnel and CH\textsubscript{2}Cl\textsubscript{2} (3 x 50 mL) was added. The organic layer was separated and dried over MgSO\textsubscript{4}. The solvent was removed \textit{in vacuo} to give 13 as a light yellow-green solid. Yield: 0.48 g, 74%. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 7.44 (d, \(J = 8\) Hz, 2H, CH\textsubscript{arom}), 6.84 (d, \(J = 8\) Hz, 2H, CH\textsubscript{arom}), 3.80 (s, 3H, OCH\textsubscript{3}), 3.02 (s, 1H, C≡C-H). MS (EI) \(m/z\): 132 [M\textsuperscript{+}].
Compound 7 (12.02 g, 54.53 mmol) was added to a suspension of Na₂CO₃ (23.12 g, 218.12 mmol) in MeOH (450 mL) and H₂O (100 mL) and the mixture was stirred for 15 h. Then water (ca. 1.0 L) was added into the reaction. The suspension was transferred to a separatory funnel and CH₂Cl₂ (3 x 100 mL) was added. The organic layer was separated and dried over MgSO₄. The solvent was removed in vacuo to give 14 as a light yellow-green solid. Yield: 4.02 g, 50%. ¹H NMR (400 MHz, CDCl₃) δ: 7.40 (d, J = 8 Hz, 2H, CH₆arom), 7.16 (d, J = 8 Hz, 2H, CH₆arom), 3.15 (s, 1H, C≡C-H), 2.42 (s, 3H, SCH₃). MS (EI) m/z: 148 [M⁺].

2.4.4 Preparation of 1,4-bis(p-R-phenyl)buta-1,3-diyne

Compound 8 (1.00 g, 6.25 mmol), CuI (0.011 g, 0.06 mmol), [PdCl₂(PPh₃)₂] (0.021 g, 0.03 mmol), I₂ (0.76 g, 3.00 mmol) and Et₃N (100 mL) were added to a round bottom flask and the reaction was stirred in air for 15 h. The reaction was monitored in situ by GC-MS, and the Et₃N was removed in vacuo once the reaction was complete. The residue was dissolved in CH₂Cl₂ (150 mL). The organic fraction was washed thoroughly with a saturated Na₂S₂O₃ solution, dried over MgSO₄ and then the solvent was removed in vacuo to give a brown solid. The solid was placed on the top of a 5 cm silica gel column and eluted with hot toluene. The toluene eluant was evaporated in vacuo to give 15 as a
white solid. Yield: 0.80 g, 80%. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 8.02 (d, $J = 8$ Hz, 4H, CH$_{arom}$), 7.59 (d, 4H, $J = 8$ Hz, CH$_{arom}$), 3.93 (s, 6H, CO$_2$CH$_3$). Anal. Calcd. For C$_{20}$H$_{14}$O$_4$: C, 75.46; H, 4.43. Found: C, 75.42, H, 4.38%. MS (EI) $m/z$: 318 [M$^+$].

16 – 1,4-bis($p$-trifluoromethylphenyl)buta-1,3-diyne$^{33,65,66}$

![16 - 1,4-bis($p$-trifluoromethylphenyl)buta-1,3-diyne](image)

Compound 9 (3.40 g, 20.00 mmol), CuI (0.038 g, 0.20 mmol), [PdCl$_2$(PPh$_3$)$_2$] (0.07 g, 0.10 mmol) and Et$_3$N (150 mL) were added to a round bottom flask and the reaction was stirred in air for 15 h. The reaction was monitored in situ by GC-MS, and the Et$_3$N was removed in vacuo once the reaction was complete. The residue was placed on the top of a 5 cm silica gel column, which was eluted with hexane. The hexane eluant was evaporated in vacuo and gave 16 as a yellow solid. Yield: 0.87 g, 26%. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 7.65 (s, 8H, CH$_{arom}$). $^{19}$F{$^1$H} NMR (376 MHz, CDCl$_3$) $\delta$: -63.42 (s, 6F, CF$_3$). Anal. Calcd. for C$_{18}$H$_8$F$_6$: C, 63.92; H, 2.38. Found: C, 63.93; H, 2.47%. MS (EI) $m/z$: 338 [M$^+$].

17 – 1,4-bis($p$-cyanophenyl)buta-1,3-diyne$^{8,33,67}$

![17 - 1,4-bis($p$-cyanophenyl)buta-1,3-diyne](image)

Compound 10 (1.00 g, 7.87 mmol), CuI (0.015 g, 0.079 mmol), [PdCl$_2$(PPh$_3$)$_2$] (0.027 g, 0.039 mmol), I$_2$ (1.14 g, 4.50 mmol) and Et$_3$N (100 mL) were added to a round bottom flask and the reaction was stirred in air for 48 h. The Et$_3$N was removed in vacuo. The resulting dark grey brown solid was transferred to the top of a 5 cm silica gel column and
eluted with boiling toluene. The toluene was removed in vacuo to give a brown-yellow solid. The brown-yellow solid was washed with CH\textsubscript{2}Cl\textsubscript{2} (150 mL) and the remaining white solid was recrystallised from hot toluene to yield pure 17. Yield: 0.56 g, 56%. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 7.64 (d, \(J = 9\) Hz, 4H, CH\textsubscript{arom}), 7.61 (d, \(J = 9\) Hz, 4H, CH\textsubscript{arom}). Anal. Calcd. for C\textsubscript{18}H\textsubscript{8}N\textsubscript{2}: C, 85.70; H, 3.20; N, 11.10. Found: C, 85.44; H, 3.24; N, 11.14%. MS (MALDI\textsuperscript{+}) \textit{m/z}: 252 [M\textsuperscript{+}].

18 – 1,4-bis(p-nitrophenyl)buta-1,3-diyne\textsuperscript{8,68-70}

\[\text{O}_2\text{N} \quad \equiv \quad \equiv \quad \text{NO}_2\]

Compound 11 (2.00 g, 13.60 mmol), CuI (0.026 g, 0.136 mmol), [PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}] (0.048 g, 0.068 mmol), I\textsubscript{2} (1.78 g, 7.00 mmol) and \(\text{Et}_3\text{N}\) (150 mL) were added to a round bottom flask and the reaction was stirred in air for 48 h. The \(\text{Et}_3\text{N}\) was removed in vacuo. The resulting dark grey-brown solid was transferred to the top of a 5 cm silica gel column and eluted with boiling toluene. The toluene was removed in vacuo and gave a brown-yellow solid in the round bottom flask. The brown-yellow solid was washed with CH\textsubscript{2}Cl\textsubscript{2} (150 mL) and the remaining yellow solid was recrystallised from hot toluene. Yield: 1.38 g, 69%. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 8.24 (d, \(J = 8\) Hz, 4H, CH\textsubscript{arom}), 7.70 (d, \(J = 8\) Hz, 4H, CH\textsubscript{arom}). Anal. Calcd. for C\textsubscript{16}H\textsubscript{8}N\textsubscript{2}O\textsubscript{4}: C, 65.76; H, 2.76; N, 9.59. Found: C, 65.89; H, 2.78; N, 9.25%. MS (MALDI\textsuperscript{+}) \textit{m/z}: 292 [M\textsuperscript{+}].

106
19 – 1,4-bis(p-tolyl)buta-1,3-diyne\textsuperscript{33, 65, 66}

![Chemical structure of 19]

Compound 12 (1.00 g, 8.62 mmol), CuI (0.016 g, 0.086 mmol), [PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}] (0.030 g, 0.043 mmol) and Et\textsubscript{3}N (100 mL) were added to a round bottom flask and the solution was stirred for 15 h in the open air. The reaction was monitored \textit{in situ} by GC-MS and the Et\textsubscript{3}N was removed \textit{in vacuo} once the reaction was complete. The residue brown-grey solid was applied to the top of a silica pad and eluted by Et\textsubscript{2}O. The Et\textsubscript{2}O was removed \textit{in vacuo} giving a brown solid, which was sublimed at 2.0 x 10\textsuperscript{-3} Torr and 240 °C to give 19 as white solid. Yield: 0.61 g, 61%. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 7.35 (d, \(J = 9\) Hz, 4H, CH\textsubscript{arom}), 7.07 (d, \(J = 9\) Hz, 4H, CH\textsubscript{arom}), 2.30 (s, 6H, CH\textsubscript{3}). Anal. Calcd. for C\textsubscript{18}H\textsubscript{14}: C, 93.87; H, 6.13. Found: C, 93.42; H, 6.11%. MS (EI) \(m/z\): 230 [M\textsuperscript{+}].

20 – 1,4-bis(p-methylthiophenyl)buta-1,3-diyne\textsuperscript{33}

![Chemical structure of 20]

Compound 14 (2.00 g, 13.51 mmol), CuI (0.026 g, 0.135 mmol), [PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}] (0.048 g, 0.068 mmol) and Et\textsubscript{3}N (100 mL) were added to a round bottom flask and the mixture was stirred open air for 15 h. The reaction was monitored \textit{in situ} by GC-MS and the Et\textsubscript{3}N was removed \textit{in vacuo} once the reaction was complete. The residual brown-grey solid was applied to the top of a silica gel pad and eluted with Et\textsubscript{2}O. The Et\textsubscript{2}O was removed \textit{in vacuo} giving a dark brown solid. The pure product was obtained via recrystallisation from hot CHCl\textsubscript{3} at 5 °C for 15 h. White solid was formed, separated, and dried \textit{in vacuo}. Yield: 1.26 g, 63%. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 7.42 (d, \(J = 8\) Hz, 4H, CH\textsubscript{arom}), 7.17
(d, J = 8 Hz, 4H, CH$_{arom}$). 2.49 (s, 6H, SCH$_3$). Anal. Calcd. for C$_{18}$H$_{14}$S$_2$: C, 73.43; H, 4.79. Found: C, 72.95; H, 4.77%. MS (MALDI$^+$) $m/z$: 294 [M$^+$].

21 – 1,4-bis($\rho$-methoxyphenyl)buta-1,3-diyne$^{33, 65, 66, 71}$

The compound Cu(OAc)$_2$ (1.13 g, 6.24 mmol), slurried in MeOH (20 mL) and pyridine (20 mL) was added dropwise to a solution of 13 (0.50 g, 3.78 mmol) in MeOH (50 mL). The mixture was refluxed at 70 °C for 15 min and allowed to cool to room temperature. Aqueous HCl (1.0 M, 20 mL) was added to the mixture and the product was extracted by Et$_2$O (3 x 30 mL). The organic fraction was washed with water (3 x 30 mL), separated and dried over MgSO$_4$. The organic solvent was removed in vacuo giving 20 as a yellow solid. Yield: 0.40 g, 81%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.39 (d, J = 9 Hz, 4H, CH$_{arom}$), 6.79 (d, J = 9 Hz, 4H, CH$_{arom}$), 3.76 (s, 6H, OCH$_3$). Anal. Calcd. for C$_{18}$H$_{14}$O$_2$: C, 82.42; H, 5.38. Found: C, 81.79; H, 5.35%. MS (EI) $m/z$: 262 [M$^+$].

2.4.5 Preparation of extended bis(arylethynyl)diarylbuta-1,3-diynes and related compounds

22 – 4-(4-bromophenyl)-2-methylbut-3-yn-2-ol$^{72}$

The compounds 1-bromo-4-iodobenzene (28.30 g, 100.04 mmol), CuI (0.38 g, 2.00 mmol) and [PdCl$_2$(PPh$_3$)$_2$] (0.70 g, 1.00 mmol) were added to dry and degassed Et$_3$N (ca. 450 mL) in a round bottom flask, which had been evacuated and refilled with N$_2$ 3 times.
2-Methylbut-3-yn-2-ol (9.26 g, 110.04 mmol) was added to the rapidly stirred mixture under N\textsubscript{2}. The reaction was stirred at room temperature for 15 h and then examined by GC-MS. Once complete, the solvent was removed in vacuo. The dark brown solid residue was transferred to the top of a 5 cm silica gel column and eluted with hexane : CH\textsubscript{2}Cl\textsubscript{2} (4 : 1 v/v) (ca. 1.5 L). The solvent was removed in vacuo to give a bright yellow solid. The product was further purified by recrystallisation from hot hexane at -20 °C for 15 h. The resulting white solid was collected by filtration and dried in vacuo. Yield: 20.4 g, 85%.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \): 7.35 (d, \( J = 9 \) Hz, 2H, CH\textsubscript{arom}), 7.20 (d, \( J = 9 \) Hz, 2H, CH\textsubscript{arom}), 3.33 (s, 1H, OH), 1.58 (s, 6H, C(CH\textsubscript{3})\textsubscript{2}). MS (EI) \( m/z \): 238 [M\textsuperscript{+}].

\textbf{23} – 4-(4-trimethylsilylethynylphenyl)-2-methylbut-3-yn-2-ol\textsuperscript{73,74}

Compound 22 (10.20 g, 42.65 mmol), CuI (0.16 g, 0.85 mmol) and [PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}] (0.30 g, 0.43 mmol) were added to a flask, which had been evacuated and refilled with N\textsubscript{2} 3 times. Dry, degassed Et\textsubscript{3}N (250 mL) was added via cannula. TMSA (4.61 g, 46.92 mmol) was added to the rapidly stirred mixture under N\textsubscript{2}. The reaction was heated at 80 °C for 15 h and then examined by GC-MS. Once complete, the solvent was removed in vacuo. The dark grey solid residue was transferred to the top of a 5 cm silica gel column and eluted with hexane : CH\textsubscript{2}Cl\textsubscript{2} (4 : 1 v/v) (ca. 1.0 L). The solvent was removed in vacuo to give 23 as a light brown solid. The product was further purified by passage through a silica gel column eluting with hexane : CH\textsubscript{2}Cl\textsubscript{2} (9 : 1 v/v). The solvent was removed in vacuo to give the pure product as a white solid. Yield: 8.50 g, 78%. \textsuperscript{1}H NMR
(400 MHz, CDCl$_3$) $\delta$: 7.37 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 7.31 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 2.52 (s, 1H, OH), 1.59 (s, 6H, C(CH$_3$)$_2$), 0.24 (s, 9H, Si(CH$_3$)$_3$). MS (EI) m/z: 256 [M$^+$].

**24** – 4-ethynlyphenylethynyltrimethylsilane$^{73,74}$

![Structure of 4-ethynlyphenylethynyltrimethylsilane](image)

Compound 23 (8.00 g, 31.25 mmol), freshly powdered NaOH (0.13 g, 3.13 mmol) and toluene (100 mL) were added to a two neck round bottom flask and the reaction mixture was refluxed at 110 °C for 2 h. The system was purged with nitrogen gas to assist the removal of acetone, which formed in the reaction, through the condenser. Once the reaction was complete, the black-brown toluene solution was filtered and the solvent was removed in vacuo to give a dark brown solid. The solid was transferred to the top of a silica gel column and eluted with hexane. The solvent was removed in vacuo to give 24 as a light yellow solid. Yield: 4.83 g, 78%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.41 (s, 4H, CH$_{arom}$), 3.16 (s, 1H, C≡CH), 0.25 (s, 9H, Si(CH$_3$)$_3$). MS (EI) m/z: 198 [M$^+$].

**25** – 4-iodobenzoic acid n-octyl ester$^{75}$

![Structure of 4-iodobenzoic acid n-octyl ester](image)

To an ice cooled and stirred solution of 4-iodobenzoic acid (7.40 g, 29.84 mmol), n-octan-1-ol (4.55 g, 34.94 mmol) and 4-$N,N$-dimethylaminopyridine (DMAP) (0.378 g, 3.09 mmol) in 150 mL of CH$_2$Cl$_2$, was added dropwise a solution of $N,N'$-dicyclohexylcarbodiimide (DCCI) (12.70 g, 61.50 mmol) in 30 mL of CH$_2$Cl$_2$. The mixture was stirred for 15 h. The solution was filtered and the solvent was removed in
vacuo. The crude product was transferred to the top of a 5 cm silica gel pad and eluted with hexane. Hexane was removed in vacuo and followed by Kugelrohr distillation (120 – 130 °C, 3.1 x 10⁻³ Torr) gave a brown-yellow oil. Yield: 5.34 g, 50%. ¹H NMR (400 MHz, CDCl₃) δ: 7.76 (d, J = 9 Hz, 2H, CHₐrom), 7.71 (d, J = 9 Hz, 2H, CHₐrom), 4.28 (t, J = 7 Hz, 2H, OCH₂), 1.73 (quint, J = 7 Hz, 2H, OCH₂CH₂), 1.34 (m, 2H, CH₂CH₃), 1.27 (m, 8H, CH₂), 0.86 (t, J = 7 Hz, 3H, CH₂CH₃). Anal. Calcd. for C₁₅H₂₁O₂I: C, 50.01; H, 5.88. Found: C, 49.91; H, 5.90%. MS (EI) m/z: 360 [M⁺].

26 – di-n-hexyl-(4-iodophenyl)-amine ⁷⁶-⁷⁸

To a solution of p-iodoaniline (10.95 g, 50.00 mmol) in DMF (ca. 160 mL) was added 1-iodohexane (34.0 g, 160.32 mmol) and Na₂CO₃ (9.20 g, 86.80 mmol). The reaction was heated at 120 °C for 40 h. Then the solvent was removed in vacuo, and the residue was dissolved in CH₂Cl₂ and passed through a 5 cm celite column. The solvent was removed in vacuo to give a dark brown oil which was purified by passing through a silica gel column eluting with CH₂Cl₂ : hexane, (1 : 10 v/v) (ca. 750 mL). The solvent was removed in vacuo to give the pure product as light brown oil. Yield: 10.73 g, 55%. ¹H NMR (400 MHz, CDCl₃) δ: 7.47 (d, J = 9 Hz, 2H, CHₐrom), 6.48 (d, J = 9 Hz, 2H, CHₐrom), 3.23 (t, 4H, N(CH₂)₂), 1.56 (quint, J = 6 Hz, 4H, N(CH₂CH₂)₂), 1.32 (m, 12H, CH₂), 0.92 (t, J = 6 Hz, 6H, 2 x CH₃). MS (EI) m/z: 387 [M⁺].
27 – 4-(4-trimethylsilylethynylphenylethynyl)-benzoic acid n-octylester

![Structure](image)

Compound 25 (1.80 g, 5.00 mmol), CuI (0.019 g, 0.10 mmol) and [PdCl$_2$(PPh$_3$)$_2$] (0.035 g, 0.05 mmol) were added to a round bottom flask, which had been evacuated and refilled with N$_2$ 3 times. Dry, degassed Et$_3$N (100 mL) was added via cannula. Compound 24 (1.09 g, 5.50 mmol) was added to the rapidly stirred mixture under N$_2$. The reaction was stirred at room temperature for 15 h and then examined by GC-MS. Once complete, the solvent was removed in vacuo. The crude solid was transferred to the top of a 5 cm silica gel pad and eluted with hexane : CH$_2$Cl$_2$, (4 : 1 v/v) (ca. 500 mL). The solvent was removed in vacuo to give a yellow solid. The product was further purified by recrystallisation by dissolution in hot hexane and then cooling to -20 °C. The pure product was isolated as a yellowish solid. Yield: 2.02 g, 94%. $^1$H NMR (200 MHz, CDCl$_3$) δ: 8.02 (d, $J = 9$ Hz, 2H, CH$_{arom}$), 7.58 (d, $J = 9$ Hz, 2H, CH$_{arom}$), 7.46 (s, 4H, CH$_{arom}$), 4.32 (t, $J = 7$ Hz, 2H, OCH$_2$), 1.75 (quint, $J = 7$ Hz, 2H, OCH$_2$CH$_2$), 1.30 (m, 10H, CH$_2$), 0.88 (t, $J = 7$ Hz, 3H, CH$_3$). Anal. Calcd. for C$_{28}$H$_{34}$O$_2$Si: C, 78.09; H, 7.96. Found: C, 77.98; H, 7.90%. MS (EI) m/z: 430 [M$^+$].

28 – di-n-hexyl-[4-(4-trimethylsilylethynylphenylethynyl)phenyl]-amine

![Structure](image)

Compound 26 (3.87 g, 9.99 mmol), CuI (0.038 g, 0.20 mmol) and [PdCl$_2$(PPh$_3$)$_2$] (0.070 g, 0.10 mmol) were added to a round bottom flask, which had been evacuated and refilled with N$_2$ 3 times. Dry, degassed Et$_3$N (150 mL) was added via cannula. Compound
(2.18 g, 11.00 mmol) was added to the rapidly stirred mixture under N₂. The reaction was stirred at room temperature for 15 h and then examined by GC-MS. Once complete, the solvent was removed in vacuo. The dark brown solid residue was transferred to the top of a 5 cm silica gel pad and eluted with hexane. The solvent was removed in vacuo to give a yellow solid. Yield: 4.02 g, 88%. ¹H NMR (400 MHz, CDCl₃) δ: 7.41 (s, 4H, CH₄), 7.34 (d, J = 9 Hz, 2H, CH₄), 6.56 (d, J = 9 Hz, 2H, CH₄), 3.27 (t, J = 7 Hz, 4H, N(CH₂)₂), 1.58 (m, 4H, N(CH₂CH₂)₂), 1.32 (m, 12H, CH₂), 0.90 (t, J = 6 Hz, 6H, 2 x CH₃), 0.25 (s, 9H, Si(CH₃)₃). Anal. Calcd. for C₃₁H₄₃NSi: C, 81.34; H, 9.47; N, 3.06. Found: C, 81.46; H, 9.46; N, 2.81%. MS (EI) m/z: 457 [M⁺].

29 – 4-(4-ethynylphenylethynyl)-benzoic acid n-octyl ester⁴⁹

Compound 27 (1.40 g, 3.25 mmol), [n-Bu₄N]F (1.0 M in THF) (3.25 mL, 3.25 mmol) and Et₂O (50.0 mL) were added to a round bottom flask and the reaction mixture was stirred for 2 h. The solvent was removed in vacuo and the residue was transferred to a sinter funnel and washed with hot water. The product was extracted with Et₂O (ca. 3 x 50 mL) in a separatory funnel. The organic layer was separated and dried over MgSO₄. The solvent was removed in vacuo to give a pale yellow-white solid. Yield: 0.78 g, 67%. ¹H NMR (200 MHz, CDCl₃) δ: 8.02 (d, J = 9 Hz, 2H, CH₄), 7.58 (d, J = 9 Hz, 2H, CH₄), 7.49 (s, 4H, CH₄), 4.32 (t, J = 7 Hz, 2H, OCH₂), 3.19 (s, 1H, C≡CH), 1.75 (quint, J = 7 Hz, 2H, OCH₂CH₂), 1.30 (m, 10H, CH₂), 0.88 (t, J = 6 Hz, 3H, CH₃). Anal. Calcd. for C₂₅H₂₆O₂: C, 83.76; H, 7.31. Found: C, 82.87; H, 7.32%. MS (MALDI⁺) m/z: 358 [M⁺].
30 – [4-(4-ethynylphenylethynyl)phenyl]-di-n-hexylamine

![Chemical structure of 30](image)

To a solution of compound 28 (2.29 g, 5.00 mmol) in Et2O (100 mL), MeOH (100 mL) and water (30 mL) was added K2CO3 (2.76 g, 20.0 mmol), and the reaction mixture was stirred at room temperature for 15 h. Then, water (ca. 600 mL) was added into the reaction. The suspension was transferred to a separatory funnel and CH2Cl2 (3 x 75 mL) was added. The organic layer was separated and dried over MgSO4. The solvent was removed in vacuo to give 30 as a yellow solid. Yield: 1.62 g, 84%. 1H NMR (400 MHz, CDCl3) δ: 7.45 (s, 4H, CHarom), 7.37 (d, J = 9 Hz, 2H, CHarom), 6.57 (d, J = 9 Hz, 2H, CHarom), 3.28 (t, J = 8 Hz, 4H, N(CH2)2), 3.16 (s, 1H, C≡CH), 1.59 (m, 4H, N(CH2CH2)2), 1.33 (m, 12H, CH2), 0.92 (t, J = 6 Hz, 6H, 2 x CH3). Anal. Calcd. for C28H35N: C, 87.22; H, 9.15; N, 3.63. Found: C, 87.20; H, 9.01; N, 3.34%. MS (EI) m/z: 385 [M+].

31 – 4,4′-bis-(4′′-carbo-n-octyloxyphenylethynyl)diphenyl-buta-1,3-diyned49

![Chemical structure of 31](image)

Compound 29 (0.50 g, 1.39 mmol), CuI (0.003 g, 0.014 mmol) and [PdCl2(PPh3)2] (0.005 g, 0.007 mmol) were added to a round bottom flask. Et3N (100 mL) was added to the mixture followed by I2 (0.36 g, 1.40 mmole). The reaction was stirred open to the air at room temperature for 24 h and then examined by GC-MS. Once complete, the solvent was removed in vacuo. The residue was transferred to the top of a 5 cm silica gel column and eluted with hexane : CH2Cl2 (4 : 1 v/v) (ca. 500 mL). The solvent was removed in
**vacuo** to give 31 as a white solid. Yield: 0.38 g, 76%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.03 (d, $J = 8$ Hz, 4H, CH$_{arom}$), 7.58 (d, $J = 8$ Hz, 4H, CH$_{arom}$), 7.52 (s, 8H, CH$_{arom}$), 4.32 (t, $J = 7$ Hz, 4H, OCH$_2$), 1.77 (quint, $J = 7$ Hz, 4H, OCH$_2$CH$_2$), 1.30 (m, 20H, CH$_2$), 0.89 (t, $J = 7$ Hz, 6H, CH$_3$). Anal. Calcd. for C$_{50}$H$_{50}$O$_4$: C, 84.00; H, 7.05. Found: C, 83.95; H, 6.99%. MS (MALDI$^+$) $m/z$: 714 [M$^+$].

32 – 4,4’-bis-(4’’-di-n-hexylaminophenylethynyl)diphenyl-buta-1,3-diyne$^{13}$

![Diagram of compound 32](https://example.com/diagram.png)

Compound 30 (1.00 g, 2.59 mmol), CuI (0.005 g, 0.026 mmol) and [PdCl$_2$(PPh$_3$)$_2$] (0.009 g, 0.001 mmol) were added to round bottom flask. Et$_3$N (100 mL) was added to the mixture, which was then stirred at room temperature for 24 h and monitored by GC-MS. Once completed, the solvent was removed *in vacuo*. The residue was transferred to the top of a 5 cm silica gel pad and eluted with hexane : CH$_2$Cl$_2$ (4 : 1 v/v) (ca. 1000 mL). The solvent was removed *in vacuo* to give an orange-brown solid. The solid was further purified by recrystallisation by dissolution in hot hexane (ca. 15 mL) and cooling to ca. -20 °C, giving a yellow solid. Yield: 0.79 g, 79%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.45 (s, 8H, CH$_{arom}$), 7.36 (d, $J = 8$ Hz, 4H, CH$_{arom}$), 6.57 (d, $J = 8$ Hz, 4H, CH$_{arom}$), 3.28 (t, $J = 8$ Hz, 8H, N(CH$_2$)$_2$), 1.58 (m, 8H, N(CH$_2$CH$_2$)$_2$), 1.33 (m, 24H, CH$_2$), 0.91 (t, $J = 6$ Hz, 12H, CH$_3$). Anal. Calcd. for C$_{56}$H$_{68}$N$_2$: C, 87.45; H, 8.91; N, 3.64. Found: C, 86.83; H, 8.85; N, 3.45%. MS (ES$^+$) $m/z$: 768 [M$^+$], 769 [M + H$^+$].
2.4.6 Preparation of 1,12-bis(p-R-phenyl)dodeca-1,3,9,11-tetraynes and related compounds

33 – 1,8-dibromo-1,7-octadiyne\textsuperscript{79, 80}

To a solution of 1,7-octadiyne (9.98 g, 94.00 mmol) in acetone (200 mL) was added recrystallised NBS (66.92 g, 376 mmol) and AgNO\textsubscript{3} (1.60 g, 9.40 mmol), and the reaction was stirred for 15 h at room temperature. Acetone was removed \textit{in vacuo} and the residue was treated with hexane (200 mL). Water (5 x 200 mL) was added to the hexane suspended solution. The organic layer was separated, dried over MgSO\textsubscript{4} and removed \textit{in vacuo} to give 33 as a yellow oil. Yield: 21.06 g, 85%. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \textit{δ}: 2.25 (m, 4H, C≡C-CH\textsubscript{2}), 1.62 (m, 4H, CH\textsubscript{2}). \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (100.4 MHz, CDCl\textsubscript{3}) \textit{δ}: 79.7 (C2), 38.1 (C1), 27.2 (C4), 19.2 (C3).

34(a) – 1,12-diphenyldodeca-1,3,9,11-tetrayne

CuCl (0.025 g, 0.25 mmol) followed by hydroxylamine hydrochloride, NH\textsubscript{2}OH-HCl, (ca. 0.50 g) was added into a degassed mixture of \textit{n}-BuNH\textsubscript{2} (20 mL) and water (45 mL) and the mixture was stirred for 1 h under N\textsubscript{2}. Phenylacetylene (1.30 g, 12.75 mmol) was added to the solution which was then cooled to 0 °C. Compound 33 (1.60 g, 6.07 mmoles) was added to the cold solution and the mixture was stirred for 5 min. The
reaction was allowed to warm to room temperature, then a large amount of NH₂OH·HCl (ca. 10 g) was added to the mixture. The mixture was stirred for 15 h, then ethyl acetate (EA) (3 x 20 mL) was added to the reaction. The organic layer was separated and dried over MgSO₄. The solvent was removed in vacuo to give a yellow-brown crude material and further purified via recrystallisation via dissolution in hot hexane and cooling to ca. -20 °C. A white solid was formed, which was separated and washed with hexane (ca. 5 mL). Yield: 0.79 g, 42%. ¹H NMR (200 MHz, CDCl₃) δ: 7.50 (m, 4H, CH₉arom), 7.33 (m, 6H, CH₉arom), 2.43 (m, 4H, C≡C-CH₂), 1.74 (m, 4H, CH₂). ¹³C{¹H} NMR (50.3 MHz, CDCl₃) δ: 132.7 (C₃ & C₅), 129.1 (C₂ & C₆), 128.6 (C₁), 122.2 (C₄), 84.1 (C₁₀), 75.2 (C₇), 74.5 (C₈), 65.9 (C₉), 27.5 (C₁₂), 19.4 (C₁₁). Anal. Calcd. for C₂₄H₁₈: C, 94.08; H, 5.92. Found: C, 93.26; H, 6.04%. MS (MALDI⁺) m/z: 306. IR (KBr) υC-H = 2937; υC≡C = 2239; υAr = 1591 cm⁻¹.

35 – 1,12-bis(p-carboxymethoxyphenyl)dodeca-1,3,9,11-tetrayne

[Pd(dba)₂] (0.30 g, 0.52 mmol), CuI (0.50 g, 0.26 mmol), and the “P-olefin ligand” (0.20 g, 0.52 mmol) were added to a two neck round bottom flask in a N₂ filled glove box. Dried, degassed DMF (80 mL), Et₃N (10 mL) and 33 (1.71 g, 6.49 mmol) were added to the round bottom flask and the mixture was stirred for 5 min. The compound 4-ethenylbenzoic acid methyl ester (8, 2.18 g, 13.63 mmol) was added to the mixture and the reaction was stirred for 15 h outside of the glove box. Upon completion, the Et₃N was removed in vacuo, then CH₂Cl₂ (50 mL) was added to the flask. The dark brown solution
was transferred to a 500 mL separatory funnel and brine (5 x 200 mL) was added. The organic layer was separated, dried over MgSO$_4$ and then the solvent was removed in vacuo. The product was purified via silica gel column chromatography slowly increasing the solvent polarity until the ratio of hexane : CH$_2$Cl$_2$ reached 2 : 3 (v/v). Compound 35 was isolated appears as an off-white solid. Single crystals of 35 were obtained by dissolution in hot CH$_2$Cl$_2$ and cooling to ca. 5 °C. Yield: 0.81 g, 30%. $^1$H NMR (200 MHz, CDCl$_3$) δ: 7.95 (d, $J = 8$ Hz, 4H, CH$_{arom}$), 7.52 (d, $J = 8$ Hz, 4H, CH$_{arom}$), 3.91 (s, 6H, CO$_2$CH$_3$), 2.44 (m, 4H, C≡C-CH$_2$), 1.74 (m, 4H, CH$_2$). $^{13}$C{$^1$H} NMR (50.3 MHz, CDCl$_3$) δ: 166.6 (C13), 132.6 (C3 & C5), 130.2 (C1), 129.7 (C2 & C6), 126.9 (C4), 85.7 (C10), 77.3 (C7), 74.3 (C8), 65.6 (C9), 52.5 (C14), 27.3 (C12), 19.4 (C11). Anal. Calcd. for C$_{28}$H$_{22}$O$_4$: C, 79.60; H, 5.25. Found: C, 78.86; H, 5.20%. MS (MALDI$^+$) m/z: 422. IR (KBr) $\nu_{C-H} = 2935; \nu_{C=C} = 2235; \nu_{C=O} = 1719; \nu_{Ar} = 1602$ cm$^{-1}$.

36 – 1,12-bis(p-dimesitylborylphenyl)dodeca-1,3,9,11-tetrayne

In a N$_2$ filled glove, the compounds [Pd(dba)$_2$] (0.014 g, 0.024 mmol), CuI (0.002 g, 0.012 mmol), and the “P-olefin ligand” (0.009 g, 0.024 mmol) were added to a 25 mL vial. Dried and degassed DMF (10.0 mL), Et$_3$N (3.0 mL) and 33 (0.079 g, 0.30 mmol) were added to the vial and the mixture was stirred for 5 min. The compound 4-ethynylphenyldimesitylborane (0.22 g, 0.63 mmol) was added to the mixture and the
reaction was stirred for 15 h in the glove box. The vial was removed from the glove box and the contents were transferred into a 100 mL round bottom flask. The Et₃N was removed in vacuo, then CH₂Cl₂ (50 mL) was added to the flask. The dark brown solution was transferred into a separatory funnel and brine (5 x 50 mL) was added. The organic layer was separated, dried over MgSO₄ and then the solvent was removed in vacuo. The product was separated via silica gel column chromatography slowly increasing solvent polarity until the ratio of hexane : CH₂Cl₂ reached 4 : 1 (v/v). Compound 36 was isolated as a light yellow solid. Yield: 0.10 g, 42%. ¹H NMR (400 MHz, CDCl₃) δ: 7.46 (s, 8H, CH₉arom), 6.82 (s, 8H, CH₉arom), 2.42 (m, 4H, C≡C-CH₂), 2.32 (s, 12H, Ar-C₂₀H₃), 2.00 (s, 24H, Ar-C₁₉H₃ & Ar-C₂₁H₃), 1.75 (m, 4H, CH₂). ¹³C{¹H} NMR (100.6 MHz, CDCl₃) δ: 146.7, 141.7, 141.0, 139.2, 136.2, 132.2, 128.5, 125.5, 85.7, 76.5, 75.5, 66.0, 29.4, 23.7, 21.5, 19.5. Anal. Calcd. for C₆₀H₆₀B₂: C, 89.77; H, 7.53. Found: C, 86.88; H, 7.61%. MS (MALDI⁺) m/z: 802, Accurate Mass MS (ASAP) m/z: 801.5075. IR (KBr) νC-H = 2135; νC≡C = 2240; νAr = 1606 cm⁻¹.

37 – 1,12-bis(p-methylthiophenyl)dodeca-1,3,9,11-tetrayne

In a N₂ filled glove box, the compounds [Pd(dba)₂] (0.349 g, 0.606 mmol), CuI (0.058 g, 0.303 mmol), and the “P-olefin ligand” (0.238 g, 0.606 mmol) were added to a 100 mL two neck round bottom flask. Dried, degassed DMF (25.0 mL), Et₃N (10.0 mL) and 33 (2.00 g, 7.58 mmol) were added to the flask and the mixture was stirred for 5 min. The compound 4-ethynylthioanisole (14, 2.36 g, 15.92 mmol) was added to the mixture and
the reaction was stirred for 15 h at room temperature outside of the glove box. Upon completion, the Et₃N was removed in vacuo then CH₂Cl₂ (50 mL) was added to the flask. The dark brown solution was transferred to a 500 mL separatory funnel and brine (5 x 200 mL) was added. The organic layer was separated, dried over MgSO₄ and then the solvent was removed in vacuo. The product was separated via silica gel column chromatography, slowly increasing solvent polarity until the ratio of hexane : CH₂Cl₂ reached 3 : 2 (v/v). Pure compound 37 was isolated as an off-white solid. Crystals of 37 were obtained by dissolution in a mixture of hot hexane/CH₂Cl₂ and cooling to ca. 5 °C. Yield: 1.0 g, 33%. ¹H NMR (400 MHz, CDCl₃) δ: 7.37 (d, J = 8 Hz, 4H, CH₉arom), 7.14 (d, J = 8 Hz, 4H, CH₉arom), 2.47 (s, 6H, SCH₃), 2.42 (m, 4H, C≡C-CH₂), 1.72 (m, 4H, CH₂). ¹³C{¹H} NMR (50.3 MHz, CDCl₃) δ: 140.1 (C1), 133.0 (C3 & C5), 125.8 (C2 & C6), 118.3 (C4), 85.7 (C10), 75.1 (C7), 74.5 (C8), 66.0 (C9), 27.5 (C12), 19.4 (C13), 15.4 (C11). Anal. Calcd. for C₂₆H₂₂S₂: C, 78.35; H, 5.56. Found: C, 78.50; H, 5.52%. MS (MALDI⁺) m/z: 398. IR (KBr) νC-H = 2935; νC≡C = 2236; νAr = 1582 cm⁻¹.
Reference:

Chapter 3

The synthesis, characterisation and investigation of the photophysical properties of 2,5-bis(arylethynyl)rhodacyclopentadienes
3.1 Introduction

Metallacyclopentadiene complexes, especially with 2,2'-bipyridine (bpy) ligands, have been extensively studied over the last few decades because of their interesting photophysical properties such as strong spin-orbit coupling (SOC), extremely fast intersystem crossing (ISC) rates and microsecond lifetimes, which make the complexes potential candidates for various applications such as probes for biological-labelling\(^1\) and two-photon absorption materials.\(^2\)\(^-\)\(^5\) More recently, [Ir(ppy)\(_3\)] has been applied in organic light emitting diode devices (OLEDs), due to its highly efficient triplet state emission.\(^6\)

In 2001, Marder and Rourke et al. reported an example of a new type of luminescent metallacyclopentadiene complex, namely a 2,5-bis(\(p\)-tolylethynyl)-3,4-bis(\(p\)-tolyl) rhodacyclopentadiene, the structure of which is shown in Figure 3.1.\(^7\)

![Figure 3.1: The structure of 2,5-bis(\(p\)-tolylethynyl)-3,4-bis(\(p\)-tolyl)rhodacyclopentadiene.](image)

The photophysical properties of this and related complexes were investigated further by Ward in his Ph.D. study,\(^8\) in which he varied the R substituents at the para-positions of the phenyl rings, and also used different kinds of ligands on the Rh centre (Figure 3.2). The ligands that were studied by Ward included trimethylsilyl ethynyl- (TMSE), methyl- (Me-), chloro- (Cl-), 4-\(N,\,N\)-dimethylaminophenylethynyl (Me\(_2\)N-C\(_6\)H\(_4\)-C≡C-) and 4-\(N,\,N\)-diphenylaminophenylbutadiynyl (Ph\(_2\)N-C\(_6\)H\(_4\)-C≡C-C≡C-). The reasons for using the
Me₂N-C₆H₄-C≡C- and Ph₂N-C₆H₄-C≡C-C≡C- ligands was to extend the conjugation length of the alkynyl ligand and also to attempt to maximise the co-planarity between the phenyl ring at the 2-position of the rhodacycle ring and the phenyl ring of the alkynyl ligand, which can subsequently increase the π-interaction of the conjugated alkynyl ligand with the rhodacycle ring. For the TMSE-based rhodacyclopentadienes, Ward investigated the effect of different R substituents including NO₂, CN, CO₂Me, CF₃, H, Me, OMe, SMe and NMe₂ on the photophysical properties.

Figure 3.2: Rhodacyclopentadienes with different R substituents and X ligands that have been studied by Ward.⁸

The photophysical results of Ward can be summarised as follows:

(i) the room temperature emissions of rhodacyclopentadienes originate from singlet excited states, which have nanosecond lifetimes;

(ii) the λ_max values in absorption and emission are bathochromically shifted for both electron donating and withdrawing R-substituents; the electron withdrawing groups have a greater effect than the electron donating groups;

(iii) changing the X ligand has little effect on the overall absorption and emission wavelengths. The alkynyl-rhodacyclopentadienes e.g. TMSE-, Me₂N-C₆H₄-C≡C-
and Ph₂N-C₆H₄-C≡C-C≡C- have similar λ_{max} values in absorption and emission; and

(iv) rhodacyclopentadienes bearing the TMSE- ligand have higher quantum yields than those with other ligands.

Comparing the emission lifetimes of the rhodacyclopentadienes (type a, Figure 3.3) to the other luminescent metallacyclopentadienes (type b, Figure 3.3), the nanosecond fluorescence lifetimes of the rhodacyclopentadienes are an unusual photophysical property.

![Figure 3.3: Comparison of the structures of rhodacyclopentadienes to other luminescent metallacyclopentadienes.](image)

Indeed, most luminescent metallacyclopentadienes do not fluoresce because of a strong spin-orbit coupling (SOC) effect from the metal centre, which causes extremely fast intersystem crossing (ISC) to convert the singlet excited states to triplet excited states. Therefore, the singlet excited state lifetimes of most of the luminescent metallacyclopentadienes should be on the femto- to picosecond timescale.

Che et al. reported the luminescent properties of a Au^{(I)} complex [TEE][Au(PCy₃)]₄ ([TEE]H₄ = tetraethynylethene, Figure 3.4). Interestingly, despite the fact that the TEE ligand is directly bonded to the Au centres, this Au^{(I)} complex also exhibits a strong
fluorescent emission at $\lambda_{\text{max}} = 412$ nm ($\Phi = 0.22$, $\tau < 50$ ns), which can be confirmed from its short lifetime and small Stokes shift (1040 cm$^{-1}$). No phosphorescence was observed even at 77 K, and the group believed that its $T_1$ state must be very close in energy to the ground state, which leads to a very low $\Phi_p$ value.$^9$

![Figure 3.4: The structure of [TEE][Au(PCy$_3$)$_4$.](image)

Besides the Au$^{(I)}$ complex, another heavy atom complex, [Pt$^{(0)}$ (binap)$_2$] (binap = 2,2'-bis(diphenylphosphino)-1,1’binaphthyl), has also been reported regarding its interesting fluorescent properties.$^{10}$ Two kinds of fluorescence were observed at room temperature, (i) prompt fluorescence with a lifetime of 3.2 ps and $\Phi_f = 1.56 \times 10^{-4}$ and (ii) delayed-fluorescence with a lifetime of 1.25 $\mu$s and $\Phi_f = 0.12$. The reason that the emission with lifetime of 1.25 $\mu$s was assigned as delayed-fluorescence is because the $\Phi_f$ value decreases when the temperature decreases. This is due to the fact that the $^1$MLCT and $^3$MLCT states are very close in energy (1200 cm$^{-1}$), therefore, the $^3$MLCT state can return back to the $^1$MLCT state and fluoresce at ambient temperature. At low temperatures, the delayed-fluorescence was then replaced by phosphorescence with a lifetime of 1.2 $\mu$s. Importantly, the authors also pointed out that the ISC rate is dependent on the effectiveness of the SOC but not the value of the SOC constant of the heavy atom.$^{10}$
In the rhodacyclopentadiene systems, $\Phi_f$ values of up to 0.18 can be achieved (TMSE-rhodacyclopentadiene, $R = \text{NO}_2$, which has a lifetime of 1.2 ns). Preliminary results of TD-DFT calculations that have been carried out on a TMSE-rhodacyclopentadiene suggest that the main $S_0 \rightarrow S_1$ transition is mainly HOMO to LUMO. The calculations also reveal that the Rh centre makes some contribution to the HOMO, but very little contribution to the LUMO (Figure 3.5). In this case, the Rh-participation should be able to generate triplet excited states in the rhodacyclopentadienes. In order to investigate the SOC effect from the Rh centre, which facilitates the ISC process, rhodacyclopentadienes with TMSE-, Me- and Cl- ligands have been investigated with regard to the quantum yields of triplet excited state generation ($\Phi_\Delta$) using singlet oxygen sensitisation experiments, which were carried out by Dr. Andreas Steffen from our group, and the results are shown in Table 3.1.

**Figure 3.5:** HOMO-LUMO diagrams for the TMSE-rhodacyclopentadiene with phenyl groups.
The principle of the singlet oxygen sensitisation experiment is to use triplet oxygen molecules to quench the molecules in the triplet excited states, and form singlet oxygen molecules. The number of singlet oxygen molecules formed corresponds to the number of molecules originally in the triplet excited states. Thus, the quantum yields of the emission from singlet oxygen molecules are related to the quantum yields of triplet excited state generation in the rhodacyclopentadienes. The results in Table 3.1 show that the quantum yields of triplet excited state formation in rhodacyclopentadienes are higher than those of fluorescence. This indicates that ISC in rhodacyclopentadienes is more efficient than the fluorescence processes. Indirectly, the results also reveal that Rh centres possibly participate in the frontier orbitals of the excited states. The rhodacyclopentadienes with Me- and Cl- ligands seem to have a generally higher SOC influence than those with

*\( k_f = \Phi_f / \tau_f \) and \( k_\Delta = \Phi_\Delta / \tau_f \)
TMSE- (except the Me-rhodacyclopentadiene with R = CO$_2$Me). Nevertheless, the results in Table 3.1 also show that non-radiative decay processes, such as internal conversion (IC), are very effective in the Me- and Cl- rhodacyclopentadienes; therefore, low $\Phi_f$ values were observed (except for the Cl-rhodacyclopentadiene with R = CO$_2$Me).

In TMSE-rhodacyclopentadienes, the $k_\Delta$ values are much smaller compared to typical luminescent organometallic complexes ($k_\Delta \approx 10^{12}$ s$^{-1}$). Since the $k_f$ values are close to the $k_\Delta$ values, the fluorescent processes are competitive with ISC; therefore, fluorescence is observed.

To date, the photophysical properties of type a metallacyclopentadienes in Figure 3.3 have been investigated only briefly by Ward, although the photophysical properties of structurally related analogues with main group elements (EC$_4$), such as phospholes,$^{11}$ siloles,$^{12}$ and thiophenes$^{13}$ have been reported in depth. In general, most of the EC$_4$ analogues fluoresce in the visible region ($\lambda_{\text{max}} = 380 – 540$ nm) with $\pi \rightarrow \pi^*$ transitions. For example, the $\lambda_{\text{max}}$ values of the absorption in 2,5-bis($p$-R-arylethynyl)thiophenes were recorded in the range of 350 and 387 nm, which are assigned to $\pi \rightarrow \pi^*$ transitions, while the $\lambda_{\text{max}}$ values of emission were in the range 382 and 435 nm, depending on the substituent R at the phenyl rings. The quantum yields range from 0.19 - 0.33 with lifetimes of 0.21 - 0.40 ns.$^{13}$

Indeed, type a metallacyclopentadienes are more well-known for their catalytic function in [2+2+2] cycloadditions of alkynes to form benzene derivatives (Figure 3.6).$^{14-16}$ As shown in Figure 3.6, a metallacyclopentadiene ii is produced when the metal (M) reacts with two equivalents of alkyne. The coordination of the third alkyne to the metal centre in the metallacyclopentadiene can lead to the formation of $\pi$-complex iii. It
is then converted to complex v, either through direct (Diels-Alder) cycloaddition, or by insertion and then reductive elimination from an intermediate seven-membered metallacycle iv. By adding another alkyne to complex v, π-complex vi is formed, and then a benzene derivative is eliminated after another alkyne binds to the metal centre to regenerate complex i.\textsuperscript{15}

**Figure 3.6:** Catalytic cycle for the cyclotrimerisation of acetylene to benzene.\textsuperscript{15}

In term of synthesis, the preparation of the type a metallacyclopentadienes in Figure 3.3 is not straightforward. This is due to the regioselectivity problems that can lead to the formation of three different isomeric products (Figure 3.7.a, b, and c), as has been reported by Nishihara et al. in 1995.\textsuperscript{17}
Figure 3.7: Formation of three regioisomers from the coupling of symmetrical buta-1,3-diynes at a transition metal centre.\textsuperscript{17}

Hill and co-workers reported the formation of a ruthenacyclopentadiene by refluxing \([\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]\) (Figure 3.8.a) in the presence of excess diphenylbutadiyne in toluene.\textsuperscript{18} They observed an intermediate \(\pi\)-complex (Figure 3.8.b), before formation of the ruthenacyclopentadiene (Figure 3.8.c).

Figure 3.8: The formation of a ruthenacyclopentadiene.
The reaction in Figure 3.8 was very slow (12 – 14 h), even under reflux conditions. Interestingly, when xylene was used as the solvent, the reaction was complete after 10 minutes at reflux.\textsuperscript{18} In his report, Hill noted that the 2,5-bis(arylethynyl) rhodacyclopentadiene synthesis published by Marder and Rourke et al. in 2001 (Figure 3.1)\textsuperscript{7} is the only example of metallacycle formation by reductive coupling of butadiynes at room temperature without any regioselectivity problems.\textsuperscript{18}

3.1.1 Objectives and outline of synthetic routes

The main objective of this project was to explore, as well as to understand, the unusual photophysical behaviour of the rhodacyclopentadienes, e.g., long-lived singlet excited states and high-intensity fluorescence, and lack of phosphorescence. These unusual photophysical properties may be due to the small Rh contribution to the frontier orbitals of the excited states. In that case, the SOC effect from the Rh centre might not sufficient to facilitate a fast ISC to convert all of the singlet excited states to triplet excited states, and thus appreciable amounts of fluorescence are observed. In order to test this hypothesis, many photophysical experiments (e.g. low-temperature lifetime measurement and singlet oxygen sensitisation) were carried out.

Apart from the photophysical experiments, several series of rhodacyclopentadienes with different types of ligand were synthesised. The first type was designed based on the suggestions from Ward’s thesis,\textsuperscript{8} in which the rhodacyclopentadienes were synthesised by reacting two equivalents of a 1,4-bis(\(\rho\)-R-phenyl)buta-1,3-diyne with one equivalent of \([\text{RhX(PMe}_3]_4\), [where \(X = 4-\{4-(N,N\text{-di-}n\text{-hexylamino})\text{phenylethynyl}\}\text{phenylethynyl]-}
(DHAPEPE-) or trimethylsilylethynyl- (TMSE-)], as shown in Figure 3.9. The reason for preparing the DHAPEPE-rhodacyclopentadienes was to investigate the effect of an extended phenylene-ethynylene as a σ-donor at the X position on the photophysical properties of rhodacyclopentadienes. Hexyl groups were employed to improve solubility.

$$[\text{RhX(PMe}_3)_4] + 2 \text{ R} \rightarrow \text{ R}$$

$$\text{ THF} \rightarrow \text{ R}$$

$X = \text{DHAPEPE or TMSE}$

$R = \text{aryl}$

**Figure 3.9:** Synthetic route to the first type of rhodacyclopentadienes.

In addition, extended phenylene-ethynylene moieties were employed at the R positions. The two extended phenylene-ethynlenes with R groups employed were: i) $R = \text{C≡C-}(\text{C}_6\text{H}_4-p-\text{CO}_2-n\text{-C}_8\text{H}_{17})$ as an electron withdrawing group; and ii) $R = \text{C≡C-[C}_4\text{H}_4-p-\text{N}(n\text{-C}_6\text{H}_{13})_2]$ as an electron donating group. The reason for preparing these two rhodacyclopentadienes was to observe the effect of extended phenylene-ethynlenes at the R-positions on the photophysical properties of the rhodacyclopentadienes by comparing them to their shorter analogues, and also to observe whether any liquid crystal phase behaviour might be present. The absorption and emission spectra were expected to be red-shifted as the conjugation length increases in the extended phenylene-ethynylene analogues.

The calculation results from Figure 3.5 show that the two phenyl rings at the 3- and 4-positions of the rhodacyle ring do not have any contribution in the HOMO-LUMO transitions. Indeed, the two phenyl rings may act as quenchers by assisting in the loss of excitation energy through rotation, and subsequently reduce the emission efficiency. Therefore, more rigid rhodacyclopentadienes, which have a cyclohexyl loop instead of
two phenyl rings at the 3- and 4-positions of the rhodacycle ring have been designed. These rhodacyclopentadienes were synthesised by reacting one equivalent of the appropriate 1,12-bis(p-R-phenyl)-dodeca-1,3,9,11-tetrayne with one equivalent of [RhX(PMe$_3$)$_4$] ($X = \text{TMSE and Me}$), as shown in Figure 3.10.

![Figure 3.10: Synthetic route to the second type of rhodacyclopentadienes.](image)

The singlet oxygen sensitisation experiment results from Table 3.1 showed that the rhodacyclopentadienes with $\sigma$-donor ligands such as Me- and Cl- generally have slightly higher $\Phi_\Delta$ values compared to TMSE-rhodacyclopentadiene, which might be due to increased Rh-participation in the frontier orbitals. To explore this further, $\sigma$- and $\pi$-donor ligands [e.g. acetylacetonato, (acac-)] were used in order to increase the Rh contribution to the frontier orbitals further by destabilising the Rh d-orbitals. Faster ISC was expected from this type of rhodacyclopentadiene, which would generate triplet excited states more efficiently. This third type of rhodacyclopentadiene was synthesised by reacting one equivalent of [RhMe(PMe$_3$)$_4$] with one equivalent of acetylacetone (acac-), followed by reaction with one equivalent of the appropriate 1,12-bis(p-R-phenyl)dodeca-1,3,9,11-tetrayne to form bis(trimethylphosphine)-$\eta^2$-acetylacetonato-rhodacyclopentadienes (Figure 3.11).
3.2 Results and discussion

3.2.1 Synthesis and characterisation of tetrakis(trimethylphosphine)methyl rhodium, [RhMe(PMe₃)₄]

The synthetic route to the precursor, [RhMe(PMe₃)₄], is shown in Figure 3.12. RhCl₃·3H₂O was reacted with 1,5-cyclooctadiene (COD) under nitrogen for 3 h to produce [RhCl(COD)]₂ dimer. Alternatively, [RhCl₃·3H₂O] can also be reacted with cyclooctene (COE) to produce [RhCl(COE)]₂ dimer. Both [RhCl(COD)]₂ and [RhCl(COE)]₂ dimers can be used to synthesise [Rh(PMe₃)₄]Cl by reaction with excess trimethylphosphine (PMe₃) to give the product in over 80% yield.

![Synthetic route to the third type of rhodacyclopentadiene.](image)

**Figure 3.11:** Synthetic route to the third type of rhodacyclopentadiene.

**Figure 3.12:** The preparation of [RhMe(PMe₃)₄].
The preparation of [RhMe(PMe$_3$)$_4$] from [Rh(PMe$_3$)$_4$]Cl was based on the method described by Price et al. with some modifications. In a nitrogen-filled glovebox, LiMe was added dropwise to a solution of [Rh(PMe$_3$)$_4$]Cl in THF. The solution colour changed from orange to yellow indicating that [RhMe(PMe$_3$)$_4$] was forming in the reaction. After LiCl was filtered off and the solvent was removed, [RhMe(PMe$_3$)$_4$] (1) was obtained as a yellow solid in high yield (> 80%).

3.2.2 4-[4-(N,N-di-n-hexylamino)phenylethynyl]phenylethynylrhodacyclopentadienes (DHAPEPE-rhodacyclopentadienes)

3.2.2.1 Synthesis and characterisation

The 4-[4-(N,N-di-n-hexylamino)phenylethynyl]phenylethynyl-based rhodacyclopentadienes (DHAPEPE-rhodacyclopentadienes) were first prepared and studied by van Leeuwen in her M. Chem. fourth-year project. Some of the DHAPEPE-rhodacyclopentadienes were resynthesised in this work in order to complete the data collection for this series of rhodacyclopentadienes.

Firstly, [RhMe(PMe$_3$)$_4$] (1) was reacted with one equivalent of 4-(4-ethynylphenylethynyl)-N,N-di-n-hexylaniline (EPEDHA) to form a rhodium complex [Rh(DHAPEPE)(PMe$_3$)$_4$] (2), which was subsequently reacted with two equivalents of the appropriate 1,4-bis(p-R-phenyl)buta-1,3-diyne in THF forming the DHAPEPE-rhodacyclopentadienes (R = H, 3(a); R = OMe, 3(b); R = CF$_3$, 3(c); R = CO$_2$Me, 3(d); Figure 3.13).
Figure 3.13: Syntheses of the DHAPEPE-rhodacyclopentadienes.

However, care must be taken to add an accurate amount of the EPEDHA to [RhMe(PMe$_3$)$_4$]. Adding excess EPEDHA (> 1 equivalent), or adding it too quickly to [RhMe(PMe$_3$)$_4$], leads to the formation of $\textit{mer,trans-}[\text{RhH}(\equiv\text{C-R})_2(P\text{Me}_3)_3]$ (Figure 3.14), a process which has been reported by Marder et al.$^{21-23}$

Figure 3.14: Formation of $\textit{mer,trans-}[\text{RhH}(\equiv\text{C-R})_2(P\text{Me}_3)_3]$ by adding excess RC≡CH to [RhMe(PMe$_3$)$_4$].$^{21-23}$
After adding two equivalents of the appropriately substituted 1,4-bis(p-R-phenyl)buta-1,3-diyne to [Rh(DHAPEPE)(PMe$_3$)$_4$], the volatiles (i.e. solvent and dissociated PMe$_3$) were removed in vacuo and the flask was refilled with fresh THF. This process was repeated at least three times in order to remove the dissociated PMe$_3$ from [Rh(DHAPEPE)(PMe$_3$)$_4$]. The reactions were monitored by in situ $^{31}$P{$^1$H} NMR spectroscopy, and the rate of reaction was found to depend on the R substituent on the 1,4-bis(p-R-phenyl)buta-1,3-diyne. For example, the buta-1,3-diyne with the electron donating OMe groups reacted more slowly compared to those with electron withdrawing substituents, such as CO$_2$Me. This may be due to the fact that the electron donating property of OMe leads to weaker back-bonding from Rh to the C≡C bonds of the buta-1,3-diyne and subsequently slows down the reductive coupling process of butadiyne. The reactions took about 15 - 48 h to complete at room temperature. An intermediate $\pi$-complex can be observed in the $^{31}$P{$^1$H} NMR spectrum (Figure 3.15) if the reaction is not complete.

**Figure 3.15:** $^{31}$P{$^1$H} NMR spectrum (122 MHz, C$_6$D$_6$) of 3(b) after 3 h reaction.
The presence of the intermediate $\pi$-complex in the reaction 3(b) was confirmed by comparing the $^{31}\text{P}\{^1\text{H}\}$ NMR signals to those of a structurally related Rh $\pi$-complex (Figure 3.16) from the reaction of $[\text{Rh(C=S-SiMe}_3]\text{(PMe}_3)_4]$ with $(p\text{-CF}_3\text{-C}_6\text{H}_4)\text{-C=S-(p-}$

$\text{C}_6\text{H}_4\text{-CF}_3$) reported by Marder and Rourke et al.$^{23}$ The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in Figure 3.15 was obtained \textit{in situ} after 3 h reaction, and the signals of the $\pi$-intermediate complex appear as a doublet of doublets at -0.82 ppm and a doublet of triplets at -20.25 ppm, in a ratio of 2:1. This implies that there are two equivalent phosphorus atoms mutually $\textit{trans}$ to each other and one unique phosphorus atom. Based on the value of the Rh to phosphorus coupling constant ($J_{\text{Rh-P}}$) of ca. 96 Hz for the doublet of doublets and 118 Hz for the doublet of triplets, the unique phosphorus is subjected to a weaker $\textit{trans}$-influence than the other two phosphorus atoms. Therefore, the structure of the intermediate $\pi$-complex is believed to be similar to the one reported by Marder and Rourke et al.$^{23}$ In addition, the magnitudes of the $J_{\text{Rh-P}}$ values (118 Hz for the doublet of triplets) clearly indicate that the intermediate complex contains Rh(I) rather than Rh(III).

\[ \text{Figure 3.16: The structure of the intermediate complex that was reported by Marder and Rourke et al.}^{23} \]

In Figure 3.15, a small doublet of doublets was found at -6.28 ppm ($J_{\text{Rh-P}} = 92$ Hz, $J_{\text{P-P}} = 26$ Hz), which is assigned to the $\textit{mer,trans}$-$[\text{RhH(-C=S-R)}_2]\text{(PMe}_3)_3]$ complex [R =
C₆H₄-C≡C-C₆H₄-\textit{p}-N(n-C₆H₁₃₂). As mentioned before, the formation of this complex was probably due to adding the alkynyl ligand too quickly into the [RhMe(PMe₃)₄] solution.

The reaction was continuously stirred until the doublet of doublets at -0.82 ppm, as well as the doublet of triplets at -20.25 ppm, disappeared in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, indicating that the reaction had gone to completion [48 h for 3(b)]. The volatiles were removed \textit{in vacuo} and the product was washed with hexane. The crude product was purified by several recrystallisations from THF and hexane or C₆D₆ and hexane in order to obtain high-purity samples for photophysical studies. The purity of the compounds was determined by elemental analysis (EA), $^{31}\text{P}\{^1\text{H}\}$, $^1\text{H}$ NMR and mass spectroscopy. The isolated yields for pure compounds 3(a), 3(b), 3(c) and 3(d) are shown in Table 3.2, and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 3(a) is shown in Figure 3.17.

<table>
<thead>
<tr>
<th>Compound</th>
<th>R Group</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3(a)</td>
<td>H</td>
<td>85</td>
</tr>
<tr>
<td>3(b)</td>
<td>OMe</td>
<td>64</td>
</tr>
<tr>
<td>3(c)</td>
<td>CF₃</td>
<td>81</td>
</tr>
<tr>
<td>3(d)</td>
<td>CO₂Me</td>
<td>51</td>
</tr>
</tbody>
</table>
Based on the $^{31}$P{$^1$H} NMR patterns in Figure 3.17, the doublet of doublets and associated doublet of triplets in a ratio of 2:1 indicate that there are two equivalent phosphorus atoms and one unique phosphorus atom. The $J_{\text{Rh-P}}$ values of ca. 98 Hz for the doublet of doublets and 81 Hz for the doublet of triplets show that the unique phosphorus atom is incurring a stronger $trans$-influence than the two equivalent ones. This clearly implies that the unique phosphorus atom is $trans$ to the rhodacycle $\alpha$-carbon and is located in the rhodacycle plane, while the other two are located at axial positions, as seen in Figure 3.13.

The $^1$H NMR spectrum of 3(a) is shown in Figure 3.18. The twenty-eight aromatic protons from the phenyl rings give rise to signals in the region of 7.65 – 6.50 ppm, which confirms that there are six different phenyl rings present. The doublet ($J_{\text{P,H}} = 8$ Hz) at 1.36 ppm belongs to the PMe$_3$ ligand which is $trans$ to the $\alpha$-carbon of the rhodacycle ring, whereas the virtual triplet at 1.30 ppm is assigned to the two mutually $trans$ PMe$_3$ ligands which are located in the axial positions.
Interestingly, the chemical shifts of the NCH$_2$CH$_2$ signal in the $^1$H NMR spectra from the DHAPEPE fragment are significantly influenced by the R groups on the phenyl substituents the rhodacycle ring. The chemical shift of this proton signal is 1.22 ppm for R = H and OMe, whereas for R = CF$_3$ and CO$_2$Me, this signal is shifted to lower field at 1.38 and 1.40 ppm, respectively. This indicates that the electronic effect of the R groups can pass through the Rh centre and reach the end of the alkynyl ligand.

The IR spectra of the complexes show four signals to be present in the region between 2000 and 2200 cm$^{-1}$, which indicates that there are four allowed C= C stretching modes present in each complex. An additional strong band at 1721 cm$^{-1}$ can be observed in the IR spectrum of 3(d), which is assigned to the C=O stretches from the CO$_2$Me groups.
3.2.2.2 Photophysical studies

The photophysical data for the DHAPEPE-rhodacyclopentadienes 3(a), 3(c) and 3(d) are given in Table 3.3, and the absorption and emission spectra of these complexes are shown in Figure 3.19.

![Table 3.3](image)

Table 3.3: Summary of the photophysical data for 3(a), 3(c) and 3(d).

<table>
<thead>
<tr>
<th>Compound</th>
<th>λ_{max} ABS (nm)</th>
<th>ε (M^{-1} cm^{-1})</th>
<th>λ_{max} EM (nm)</th>
<th>Stokes shift (cm^{-1})</th>
<th>Φ</th>
<th>τ_f (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3(a), R = H</td>
<td>454</td>
<td>27000</td>
<td>497</td>
<td>1900</td>
<td>0.04</td>
<td>0.26 (82%)</td>
</tr>
<tr>
<td>3(c), R = CF_3</td>
<td>465</td>
<td>31000</td>
<td>510</td>
<td>1900</td>
<td>0.04</td>
<td>0.18 (82%)</td>
</tr>
<tr>
<td>3(d), R = CO_2Me</td>
<td>484</td>
<td>26000</td>
<td>535</td>
<td>2010</td>
<td>0.14</td>
<td>0.55 (85%)</td>
</tr>
</tbody>
</table>

Note: All of the data (except ε) above were recorded in degassed toluene solution at room temperature. ε values were recorded in non-degassed toluene solution. No data were recorded for 3(b) due to sample decomposition in low concentration solutions.

The progressional spacings in the emission spectra (Figure 3.19) are in the range of 1320 – 1290 cm^{-1}. The absorption and emission maxima (λ_{max}) for those DHAPEPE-rhodacyclopentadienes with electron withdrawing substituents such as R = CF_3 [3(c)] and CO_2Me [3(d)] are red-shifted compared to those of 3(a). This can be rationalised by the fact that the rhodacyclopentadienes with these electron withdrawing groups have a smaller energy gap between the excited and ground states. However, comparing the λ_{max} values of absorption and emission between the DHAPEPE- and the TMSE-rhodacyclopentadienes reported by Ward (Table 1.5, Chapter 1), the extended phenylene-ethynylene alkynyl ligand in the DHAPEPE-rhodacyclopentadienes did not impart any bathochromic effect.
All of the lifetimes of the DHAPEPE-rhodacyclopentadienes are on the nanosecond timescale. These results are parallel to the results from Ward, and confirm that the emissions arise from fluorescence, i.e., they originate from singlet excited states. As mentioned before, the fluorescence emission from the DHAPEPE-rhodacyclopentadienes is an unusual photophysical property because fluorescence is rarely observed in metallacyclopentadiene complexes, especially those containing Rh. In most cases, Rh complexes do not fluoresce, but phosphoresce at 77 K in a rigid glass with micro- to
millisecond lifetimes. The dominant phosphorescent emissions are mainly from ligand-centred $3\pi \rightarrow \pi^*$ transitions with small amounts of metal contributions.$^{24-27}$

The DHAPEPE-rhodacyclopentadienes were observed to have two fluorescence lifetime ($\tau_f$) components compared to one for the TMSE-series in Table 1.5. This may be due to partial decomposition of the DHAPEPE-rhodacyclopentadienes when they were prepared in low-concentration ($10^{-6}$ M) solutions. Fast decomposition was noticed for the more electron rich compound, 3(b), when it was prepared for lifetime measurement: 30 minutes after preparation, the emission colour was found to have changed from yellow to blue, even in degassed solution, which indicated that decomposition had occurred. However, the fact that two lifetime components occur in essentially identical ratios for all three compounds, which should have different stabilities, suggests that an alternative process might be responsible such as a second localised transition.

The $\Phi_f$ values of the DHAPEPE-series are relatively low compared to the TMSE-rhodacyclopentadienes in Table 1.5, which are in the range of $\Phi_f = 0.03 - 0.18$. This may be due to the excitation energy lost through the long alkynyl ligand, which increases the quenching possibilities from C-H stretching motions and poor rigidity in the hexyl chains. For example, the $\Phi_f$ values for TMSE-rhodacyclopentadienes with $R = H$ and CF$_3$ in Ward’s study$^8$ were reported as 0.15 and 0.08, respectively, but for the DHAPEPE-rhodacyclopentadienes with the same $R$-substituents, the $\Phi_f$ values are 0.04. However, the $\Phi_f$ values for the rhodacyclopentadienes with $R = CO_2Me$ are very similar: 0.14 (for the DHAPEPE-rhodacyclopentadiene) and 0.16 (for the TMSE-analogue).

The fluorescence rate constant ($k_f$) can be calculated from the formula $k_f = \Phi_f/\tau_f$; thus, the $k_f$ values in DHAPEPE-rhodacyclopentadienes 3(a), 3(c) and 3(d) must be in the
range of $0.26 - 2.54 \times 10^8 \text{ s}^{-1}$. If it is assumed, and this is unlikely, that no IC from the $S_1$ state is occurring, the $\Phi_\Delta$ values for 3(a) and 3(c) would be 0.96. As the rate constant of ISC ($k_\Delta$) is calculated from the formula $k_\Delta = \Phi_\Delta/\tau_f$, the $k_\Delta$ values of these three DHAPEPE-rhodacyclopentadienes can be up to $5 \times 10^9 \text{ s}^{-1}$ [for 3(c)]. This value is still over two orders of magnitude slower than the ISC rates of typical organometallic complexes, which are in the range of $10^{12} \text{ s}^{-1}$. This explains why significant fluorescence can occur in the DHAPEPE-rhodacyclopentadienes.

3.2.3 Me-rhodacyclopentadiene with NMe$_2$ groups at the para-position of the phenyl rings

3.2.3.1 Synthesis and characterisation

The synthesis of a Me-rhodacyclopentadiene bearing -NMe$_2$ groups at the para-positions of the phenyl rings (Figure 3.20) is much more difficult than those with other para-substituents because 1,4-bis($p,N,N$-dimethylaminophenyl)butadiyne contains strong electron donor substituents, which significantly affect the back-bonding from the Rh centre to the C≡C bonds and slows down the reaction. In this case, the reaction needs to be heated in order for it to reach completion at a reasonable rate. However, the optimum synthesis conditions were not found by Ward.$^8$ In a continuation of Ward’s work, one of the objectives in the early part of this project was to ascertain the optimum synthesis conditions for this rhodacyclopentadiene.
In the synthesis of 4, two equivalents of 1,4-bis(p-N,N-dimethylaminophenyl)butadiyne were added to [RhMe(PMe$_3$)$_4$] in degassed THF solution, the volatiles (e.g. THF and PMe$_3$) were removed in vacuo and the flask was refilled with fresh THF. This process was repeated three times. Then, the reaction was heated at 50 °C for five days under nitrogen condition, and the reaction progress was monitored in situ using $^{31}$P{${}^1$H} NMR spectroscopy. It is worth noting that the reaction time is temperature-dependent: at 45 °C, the reaction took about six weeks to complete; but surprisingly, it can be completed within five days at 50 °C, although there is only a 5 °C difference in temperature.

When the reaction was complete, the solvent was removed in vacuo, and the crude product was crystallised via slow diffusion of hexane vapour into a concentrated toluene solution in order to obtain high-purity product with EA results within the acceptable range. In the mass spectrum [electrospray (ES), positive ion mode], the major signal occurred at $m/z = 907$, which is associated with the fragment [M$^+$ - CH$_3$].

The $^{31}$P{${}^1$H} NMR spectrum of 4 is similar to those shown in Figure 3.17, which indicates that the PMe$_3$ ligands in 4 are at similar positions to those in 3(a) - 3(d). The $J_{\text{Rh-P}}$ values (dd, 106 Hz; dt, 89 Hz) are higher than those in 3(a) - 3(d), which confirms that the Me- group is a stronger donor ligand that increases the electron density at the Rh
centre. In the $^1$H NMR spectrum, the protons from this Me- ligand appear as a doublet of quartets (dq) at 0.15 ppm ($^2J_{\text{Rh-H}} = 2$ Hz, $^3J_{\text{P-H}} = 7$ Hz) because they are coupled with the Rh centre and three PMe$_3$ ligands. The coupling to Rh is smaller than the couplings to P, and therefore a doublet of quartets is observed. Four singlets for the protons of the NMe$_2$ groups were observed in the 2.50 – 2.36 ppm region, which confirms that they are in four different environments. Similarly, for the aromatic protons, there are eight sets of doublets from four different phenyl rings, which appear in the 7.68 – 6.43 ppm region.

In the IR spectrum, a band appears at 2121 cm$^{-1}$ which is assigned to a C≡C stretching mode of the two ethynyl moieties at the 2- and 5-positions of the rhodacycle ring.

### 3.2.3.2 Crystallographic data for 4

The crystallographic data for 4 are listed in Table 3.4. Me-rhodacyclopentadiene 4 crystallises in the triclinic space group $P\overline{1}$ and the molecular structure is shown in Figure 3.21.

![Molecular structure of 4](image)

**Figure 3.21:** Molecular structure of 4, with thermal ellipsoids plotted at 50% probability (hydrogen atoms, H$_2$O and C$_7$H$_8$ molecules are omitted for clarity).
Table 3.4: Crystallographic data for 4.

<table>
<thead>
<tr>
<th>Compound</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>$0.85(C_{50}H_{70}N_{4}P_{3}Rh)0.15(C_{49}H_{67}ClN_{4}P_{3}Rh)0.5(C_{7}H_{8})0.5(H_{2}O)$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>981.06</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>120(2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$P1$</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>9.6364(6)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>15.4817(10)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>18.2839(14)</td>
</tr>
<tr>
<td>$\alpha$ (°)</td>
<td>99.844(14)</td>
</tr>
<tr>
<td>$\beta$ (°)</td>
<td>101.008(13)</td>
</tr>
<tr>
<td>$\gamma$ (°)</td>
<td>102.875(15)</td>
</tr>
<tr>
<td>Volume (Å³)</td>
<td>2544.4(3)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Density (calculated) (Mg/m³)</td>
<td>1.280</td>
</tr>
<tr>
<td>Absorption coefficient (mm⁻¹)</td>
<td>0.478</td>
</tr>
<tr>
<td>Crystal size (mm³)</td>
<td>0.13 x 0.09 x 0.05</td>
</tr>
<tr>
<td>$\Theta$ range for data collection (°)</td>
<td>2.23 to 29.98</td>
</tr>
<tr>
<td>Reflection collected</td>
<td>15803</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>8950</td>
</tr>
<tr>
<td>Data / Restraints / Parameters</td>
<td>8950 / 6 / 583</td>
</tr>
<tr>
<td>Final R indices [I&gt;2σ(I)]</td>
<td>$R1 = 0.0491$ $wR2 = 0.0986$</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>$R1 = 0.0901$ $wR2 = 0.1104$</td>
</tr>
</tbody>
</table>

In compound 4, the bond length of Rh-C1 [2.201(4) Å] is slightly longer than Rh-C15 [2.087(4) Å] and Rh-C18 [2.078(4) Å], because C1 is sp³-hybridised, whereas C15 and C18 are sp²-hybridised. The bond lengths of Rh-P1 [2.3049(13) Å] and Rh-P2 [2.3088(13) Å] are shorter than Rh-P3 [2.3544(13) Å], which indicates that the $\alpha$-carbon has a stronger trans-influence than the PMe₃ ligand. The two NMe₂- phenyl rings at C16 and C17 are twisted suggesting the presence of unfavourable steric interactions, which
prevent a co-planar arrangement of these two phenyl rings. The C-C≡C-C moiety at C15 is slightly more distorted from linearity than the one at C18, by comparison of the bond angles of C15-C19-C20 [173.9(5)°] and C18-C39-C40 [176.6(5)°]. The NMe$_2$ group at C36 is disordered between positions a and b with equal occupancies. In addition, the methyl ligand, -C1H$_3$, at the Rh centre is partially refined as a chlorine (Cl) atom with a 0.15 probability. The Cl incorporation probably arises from LiCl, which was formed during the [RhMe(PMe$_3$)$_4$] synthesis. Indeed, this problem was also found in the molecular structures of the other Me-rhodacyclopentadienes (e.g. Ward’s Me-rhodacyclopentadienes). However, the Cl contamination is believed very small because other spectroscopic data such as mass spectra, and $^{31}$P($^1$H) and $^1$H NMR spectra did not detect the presence of any Cl-rhodacyclopentadienes. In addition, it is also possible that it is Br rather than Cl which is present, arising from LiBr in the MeLi used. In this case, even less Br would be required to account in the extra electron density peak. It is also likely that the halide is enriched in the crystals due to lower solubility of the halide complex.

3.2.3.3 Photophysical studies

Photophysical data for 4 are presented in Table 3.5, and the absorption and emission spectra are shown in Figure 3.22.
Table 3.5: Summary of the photophysical data of 4.

<table>
<thead>
<tr>
<th>$\lambda_{\text{max}}$ ABS (nm)</th>
<th>$\varepsilon$ (mol$^{-1}$ cm$^{-1}$ dm$^3$)</th>
<th>$\lambda_{\text{max}}$ EM (nm)</th>
<th>Stokes shift (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>474</td>
<td>40000</td>
<td>523</td>
<td>2000</td>
</tr>
</tbody>
</table>

Note: all of the data above (except $\varepsilon$) were measured in degassed toluene at room temperature. $\varepsilon$ value was recorded in non-degassed toluene solutions.

Figure 3.22: Absorption and emission spectra of 4.

Me-rhodacyclopentadiene 4 exhibits a yellow emission at $\lambda_{\text{max}} = 523$ nm. Similar to 3(a), 3(c) and 3(d), 4 also has a small Stokes shift (ca. 2000 cm$^{-1}$), which indicates that the emission originates from the singlet excited states. The progressional spacings of ca. 1250 cm$^{-1}$ in the emission spectrum are probably due to a stretching mode of the $\pi$-system in the structure.
3.2.4 Trimethylsilylethynyl- (TMSE-) rhodacyclopentadienes containing extended phenylene-ethynylene groups

3.2.4.1 Synthesis and characterisation

From the photophysical results of the DHAPEPE-rhodacyclopentadienes, we know that the extended phenylene-ethynylene alkynyl ligand on the Rh centre does not impart any bathochromic effects on the absorption and emission $\lambda_{\text{max}}$ values. In addition, the extended alkynyl ligand decreases the $\Phi$ values compared to shorter alkynyl ligands such as TMSE-. Two TMSE-rhodacyclopentadienes containing extended phenylene-ethynylene moieties at the 2- and 5-positions of the rhodacycle ring were thus synthesised (Figure 3.23). The reason for including these extended moieties was to study their effects on the photophysical properties of the rhodacyclopentadienes by comparison to the simple TMSE-rhodacyclopentadienes reported by Ward. Another reason was to see whether these two systems might display liquid crystal phase behaviour.

Figure 3.23: Synthetic route to TMSE-rhodacyclopentadienes containing extended phenylene-ethynylene moieties at the 2- and 5-positions of the rhodacycle ring.
About 1.2 equivalents of trimethylsilylacetylene (TMSA) in THF solution were added dropwise to a stirred solution of [RhMe(PMe₃)₄] in THF to give 5. Then two equivalents of the appropriate extended bis(p-R-phenylethynyl)diarylbutadiyne with different R substituents [R = C≡C₆H₄-p-CO₂-n-C₈H₁₇ and C≡C₆H₄-p-N(n-C₆H₁₃)₂, the syntheses of which have already been discussed in Chapter 2] were added, respectively, to solutions of 5, and the volatiles were repeatedly removed in vacuo and fresh solvent was added at least three times, to form the respective 6(a) and 6(b) [R = C≡C₆H₄-p-CO₂-n-C₈H₁₇, 6(a); R = C≡C₆H₄-p-N(n-C₆H₁₃)₂, 6(b)]. The colour of the solutions changed from yellow to dark red indicating that the rhodacyclopentadienes were forming in the reaction.

The progress of both reactions was monitored in situ using $^{31}$P{$^1$H} NMR spectroscopy, and similar NMR spectra to those shown Figure 3.17 were obtained when the reactions were complete. The pattern of a doublet of doublets associated with a doublet of triplets (in a 2:1 ratio) indicates that there are two phosphine environments. The $J_{Rh-P}$ values of ca. 97 Hz for the doublet of doublets and 82 Hz for the doublet of triplets, which are similar to the DHAPEPE-rhodacyclopentadienes, indicate that one phosphine is located in the plane of the rhodacycle, while the other two phosphines are located at mutually-trans axial positions.

At room temperature, the volatility of TMSA can result in some loss of the reagent and thus some unreacted [RhMe(PMe₃)₄] remaining in the solution following reaction with the alkyne. When two equivalents of butadiyne are then added to the solution, two kinds of rhodacyclopentadiene will be formed, namely TMSE-based and Me-based...
rhodacyclopentadienes, which reduces the isolated yields of the desired product. This is a common problem when synthesising the TMSE-rhodacyclopentadienes.

### 3.2.4.2 Photophysical studies

The absorption and emission spectra of 6(a) and 6(b) are shown in Figure 3.24, and a summary of the photophysical data for 6(a) and 6(b) is given in Table 3.6.

![Absorption and Emission Spectra](image)

**Figure 3.24:** Absorption (top) and emission (bottom) spectra of 6(a) and 6(b).
Table 3.6: Summary of the photophysical data of 6(a) and 6(b), and comparison of the photophysical data between 6(a) and 6(b), and the simple TMSE-rhodacyclopentadiene (R = CO₂Me) reported by Ward.²⁸

<table>
<thead>
<tr>
<th>Compounds, R</th>
<th>λ_{max} ABS (nm)</th>
<th>ε (M⁻¹ cm⁻¹)</th>
<th>λ_{max} EM (nm)</th>
<th>Stokes shift (cm⁻¹)</th>
<th>Φ</th>
<th>τ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6(a), R = C≡C-C₆H₄-p-CO₂-n-C₈H₁₇</td>
<td>500</td>
<td>40000</td>
<td>556</td>
<td>2010</td>
<td>0.02</td>
<td>0.096 (47%)</td>
</tr>
<tr>
<td>6(b), R = C≡C-C₆H₄-p-N(n-C₆H₁₃)₂</td>
<td>494</td>
<td>48000</td>
<td>549</td>
<td>2030</td>
<td>0.01</td>
<td>0.059 (27%)</td>
</tr>
<tr>
<td>R = CO₂Me</td>
<td>485</td>
<td>21000</td>
<td>536</td>
<td>1960</td>
<td>0.16</td>
<td>1.640 (73%)</td>
</tr>
</tbody>
</table>

Note: All data above (except ε) were recorded in degassed toluene solution at room temperature. ε values were recorded in non-degassed toluene solution.

From the results in Figure 3.24, the λ_{max} values for absorption and emission of the rhodacyclopentadiene with the electron withdrawing substituent, namely R = C≡C-C₆H₄-p-CO₂-n-C₈H₁₇ [6(a)], are slightly red-shifted compared to that with the electron donating substituent, R = C≡C-C₆H₄-p-N(n-C₆H₁₃)₂, [6(b)]. This indicates that the energy gap between the excited and ground states in the compound containing the electron withdrawing substituent is smaller than that in the compound with the electron donating substituent. The small Stokes shifts (~2000 cm⁻¹) and the nanosecond lifetimes of these two rhodacyclopentadienes imply that the emissions are from fluorescence, which occurs from singlet excited states.

The Φ_f values for these two rhodacyclopentadienes are only 0.02 [6(a)] and 0.01 [6(b)]. These low Φ_f values are possibly due to external quenching processes, such as energy transfer from the excited molecules to solvent molecules, and the increased molecular vibrations and rotations when the molecular size increases.²⁸ On the other hand, they are also possibly due to the flexibility of the long alkyl chains in 6(a) and 6(b). In addition,
the low $\Phi_f$ values in $6(\text{a})$ and $6(\text{b})$ might be also due to efficient ISC leading to non-radiative triplet excited states.

A comparison of the photophysical data between the extended phenylene-ethynylene-rhodacyclopentadiene and its shorter analogue with $R = \text{CO}_2\text{Me}$ is also given in Table 3.6. The $\lambda_{\text{max}}$ values of $6(\text{a})$ and $6(\text{b})$ in both absorption and emission showed bathochromic shifts compared to the simple TMSE-rhodacyclopentadiene. These bathochromic shifts are due to the increase in the conjugation lengths of the extended phenylene-ethynylene moieties that consequently reduces the HOMO-LUMO gap, which is assumed to dominate the transition (Figure 3.5).

A smaller energy gap between the HOMO and LUMO can increase the Frank-Condon factors because of increasing overlap between the ground and excited states, leading to more effective IC processes. Thus, the $\Phi$ values of both $6(\text{a})$ and $6(\text{b})$ are lower than the simple TMSE-rhodacyclopentadienes.

The extinction coefficient values ($\varepsilon$) of both $6(\text{a})$ and $6(\text{b})$ are greater than those of the simple TMSE-rhodacyclopentadienes. This is consistent with the result of Ward, who found that the extended bis(arylethynyl)diarylbutadiynes themselves have greater $\varepsilon$ values than the shorter butadiyne analogues (see the Introduction section in Chapter 2).

Neither $6(\text{a})$ nor $6(\text{b})$ shows any liquid crystal phases when they were analysed by a transmission polarised light microscope, fitted with a temperature-controlled hot-stage. The melting points of $6(\text{a})$ and $6(\text{b})$ are 102 – 104 and 112 – 113 °C, respectively. Both compounds melted directly into isotropic liquids. One possible reason for the lack of liquid crystal phases in both compounds may be that the alkyl chains are not sufficiently long.
3.2.5 Second-generation TMSE-rhodacyclopentadienes

The preliminary results of DFT calculations (Figure 3.5) show that the two phenyl rings at the 3- and 4-positions of the rhodacycle ring are not involved in the frontier orbitals; indeed, they are suspected to act as luminescence quenchers because both rings can rotate and lead to loss of excitation energy. Therefore, second-generation rhodacyclopentadienes with a more rigid structure have been designed by attaching a cyclohexyl loop at the 3- and 4-positions of the rhodacycle ring in order to eliminate the quenching possibilities from the two phenyl rings at these two positions.

3.2.5.1 Synthesis and characterisation

The synthesis of the second-generation TMSE-rhodacyclopentadienes (Figure 3.25) is similar to the synthesis of the first-generation TMSE-rhodacyclopentadienes. The only difference is the use of 1,12-(p-R-phenyl)dodeca-1,3,9,11-tetraynes, the syntheses of which have been discussed in Chapter 2, rather than using 1,4-di(p-R-phenyl)buta-1,3-diynes.

![Figure 3.25: Synthetic route to the second-generation TMSE-rhodacyclopentadienes.](image)

[Figure 3.25: Synthetic route to the second-generation TMSE-rhodacyclopentadienes.]
One equivalent of the appropriate 1,12-(p-R-phenyl)dodeca-1,3,9,11-tetrayne was added to the [Rh(C≡C-SiMe₃)(PMe₃)₄] in THF solution and the reactions were stirred at room temperature for 15 h to give the respective second-generation TMSE-rhodacyclopentadienes [R = H, 7(a); R = SMe, 7(b); R = C≡C-SiMe₃, 7(e); R = CO₂Me, 7(d); R = BMes₂ (Mes = mesityl), 7(e)]. As the reaction progressed, the solvent was repeatedly removed in vacuo and the flask was refilled with fresh THF in order to remove the dissociated PMe₃. The solution colour changed from yellow to yellow-brown, with strong yellow-green luminescence observed for 7(a). Upon completion, the ³¹P{¹H} NMR spectra were similar to those shown in Figure 3.17. As expected, the $J_{\text{Rh-P}}$ value of the doublets of doublets is ca. 90 Hz and for the doublets of triplets is ca. 83 Hz. In their ¹H NMR spectra [e.g. 7(d) in Figure 3.26], two additional multiplets appear at 2.85 and 1.62 ppm, indicating the presence of the -CH₂-CH₂- moiety from the cyclohexyl ring.

Figure 3.26: ¹H NMR spectrum (400 MHz, C₆D₆) of 7(d).
Two different proton environments are observed for the CO$_2$Me groups. This is due to the fact that two different ligands, C≡C-SiMe$_3$ and PMe$_3$, are located in the equatorial plane of rhodacyclopentadiene. For the same reason, there are also two sets of signal for aromatic protons in the spectrum, which represent the presence of two different phenyl ring environments in the rhodacyclopentadiene.

TMSE-rhodacyclopentadiene 7(f) [R = C≡CH] was synthesised from 7(c) by deprotecting the para-substituted trimethylsilyl (TMS) groups on the phenyl rings (Figure 3.27). Compound 7(c) was stirred with four equivalents of nBu$_4$NF (TBAF, 1M solution in THF) in degassed THF at room temperature for 15 h. Once the reaction was complete, the solvent was removed in vacuo, and the residual solid was dissolved in CH$_2$Cl$_2$ and then washed with water, in order to remove the TBAF. Interestingly, the TMS group of the TMSE ligand was not affected by the deprotection conditions. The growth of single crystals of the compound was attempted via slow diffusion of a layer of hexane into a concentrated solution in degassed THF. Unfortunately, a black solid was found at the bottom of the vial, indicating that some decomposition during the recrystallisation attempt. However, re-dissolving in C$_6$D$_6$ and subsequent filtration allowed the recovery of a sample which was pure by $^{31}$P{$^1$H} NMR and elemental analysis.

**Figure 3.27:** Deprotection of the TMS groups at the para-positions of the phenyl rings.
3.2.5.2 Crystallographic data for 7(a), 7(b) and 7(d)

The crystallographic data for 7(a), 7(b) and 7(d) are listed in Table 3.7. Molecular structures of 7(a), 7(b) and 7(d) were obtained from single-crystal X-ray diffraction data.

Table 3.7: Crystallographic data for 7(a), 7(b) and 7(d).

<table>
<thead>
<tr>
<th>Compound</th>
<th>7(a)</th>
<th>7(b)</th>
<th>7(d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{38}H_{54}P_{3}RhSi</td>
<td>C_{40}H_{58}P_{3}RhS_{2}Si</td>
<td>C_{43}H_{58}O_{3}P_{3}RhSi·C_{6}H_{14}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>734.72</td>
<td>826.89</td>
<td>936.97</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>120(2)</td>
<td>120(2)</td>
<td>120(2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Triclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>(P2_1/c)</td>
<td>(P\bar{1})</td>
<td>(P2_1/c)</td>
</tr>
<tr>
<td>(a) (Å)</td>
<td>9.1905(9)</td>
<td>10.404(1)</td>
<td>9.513(3)</td>
</tr>
<tr>
<td>(b) (Å)</td>
<td>27.141(3)</td>
<td>11.562(1)</td>
<td>18.154(6)</td>
</tr>
<tr>
<td>(c) (Å)</td>
<td>15.4133(16)</td>
<td>20.121(2)</td>
<td>28.872(8)</td>
</tr>
<tr>
<td>(\alpha) (º)</td>
<td>90.00</td>
<td>76.48(2)</td>
<td>90.00</td>
</tr>
<tr>
<td>(\beta) (º)</td>
<td>94.39(1)</td>
<td>89.22(2)</td>
<td>95.16(2)</td>
</tr>
<tr>
<td>(\gamma) (º)</td>
<td>90.00</td>
<td>64.46(2)</td>
<td>90.00</td>
</tr>
<tr>
<td>Volume (Å(^3))</td>
<td>3833.5(7)</td>
<td>2112.6(4)</td>
<td>4966(3)</td>
</tr>
<tr>
<td>(Z)</td>
<td>4</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated) (Mg/m(^3))</td>
<td>1.273</td>
<td>1.300</td>
<td>1.253</td>
</tr>
<tr>
<td>Absorption coefficient (mm(^{-1}))</td>
<td>0.626</td>
<td>0.671</td>
<td>0.50</td>
</tr>
<tr>
<td>Crystal size (mm(^3))</td>
<td>0.29 x 0.18 x 0.16</td>
<td>0.40 x 0.20 x 0.06</td>
<td>0.25 x 0.10 x 0.05</td>
</tr>
<tr>
<td>(\Theta) range for data collection (º)</td>
<td>2.61 to 29.98</td>
<td>2.18 to 29.97</td>
<td>2.24 to 29.62</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>39036</td>
<td>30305</td>
<td>43458</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>10880</td>
<td>11813</td>
<td>8743</td>
</tr>
<tr>
<td>Data / Restraints / Parameters</td>
<td>10880 / 0 / 412</td>
<td>11813 / 0 / 452</td>
<td>8743 / 0 / 532</td>
</tr>
<tr>
<td>Final R indices [I&gt;2(\sigma) (I)]</td>
<td>(R_1 = 0.0316)</td>
<td>(R_1 = 0.0291)</td>
<td>(R_1 = 0.0907)</td>
</tr>
<tr>
<td>(wR_2 = 0.0665)</td>
<td>(wR_2 = 0.0678)</td>
<td>(wR_2 = 0.1599)</td>
<td></td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>(R_1 = 0.0436)</td>
<td>(R_1 = 0.0378)</td>
<td>(R_1 = 0.1115)</td>
</tr>
<tr>
<td>(wR_2 = 0.0701)</td>
<td>(wR_2 = 0.0713)</td>
<td>(wR_2 = 0.1656)</td>
<td></td>
</tr>
</tbody>
</table>
Orange monoclinic (space group P2$_1$/c) single crystals of 7(a) formed in a 5 mm diameter glass tube by slow diffusion of a layer of hexane into a concentrated C$_6$D$_6$ solution. The molecular structure of 7(a) is shown in Figure 3.28, and selected bond lengths and angles are listed in Table 3.8.

**Table 3.8:** List of selected bond lengths (Å) and angles (º) for 7(a), 7(b) and 7(d).

<table>
<thead>
<tr>
<th></th>
<th>7(a)</th>
<th>7(b)</th>
<th>7(d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh-P1</td>
<td>2.3153(5)</td>
<td>2.3163(7)</td>
<td>Disorder</td>
</tr>
<tr>
<td>Rh-P2</td>
<td>2.3160(5)</td>
<td>2.3111(7)</td>
<td>Disorder</td>
</tr>
<tr>
<td>Rh-P3</td>
<td>2.3606(5)</td>
<td>2.3608(5)</td>
<td>Disorder</td>
</tr>
<tr>
<td>Rh-C1</td>
<td>2.0479(18)</td>
<td>2.0458(19)</td>
<td>Disorder</td>
</tr>
<tr>
<td>Rh-C15</td>
<td>2.0806(17)</td>
<td>2.0857(16)</td>
<td>Disorder</td>
</tr>
<tr>
<td>Rh-C18</td>
<td>2.0993(17)</td>
<td>2.1010(18)</td>
<td>Disorder</td>
</tr>
<tr>
<td>C1≡C2</td>
<td>1.218(2)</td>
<td>1.210(2)</td>
<td>1.207(9)</td>
</tr>
<tr>
<td>C19≡C20</td>
<td>1.206(2)</td>
<td>1.208(2)</td>
<td>1.203(9)</td>
</tr>
<tr>
<td>C31≡C32</td>
<td>1.205(3)</td>
<td>1.207(2)</td>
<td>1.217(8)</td>
</tr>
<tr>
<td>C15=C16</td>
<td>1.365(2)</td>
<td>1.368(2)</td>
<td>1.371(9)</td>
</tr>
<tr>
<td>C17=C18</td>
<td>1.374(2)</td>
<td>1.371(2)</td>
<td>1.360(10)</td>
</tr>
<tr>
<td>C16-C17</td>
<td>1.447(2)</td>
<td>1.447(2)</td>
<td>1.429(8)</td>
</tr>
<tr>
<td>C16-C27</td>
<td>1.516(2)</td>
<td>1.515(2)</td>
<td>1.494(10)</td>
</tr>
<tr>
<td>C27-C28</td>
<td>1.523(3)</td>
<td>1.523(3)</td>
<td>1.504(12)</td>
</tr>
<tr>
<td>C28-C29</td>
<td>1.526(3)</td>
<td>1.523(3)</td>
<td>1.526(10)</td>
</tr>
<tr>
<td>C29-C30</td>
<td>1.521(3)</td>
<td>1.524(2)</td>
<td>1.509(11)</td>
</tr>
<tr>
<td>C17-C30</td>
<td>1.514(2)</td>
<td>1.508(2)</td>
<td>1.508(10)</td>
</tr>
<tr>
<td>P1-Rh-P2</td>
<td>169.571(18)</td>
<td>170.535(16)</td>
<td>Disorder</td>
</tr>
<tr>
<td>C1-Rh-C18</td>
<td>173.81(7)</td>
<td>173.47(6)</td>
<td>Disorder</td>
</tr>
<tr>
<td>P3-Rh-C15</td>
<td>173.00(5)</td>
<td>172.85(5)</td>
<td>Disorder</td>
</tr>
</tbody>
</table>
Figure 3.28: Molecular structure of 7(a), the hydrogen atoms are omitted for clarity (thermal ellipsoids drawn at 50% probability).

Compound 7(b) was recrystallised via slow vapour diffusion of hexane into a concentrated solution of 7(b) in degassed THF. Orange crystals grew at the bottom of the vial overnight. They crystallised in the triclinic space group \( P\bar{1} \). The molecular structure of 7(b) is shown in Figure 3.29, and selected bond lengths and angles are listed in Table 3.8.

Figure 3.29: Molecular structure of 7(b), the hydrogen atoms are omitted for clarity (thermal ellipsoids drawn at 50% probability).
Compound **7(d)** was recrystallised by slow vapour diffusion of hexane into a concentrated solution of **7(d)** in degassed THF. Red crystals of **7(d)** grew in the vial at room temperature overnight. The molecular structure of **7(d)** is shown in **Figure 3.30** and selected bond lengths are listed in **Table 3.8**. An *n*-hexane molecule of crystallisation is disordered between two positions partially overlapping with one another. One of the CO$_2$Me groups was found to be disordered between two opposite orientations. In addition, the Rh centre is also disordered giving alternative positions for Rh, P1, P3, C6, C7, C12, C13 and C14 with their attached hydrogens. The occupancies were refined to 0.434(5) for the minor component and 0.566(5) for the major component.

**Figure 3.30**: Molecular structure of **7(d)**. Thermal ellipsoids are drawn at the 50% probability level (hydrogen atoms and the *n*-hexane molecule are omitted for clarity).

In general, the bond lengths of Rh-C1 [2.0458(19) – 2.0479(18) Å] are slightly shorter than Rh-C15 [2.0806(17) – 2.0857(16) Å] and Rh-C18 [2.0993(17) – 2.1010(18) Å], which is due the fact that C1 is sp-hybridised, whereas C15 and C18 are sp$^2$-hybridised. The C≡C bond lengths of the TMSE ligands [C1-C2, 1.207(9) – 1.218(2) Å] are similar to the C≡C bond lengths at the 2- and 5-positions of the rho dacycles [1.203(9) – 1.208(2) Å].
and 1.205(3) – 1.217(8) Å]. Comparing the bond lengths of Rh-C15 to Rh-C18, the latter are ca. 0.02 Å longer, which indicates that the TMSE ligand has a slightly stronger trans-influence than PMe₃. The Rh-P1 and Rh-P2 bond lengths are almost the same [2.3153(5) – 2.3163(7) and 2.3160(5) – 2.3111(7) Å, respectively]. However, the Rh-P3 bond lengths are longer than the Rh-P1 and Rh-P2 bond lengths [2.3606(5) – 2.3608(5) Å], which is in agreement with the Rh-P coupling constants observed by ³¹P{¹H} NMR spectroscopy. Thus, the coupling constants for the doublets of doublets for P1 and P2 (J_{Rh-P} = 98 – 99 Hz) are always greater than for the doublets of triplets for P3 (J_{Rh-P} = 83 – 84 Hz). This indicates that the trans-influence of the α-carbon of the rhodacycle is stronger than that of a PMe₃ group. The C=C bond lengths of C15-C16 and C17-C18 are 1.365(2) – 1.371(9) and 1.374(2) – 1.360(10) Å, respectively. However, the C-C single bond lengths of C16-C17 [1.447(2) – 1.429(8) Å] are slightly shorter than the typical C-C single bond length. This is because C16 and C17 are sp² hybridised carbons. For similar reasons, the bond lengths of C16-C27 and C17-C30 are slightly shorter (ca. 0.012 – 0.032 Å) than the other single bonds in the cyclohexyl ring because C16 and C17 are sp²-hybridised carbons and the others are sp³-hybridised carbons.

### 3.2.5.3 Photophysical studies

The second-generation TMSE-rhodacyclopentadienes (Table 3.9) showed a significant increase in the Φ values compared to the first-generation TMSE-rhodacyclopentadienes (Table 3.10). For example, the Φ value of 7(a) are 0.33, but its first-generation analogue (Table 3.10), has a Φ value of 0.15. Moreover, the second-generation TMSE-rhodacyclopentadienes with R = CO₂Me and BMes₂, respectively, have the highest Φ
values \[ \Phi = 0.69 \] for both \( 7(d) \) and \( 7(e) \) of any rhodacypentadiene synthesised thus far. Indeed, these values are comparable to some of the best organic fluorophores. This proves that the two phenyl rings at the 3- and 4-positions in the rhodacyle cycle ring act as quenchers. The \( \lambda_{\text{max}} \) values of absorption and emission of the second-generation TMSE-rhodacypentadienes are also shifted to the lower energy region compared to the first-generation ones (12 nm for absorption and 24 nm for emission for the compound with \( R = \text{CO}_2\text{Me} \)). The absorption and emission spectra of \( 7(a) \) – (f) are shown in Figure 3.31.

**Table 3.9:** Summary of the photophysical data for \( 7(a) \) – (f).

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \lambda_{\text{max}} ) ABS (nm)</th>
<th>( \varepsilon ) (mol(^{-1}) cm(^{-1}) dm(^3))</th>
<th>( \lambda_{\text{max}} ) EM (nm)</th>
<th>Stokes shift (cm(^{-1}))</th>
<th>( \Phi )</th>
<th>( \tau ) (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 7(a) ), ( R = \text{H} )</td>
<td>456</td>
<td>30000</td>
<td>501</td>
<td>2000</td>
<td>0.33</td>
<td>1.2</td>
</tr>
<tr>
<td>( 7(b) ), ( R = \text{SMe} )</td>
<td>467</td>
<td>41000</td>
<td>518</td>
<td>2100</td>
<td>0.34</td>
<td>1.8</td>
</tr>
<tr>
<td>( 7(c) ), ( R = \text{C}≡\text{CTMS} )</td>
<td>491</td>
<td>47000</td>
<td>550</td>
<td>2200</td>
<td>-*</td>
<td>-*</td>
</tr>
<tr>
<td>( 7(d) ), ( R = \text{CO}_2\text{Me} )</td>
<td>497</td>
<td>44000</td>
<td>560</td>
<td>2300</td>
<td>0.69</td>
<td>3.0</td>
</tr>
<tr>
<td>( 7(e) ), ( R = \text{BMes}_2 )</td>
<td>532</td>
<td>48000</td>
<td>606</td>
<td>2400</td>
<td>0.69</td>
<td>2.6</td>
</tr>
<tr>
<td>( 7(f) ), ( R = \text{C}≡\text{CH} )</td>
<td>484</td>
<td>31000</td>
<td>542</td>
<td>2200</td>
<td>-*</td>
<td>-*</td>
</tr>
</tbody>
</table>

Note: All of the data above (except \( \varepsilon \)) were recorded in degassed toluene solutions at room temperature. \( \varepsilon \) values were recorded in non-degassed toluene solutions.

* The \( \Phi \) and \( \tau \) values of \( 7(e) \) and \( 7(f) \) have not been recorded yet.
Table 3.10: The photophysical data for the first-generation TMSE-rhodacyclopentadienes in toluene solution at room temperature.\textsuperscript{8}

![Diagram of TMSE-rhodacyclopentadienes]

<table>
<thead>
<tr>
<th>substituent</th>
<th>$\lambda_{\text{max}}$ ABS (nm)</th>
<th>$\varepsilon$ (mol$^{-1}$ cm$^{-1}$ dm$^3$)</th>
<th>$\lambda_{\text{max}}$ EM (nm)</th>
<th>Stokes shift (cm$^{-1}$)</th>
<th>$\Phi$</th>
<th>$\tau$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = H</td>
<td>453</td>
<td>26000</td>
<td>496</td>
<td>1910</td>
<td>0.15</td>
<td>0.87</td>
</tr>
<tr>
<td>R = SMe</td>
<td>468</td>
<td>35000</td>
<td>515</td>
<td>1950</td>
<td>0.10</td>
<td>0.55</td>
</tr>
<tr>
<td>R = CO$_2$Me</td>
<td>485</td>
<td>21000</td>
<td>536</td>
<td>1960</td>
<td>0.16</td>
<td>0.98</td>
</tr>
</tbody>
</table>

From the results in Table 3.9, it can be seen that both electron donating and withdrawing substituents at the \textit{para}-positions of the phenyl rings cause bathochromic shifts. However, electron accepting substituents have a greater influence on the bathochromic shift than electron donating ones: the stronger the electron accepting ability, the greater the bathochromic shift. Therefore, the largest Stokes shift was observed in 7(e) because the BMes$_2$ substituent is a very strong electron accepting group. The electron accepting substituents stabilise the LUMO to a greater extent than the HOMO, whereas the electron donating substituents destabilise the HOMO to a greater extent than the LUMO. As a result, both types of substituents are able to decrease the HOMO-LUMO energy gap, as previously reported for related 2,5-bis(arylethynyl)thiophenes.\textsuperscript{13}
The absorption and emission spectra of 7(a) are shown in Figure 3.32. The small Stokes shifts (ca. 2000 cm\(^{-1}\)) and the nanosecond lifetimes suggest that the emission occurs from the singlet excited state. Unprecedented \(\Phi_f\) values for metallacyclopentadienes of up to 0.69 have been achieved for 7(d) and 7(e) with lifetimes of 3.0 and 2.6 ns, respectively.
Singlet oxygen sensitisation experiments\(^2\) on 7(a), 7(b) and 7(d) have been conducted by Dr. Andreas Steffen in order to determine the quantum yields of triplet excited state generation (\(\Phi_\Delta\)) as shown in Table 3.11. For 7(a), the \(\Phi_\Delta\) value was ca. 0.65. This indicates that the singlet excited state is decaying effectively only by fluorescence and ISC to the triplet excited state, with no \(S_1 \rightarrow S_0\) internal conversion (IC) [as \(\Phi_\Delta (0.65) + \Phi_f (0.33) \approx 1.00\)]. For 7(b) and 7(d), the sums of \(\Phi_\Delta + \Phi_f\) are less than unity (0.74 and 0.95, respectively) indicating that some IC is taking place. Nevertheless, the \(k_f\) and \(k_\Delta\) values of 7(a), 7(b) and 7(d) are close to each other (\(k_f \approx k_\Delta \approx 10^8 \text{ s}^{-1}\)), which allows fluorescence to occur to an appreciable extent in the TMSE-rhodacyclopentadienes. Although ISC to the triplet excited states was confirmed in the TMSE-rhodacyclopentadienes, no phosphorescence was observed between 400 – 1000 nm at room temperature in these rhodacyclopentadienes.
Table 3.11: The $\Phi_\Delta$, $\tau_0$, $k_f$ and $k_\Delta$ formation of 7(a), 7(b) and 7(d).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Phi_\Delta$</th>
<th>$\tau_0$ (ns)</th>
<th>$k_f$ [$10^8$ s$^{-1}$]</th>
<th>$k_\Delta$ [$10^8$ s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>7(a)</td>
<td>0.65</td>
<td>3.6</td>
<td>2.75</td>
<td>5.42</td>
</tr>
<tr>
<td>7(b)</td>
<td>0.40</td>
<td>5.3</td>
<td>1.89</td>
<td>2.22</td>
</tr>
<tr>
<td>7(d)</td>
<td>0.26</td>
<td>4.3</td>
<td>2.30</td>
<td>0.87</td>
</tr>
</tbody>
</table>

*Quantum yield for $^1O_2$ formation in $O_2$-saturated toluene solution.

$\tau_0$ is the natural lifetime calculated from the equation $\tau_0 = \tau_f/\Phi_f$.

A low-temperature lifetime measurement on 7(a) was carried out by Dr. Andrew Beeby from the Department of Chemistry, Durham University. The idea behind the low-temperature experiment is to slow down all vibrational relaxation modes and non-radiative processes in an excited molecule by freezing the sample in an iso-pentane/Et$_2$O/EtOH glass at 77 K. Thus, emission (i.e. fluorescence and phosphorescence) should be the only means of the decay to the ground state, and the lifetime from low temperature experiment should be the pure natural radiative lifetime ($\tau_0$). The calculated $\tau_0$ value for 7(a) is 3.6 ns, close to the experimental value ($\tau_f = 3.2$ ns at 77 K). This means that the $\Phi_\Delta$ value for 7(a) at 77 K must be significantly less than 0.65. The fact that $\tau_0$ occurs on the nanosecond timescale in 7(a) confirms that only fluorescence rather than phosphorescence occurs at 77 K (within the wavelength of 400 – 1000 nm). This observation is different from other luminescent rhodium complexes; for example, at 77 K, [Rh(bpy)$_3$]$^{3+}$ emits at 448 nm with a lifetime of 2.2 ms in a rigid glass, whereas no emission occurs at room temperature.$^{24}$

The fact that no phosphorescence was observed at 77 K in TMSE-rhodacyclopentadienes can be explained by two possibilities: (i) the triplet excited states are not populated at 77 K, or (ii) the lowest triplet excited ($T_1$) state is close in energy to
the ground state (i.e. emission occurs at \( \lambda > 1000 \) nm); therefore, the emission was not detected in the experiment.

Preliminary TD-DFT calculations for 7(d) (Figure 3.33) by Prof. Marder show that the energy gap between \( S_1 \) and \( S_0 \) states is 2.24 eV [554 nm; recorded \( \lambda_{\text{max}} \) emission for 7(d) = 560 nm], the \( S_1 \) state is only slightly below the \( T_2 \) state by ca. 0.07 eV, but above the \( T_1 \) state ca. 1.10 eV. The energy gap between \( T_1 \) and \( S_0 \) states is ca. 1.14 eV (1087 nm). Thus, ISC from \( S_1 \) to \( T_1 \) is very slow (\( k_\Delta = 10^8 \) s\(^{-1}\)), which may be due to the large energy gap (1.10 eV) between them. However, the \( S_1 \) state may thermally populate the \( T_2 \) state at room temperature because of the very small energy gap (0.07 eV) between them. This calculations also indicate that any possible phosphorescence would not have been observed either at room or low-temperature experiment, because emission at ca. 1100 nm would be out of the range of the wavelengths that we measured.

![Energy levels diagram of S0, S1, T1 and T2 states of 7(d).](image)

**Figure 3.33:** The energy levels diagram of \( S_0 \), \( S_1 \), \( T_1 \) and \( T_2 \) states of 7(d).

Comparing the photophysical properties of 7(a) – (f) to those of the structurally related 2,5-bis(arylethynyl)thiophenes\(^{13} \) (\( \Phi_f = 0.2 - 0.3 \), \( \tau_f = 0.2 - 0.3 \) ns), the rhodacypentadienes exhibit higher \( \Phi_f \) values and longer lifetimes than the bis(arylethynyl)thiophenes despite the fact that the spin-orbit coupling (SOC) constant of Rh (1200 cm\(^{-1}\)) is more than three times higher than that of sulphur (380 cm\(^{-1}\)). In
addition, the greater $\lambda_{\text{max}}$ values in both the absorption and emission spectra of 7(a) – (f) than those of their thiophene-based analogues clearly indicate that the Rh centre is participating in the transitions. This strongly implies that the effectiveness of SOC from the Rh in the ISC from the $S_1$ to $T_1$ state is less than that in most luminescent organometallic complexes. Therefore, the fluorescence rate is competitive to the ISC rate ($k_f \approx k_\Delta \approx 10^8 \text{ s}^{-1}$). It is generally thought that the SOC constant from the metal centre is the main factor which facilitates the ISC ($S_1 \rightarrow T_1$ state) in organometallic complexes: the greater the SOC, the more efficient the ISC is. However, in the case of rhodacyclopentadienes, despite the fact that the Rh has a large SOC coefficient, 7(a), 7(b), 7(d) and 7(e) are still able to exhibit high-intensity fluorescent emissions with nanosecond lifetimes. This brings us to another issue, i.e., how effective the SOC of the Rh is in influencing the ISC from the $S_1$ to the $T_1$ state, or, in other words, how much the Rh-centre participates in the excited states.

The emission solvatochromism for 7(e) (Figure 3.34) implies significant charge transfer (CT) in the excited state. In polar solvents (e.g. MeCN), the emission $\lambda_{\text{max}}$ values are shifted to lower energy than in less polar solvents. In addition, the structureless emission spectrum shows that there is a significant interaction between the excited 7(e) molecules and the polar solvent molecules. As a result, the emission from 7(e) is quenched by Coulombic interactions in polar solvents.
In collaboration with Prof. Michael George from the School of Chemistry at the University of Nottingham, time-resolved infrared (TRIR) absorption measurements have been carried out for 7(a) in DCM in order to obtain additional information about the excited states. In TRIR experiments, a strong IR-active band (e.g. ester C=O, C≡N or C≡C) is selected for observation at several time intervals in the range of 11 – 3000 ps after the molecule has been excited. In 7(a), a particular IR band (2128 cm\(^{-1}\)), which belongs to a C≡C stretch of the alkynyl moieties at the 2- and 5-positions of the rhodacycle ring, was investigated. The changes in intensity vs. time, on the picosecond (ps) timescale, over which the molecule was excited and then decayed to the ground state, were recorded in different TRIR spectra (Figure 3.35). After 10 ps, the TRIR spectrum shows that the band at 2128 cm\(^{-1}\) was bleached, and another band at 2008 cm\(^{-1}\), which is putatively assigned to the \(S_1\) state, was observed. This band decays at the same rate \([\tau = 1.6 \pm 0.6\) ns\] as a new IR band at 1941 cm\(^{-1}\) appears, which is believed to arise from the \(T_1\) state. The decay rate is in close agreement with the fluorescence lifetime of 7(a) in
Table 3.9, which is about 1.2 ns. Moreover, the IR frequency is reduced from 2128 to 1941 cm\(^{-1}\) which indicates decreasing C≡C triple bond character in the putative triplet excited state.

![Figure 3.35: Pico-second (ps)-TRIR spectra of 7(a).](image)

Based on the results presented in Figures 3.35 and 3.36, it can be surmised that about 35% of the ground state is reformed at the same rate as the \(S_1\) state decays, and another 65% is formed from the decay of a state postulated to be a \(T_1\) state. This is consistent with the result from the singlet oxygen sensitisation experiment in Table 3.11, which stated that the \(\Phi_\Delta\) for 7(a) is 65%.

The state associated with the band at 1941 cm\(^{-1}\) (believed to be the \(T_1\) state) decays to the ground state with \(\tau = 55\) ns in a concentrated degassed solution (\(10^{-3}\) M). The short lifetime of the \(T_1\) state lifetime is probably due to a small energy gap between the triplet excited state and the ground state, facilitating a non-radiative process.
3.2.6 Second-generation Me-rhodacyclopentadienes

3.2.6.1 Synthesis and characterisation

The second-generation of TMSE-rhodacyclopentadienes has proved that the removal of the two phenyl rings at the 3- and 4-positions of the rhodacyle ring significantly increases the $\Phi$ values of the rhodacyclopentadienes. In addition, the singlet oxygen sensitisation experiment results from Table 3.1 (for the first-generation TMSE- and Me-rhodacyclopentadienes) also show that strong $\sigma$-donors such as Me-ligand tend to have higher $\Phi_\Delta$ values compared to TMSE- ones. This may be due to the increase in metal contribution to the frontier orbitals, which could impact on $k_\Delta$. In order to investigate further the function of the in-plane donor ligand set, second-generation Me-rhodacyclopentadienes have been synthesised.

Figure 3.36: Kinetic traces: (a) the decay of the $S_1$ state at 2008 cm$^{-1}$ (■) and the growth of the $T_1$ state at 1941 cm$^{-1}$ (●); (b) the decay of $T_1$ state at 1941 cm$^{-1}$ (●) and the recovery of the ground state bleach at 2128 cm$^{-1}$ (▲).
The synthesis of Me-rhodacyclopentadienes (Figure 3.37) is much easier than for the TMSE-rhodacyclopentadienes. One equivalent of the appropriate 1,3,9,11-dodecatetrayne in degassed THF solution was added to the [RhMe(PMe$_3$)$_4$] solution, and the reaction was stirred for 4 – 15 h at room temperature to obtain the Me-rhodacyclopentadienes [R = H, 8(a); R = SMe, 8(b); R = CO$_2$Me, 8(c)].

![Figure 3.37: Synthetic route to the second-generation Me-rhodacyclopentadienes.](image)

Upon completion of the reactions, the $^{31}$P{$^1$H} NMR spectra of the Me rhodacyclopentadienes were found to be similar to those shown in Figure 3.17. As expected, the $J_{\text{Rh-P}}$ values for the doublets of doublets are ca. 106 Hz, and for the doublets of triplets are ca. 90 Hz, which are slightly higher than those of the DHAPEPE- and TMSE-rhodacyclopentadienes, showing a higher electron density at the Rh centre due to the strong $\sigma$-donor nature of the Me- ligand. The $^1$H NMR spectrum of 8(c) (Figure 3.38) shows the appearance of an approximate doublet of quartets at -0.08 ppm ($^2J_{\text{Rh-H}} = 2$ Hz, $^3J_{\text{P-H}} = 7$ Hz), which indicates that the Me- group is present on the Rh. In addition, the two multiplets at 2.95 and 1.69 ppm indicate the presence of the -CH$_2$-CH$_2$- moiety from the cyclohexyl loop.
Figure 3.38: $^1$H NMR (400 MHz, C$_6$D$_6$) spectrum of 8(c).

### 3.2.6.2 Photophysical studies

A summary of the photophysical data for 8(a) – (c) is shown in Table 3.12. Unlike the TMSE-rhodacyclopentadienes, the second-generation Me-rhodacyclopentadienes appear to exhibit very weak emission, but no quantum yields have yet been measured (Figure 3.39). These results are similar to the first-generation Me-rhodacyclopentadienes, for which the $\Phi_t$ values are only about 0.003 for the compounds where the para-substituents at the phenyl rings are H and CO$_2$Me (Table 3.1). Weak emission from the Me-rhodacyclopentadienes is due to effective IC processes taking place in the excited states or the singlet excited states undergoing ISC to triplet excited states, or both.
Figure 3.39: Absorption (top) and emission (bottom) spectra of 8(a) – (c).

Table 3.12: Summary of the photophysical data of 8(a) – (c).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$ ABS (nm)</th>
<th>$\varepsilon$ (mol$^{-1}$ cm$^{-1}$ dm$^3$)</th>
<th>$\lambda_{\text{max}}$ EM (nm)</th>
<th>Stokes shift (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8(a), R = H</td>
<td>463</td>
<td>34000</td>
<td>512</td>
<td>2100</td>
</tr>
<tr>
<td>8(b), R = SMe</td>
<td>475</td>
<td>39000</td>
<td>532</td>
<td>2300</td>
</tr>
<tr>
<td>8(c), R = CO$_2$Me</td>
<td>509</td>
<td>27000</td>
<td>580</td>
<td>2400</td>
</tr>
</tbody>
</table>

Note: All of the data above (except $\varepsilon$) were obtained in degassed toluene solution at room temperature. $\varepsilon$ values were recorded in non-degassed toluene solutions.
Comparing their absorption and emission spectra to those of the TMSE-rhodacyclopentadienes, the $\lambda_{\text{max}}$ values of absorption and emission of the Me-rhodacyclopentadienes are slightly shifted to the lower energy region by 10 - 12 nm, supporting the fact that the Me ligand is a stronger electron donating group than the acetylide ligand. This also indicates that the Rh centre is involved in the transitions, because changing the ligand can influence the $\lambda_{\text{max}}$ values in both absorption and emission. However, the small Stokes shift (ca. 2400 cm$^{-1}$) indicates that the emissions originate from $S_1$ states.

### 3.2.7 Discovery of trans-[bis(trimethylphosphine)-µ-η$^2$-succinato-2,5-bis(p-$N,N$-dimethylaminophenylethynyl)-3,4-(p-$N,N$-dimethylaminophenyl)rhodacyclopenta-2,4-diene] dimer [9(b)]

#### 3.2.7.1 Synthesis and characterisation

Compound 9(b) was discovered by accident in the process of synthesising 4. When preparing 4, the reaction needs to be heated at 50 °C in a Young’s tube in order to complete the reaction in a reasonable time period. We suspected that a small amount of succinic acid, presumably formed by hydrolysis of NBS used in a previous reaction, was present in the Young’s tube, which reacted with 4 at 50 °C to form 9(b). During the recrystallisation process, undertaken with the aim of obtaining crystals of 4, compound 9(b) crystallised and was analysed by X-ray diffraction; thus, this compound was discovered. The intentional formation of 9(b) was investigated by adding one equivalent of succinic acid to a toluene solution of 4 and monitoring the progress of the reaction by
$^{31}$P{$^1$H} NMR spectroscopy (Figure 3.40). After stirring for 15 h at room temperature and then removal of the solvent, a doublet of doublets at -8.63 ppm ($J_{\text{Rh-P}} = 108$ Hz, $J_{\text{P-P}} = 31$ Hz) and a doublet of triplets at -20.74 ppm ($J_{\text{Rh-P}} = 89$ Hz, $J_{\text{P-P}} = 31$ Hz) were observed to be the major peaks in an NMR spectrum in C$_6$D$_6$. These were assigned to an $\eta^1$-succinato-rhodacyclopentadiene dimer, 9(a). Small peaks were also observed for 4 and 9(b), a doublet at -1.23 ppm ($J_{\text{Rh-P}} = 117$ Hz) being assigned to the latter.

Figure 3.40: $^{31}$P{$^1$H} NMR (162 MHz) spectra of the conversion of 9(a) to 9(b).

The reaction was driven to form the $\eta^2$-succinato complex 9(b) by heating at 50 °C for 15 minutes, followed by removal of the volatiles (solvent and dissociated PMe$_3$) and refilling with the fresh solvent. This process was repeated ca. 20 times until all of the 9(a) was converted to 9(b).
The doublet in the top spectrum in Figure 3.40 is slightly shifted to -2.29 ppm compared to the ones below; the lower spectra were recorded in a mixture of C₆D₆ and THF, whereas the upper spectrum is in pure THF-d₈ in which 9(b) is more soluble. It is worth noting that chlorinated solvents such as chloroform (CHCl₃) can lead to the decomposition of both 9(a) and 9(b). This problem was noticed when the reaction was monitored using ³¹P{¹H} NMR spectroscopy in CDCl₃.
An ESI$^+$ mass spectrum of 9(b) shows signals at $m/z = 890$ and 904, which are assigned to [M + 2H]$^{2+}$ and [M$/2 + \text{CH}_2$], respectively. The $m/z = 890$ peak is probably due to doubly protonated and charged 9(b), and therefore, appears at M/2.

3.2.7.2 Crystallographic data for 9(b)

The crystallographic data for 9(b) are listed in Table 3.13. Crystals of 9(b) were grown in a 5 mm diameter glass tube by slow diffusion of a layer of hexane into a C$_6$D$_6$ solution. Compound 9(b) crystallised in the triclinic space group $P\bar{1}$ and its molecular structure is shown in Figure 3.42.

![Molecular structure of 9(b)](image)

**Figure 3.42:** Molecular structure of 9(b) with thermal ellipsoids plotted at 50% probability (hydrogen atoms and C$_6$D$_6$ molecules are omitted for clarity).
Table 3.13: Crystallographic data for 9(b).

<table>
<thead>
<tr>
<th>Compound</th>
<th>9(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{96}H_{120}N_8O_4P_4Rh_2·3(C_6D_6)</td>
</tr>
<tr>
<td>Formula weight</td>
<td>2014.02</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>120(2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P̅1</td>
</tr>
<tr>
<td>a (Å)</td>
<td>9.5957(7)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>12.7868(9)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>22.5429(16)</td>
</tr>
<tr>
<td>α (°)</td>
<td>88.381(11)</td>
</tr>
<tr>
<td>β (°)</td>
<td>79.043(10)</td>
</tr>
<tr>
<td>γ (°)</td>
<td>82.887(10)</td>
</tr>
<tr>
<td>Volume (Å^3)</td>
<td>2694.6(3)</td>
</tr>
<tr>
<td>Z</td>
<td>1</td>
</tr>
<tr>
<td>Density (calculated) (Mg/m^3)</td>
<td>1.241</td>
</tr>
<tr>
<td>Absorption coefficient (mm^{-1})</td>
<td>0.419</td>
</tr>
<tr>
<td>Crystal size (mm^3)</td>
<td>0.29 x 0.07 x 0.04</td>
</tr>
<tr>
<td>Θ range for data collection (°)</td>
<td>2.45 to 24.99</td>
</tr>
<tr>
<td>Reflection collected</td>
<td>21250</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>9505</td>
</tr>
<tr>
<td>Data / Restraints / Parameters</td>
<td>9505 / 6 / 647</td>
</tr>
<tr>
<td>Final R indices [I&gt;2σ(I)]</td>
<td>R1 = 0.0750</td>
</tr>
<tr>
<td></td>
<td>wR2 = 0.1566</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.1178</td>
</tr>
<tr>
<td></td>
<td>wR2 = 0.1752</td>
</tr>
</tbody>
</table>

The centres of the molecules in 9(b) are co-incident with crystallographic inversion centres. The Rh-O1 and Rh-O2 bond lengths are 2.300(4) and 2.233(4) Å, respectively (which is significantly different but probably due to crystal packing forces), whereas the Rh-C9 and Rh-C12 bond lengths are 2.011(6) and 1.979(6) Å. The C1-C2 and C2-C2\^i bond lengths of are 1.519(9) and 1.478(14) Å, respectively. The O1-Rh-O2 bond angle is 57.64(17)°, which is relatively close to related bond angles that were reported in the
literature (60.2(1)° for [Rh(η²-O₂CMe)(P̂Pr₃)₂], 58.9(3)° for [RhCp*(η¹-O₂CPh)(η²-O₂CPh)] and 58.5(2)° for [Rh(η²-O₂CMe)(ppy)₂]). The C=C=C moiety at C9 is more distorted from linearity than the one at C12 by comparison of the bond angle of C9-C13-C14 [168.8(7)°] to that of C12-C33-C34 [176.7(7)°]. The P̂Me₃ ligand is rotationally disordered: C6, C7 and C8 with attached hydrogens are distributed between positions a and b in a 2:1 ratio. In addition, the dimethylaminophenyl group at C10 is disordered between positions a and b in a 4:1 ratio.

3.2.7.3 Photophysical studies

Photophysical data for 9(b) are presented in Table 3.14, whereas absorption and emission spectra are shown in Figure 3.43. Compound 9(b) is barely soluble in toluene, benzene and THF; however, chlorinated solvents, such as CHCl₃, can lead to its decomposition. For these reasons, its extinction coefficient was not measured.

<table>
<thead>
<tr>
<th>λ_max ABS (nm)</th>
<th>ε (mol⁻¹ cm⁻¹ dm³)</th>
<th>λ_max EM (nm)</th>
<th>Stokes shift (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>486</td>
<td>-</td>
<td>578</td>
<td>3300</td>
</tr>
</tbody>
</table>

Note: The absorption and emission spectra were measured in degassed toluene at room temperature.
- No data was recorded due to the poor solubility of 9(b) in toluene, benzene and THF.
Figure 3.43: Absorption and emission spectra of 9(b) in toluene.

The $\lambda_{\text{max}}$ values for absorption and emission of 9(b) show bathochromic shifts compared to 4 (12 nm in absorption and 55 nm in emission). Indeed, the emission from 9(b) is very weak with a broad signal at $\lambda_{\text{max}} = 578$ nm. There are no differences in the emission spectra between degassed and non-degassed solutions at room temperature, which indicates that the emission at room temperature does not originate from the triplet excited states. The weak emission is possibly due to the $\pi$-donor succinato ligand destabilises the Rh d-orbitals in 9(b), facilitating a metal-centred (MC) transition, which is a well-known non-radiative transition. However, this is purely speculative at present.

3.2.8 Benzoato-rhodacyclopentadienes

3.2.8.1 Synthesis and characterisation

The discovery of 9(b) initiated the idea of synthesising a new series of rhodacyclopentadienes bearing $\sigma$- and $\pi$-donor ligands such as $\eta^2$-benzoato (Figure
1.43.a) and acetylacetonato (acac-) (Figure 1.43.b), in order to examine the hypothesis that strong $\sigma$- and $\pi$-donor ligands can increase the Rh character of the frontier orbitals, and consequently enhance the ISC rates in the rhodacyclopentadienes.

Apart from using the synthetic route as described in Section 3.2.7, the benzoato-rhodacyclopentadienes were also synthesised using the route shown in Figure 3.44. In all cases, the benzoic acid was dried in the oven for a week before use. One equivalent of benzoic acid in THF solution was added to $[\text{RhMe(PMe}_3\text{)}_4]$ in THF solution, then the volatiles (e.g. THF and dissociated PMe$_3$) were removed in vacuo and the flask was refilled with fresh solvent. This removal and refilling of solvent was repeated three times before the reaction was stirred at room temperature for 1 h in order to produce $[\text{Rh}(\eta^1$-$\text{O}_2\text{CPh})(\text{PMe}_3)_3]$, 10.

![Figure 3.44: Synthetic route to $\eta^2$-benzoato-rhodacyclopentadienes.](image-url)
At room temperature, it was found that the original broad signal at -24.0 ppm in $^{31}\text{P}^{1}\text{H}$ NMR spectrum of [RhMe(PMe$_3$)$_4$] was shifted to lower field at -6.5 ppm, which implies that [RhMe(PMe$_3$)$_4$] has been converted to 10. The dynamics may be due to the presence of traces of PMe$_3$ or the formation of a pseudo five-coordinate species via an $\eta^1$-$\eta^2$-transformation of the benzoato ligand. At 203 K (Figure 3.45), a doublet of triplets ($J_{\text{Rh-P}} = 168$ Hz, $J_{\text{P-P}} = 48$ Hz) associated with doublet of doublets ($J_{\text{Rh-P}} = 139$ Hz, $J_{\text{P-P}} = 48$ Hz) at 3.85 and -9.55 ppm, respectively, in a ratio of 1:2 are observed in the $^{31}\text{P}^{1}\text{H}$ NMR spectrum of 10. This shows that two of the PMe$_3$ ligands are in a different environment than the third one. The molecular structure of 10 in the solid state was confirmed by X-ray diffraction analysis, which showed that the complex is square planar.

![Figure 3.45: $^{31}\text{P}^{1}\text{H}$ NMR spectra of 10 at room temperature (top, 162 MHz, C$_6$D$_6$) and 203 K (bottom, 202 MHz, 10% C$_6$D$_6$ in THF).](image)

Rhodium complex 10 was synthesised by Darensbourg et al. in 1987, via reaction of [RhPh(PMe$_3$)$_3$] with CO$_2$ to form [Rh($\eta^2$-O$_2$CPh)(PMe$_3$)$_2$] (Figure 3.46). The group monitored the reaction progress using IR spectroscopy, and reported that 10, an
intermediate en route to \([\text{Rh(} \eta^2\text{-O}_2\text{CPh})(\text{PMe}_3)_2]\), is unstable in the absence of a CO\(_2\) atmosphere. Upon removal of CO\(_2\), 10 can revert to [RhPh(\text{PMe}_3)_3].\(^{33}\) However, the rhodium complex 10 that was synthesised in this work was found to be stable in an N\(_2\) atmosphere, without CO\(_2\) being present.

![Figure 3.46: Synthesis of [Rh(\eta^2\text{-O}_2\text{CPh})(\text{PMe}_3)_2] by Darensbourg and co-workers.\(^{33}\)](image)

It is worth noting that Darensbourg et al. also attempted to synthesise 10 by reaction of [Rh(\text{PMe}_3)_4]Cl with AgO\(_2\)CPh, but this was unsuccessful because of a redox process involving Ag\(^{1}\) and Rh\(^{1}\).\(^{33}\) Our attempt to synthesise 10 by reaction of [(\text{PMe}_3)_4\text{Rh}]Cl with NaO\(_2\)CPh in degassed water at 60 °C was also unsuccessful.

In order to prove that this reaction can be further applied to other carboxylic acids, a similar reaction was also carried out with succinic acid (Figure 3.47). Analogously to 10, a di-rhodium complex 13 was obtained, and its molecular structure was also confirmed by X-ray crystallography. Moreover, the \(^{31}\text{P}\{^{1}\text{H}\}\) NMR spectrum of 13 at 203 K also displays a doublet of triplets at 3.41 ppm (\(J_{\text{Rh-P}} = 168 \text{ Hz}, J_{\text{P-P}} = 45 \text{ Hz}\)) and a doublet of doublets at -9.41 ppm (\(J_{\text{Rh-P}} = 143 \text{ Hz}, J_{\text{P-P}} = 45 \text{ Hz}\)) in a ratio of 1:2.

![Figure 3.47: Synthesis of the di-rhodium complex 13 using succinic acid.](image)
After confirmation of the structure of 10, it was reacted with one equivalent of the appropriate 1,12-bis(p-R-phenyl)dodeca-1,3,9,11-tetrayne in THF at room temperature for 15 h. After removal of the solvent, $^{31}$P{$^1$H} NMR spectroscopy in C$_6$D$_6$ revealed a doublet of doublets and doublet of triplets to be the major peaks. These were assigned to η$^1$-benzoato-rhodacyclopentadienes with R = H, 11(a); R = SMe, 11(b); and R = CO$_2$Me, 11(c). Minor doublets were assigned to η$^2$-benzoato-rhodacyclopentadienes with R = H, 12(a); R = SMe, 12(b); and R = CO$_2$Me, 12(c). For example, for the reaction with 1,12-bis(phenyl)dodeca-1,3,9,11-tetrayne, the doublet of doublets and doublet of triplets at -7.52 ppm ($J_{Rh-P} = 107$ Hz, $J_{P-P} = 31$ Hz) and -18.86 ppm ($J_{Rh-P} = 91$ Hz, $J_{P-P} = 31$ Hz), respectively are assigned to 11(a), whereas the doublet at -1.04 ppm ($J_{Rh-P} = 115$ Hz) is assigned to 12(a) (Figure 3.48).

The η$^1$-benzoato-products were able to be separated from the η$^2$-benzoato-products in pure form by repeated recrystallisations from THF/hexane mixtures. After this, the residues from the recrystallisations were driven to form the η$^2$-benzoato products by dissolving them in toluene and heating at 50 °C for 15 minutes, followed by removal of the volatiles (toluene and dissociated PMe$_3$) and refilling with fresh toluene. This process was repeated ca. 11 times until the η$^1$-benzoato-rhodacyclopentadienes were completely converted to their η$^2$-benzoato-analogues. The progress of this for 12(a) is shown in Figure 3.48.
Figure 3.48: $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz) spectra in the conversion of $11(\text{a}) \rightarrow 12(\text{a})$.

Comparing the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the $\eta^1$-benzoato-rhodacyclopentadienes to those of the TMSE-rhodacyclopentadienes, it can be concluded that the positions of the PMe$_3$ ligands in the $\eta^1$-benzoato-rhodacyclopentadienes are similar to those in the TMSE-rhodacyclopentadienes. However, the $J_{\text{Rh-P}}$ values for the $\eta^1$-benzoato-rhodacyclopentadienes are larger than those of the TMSE-ones (dd, $J_{\text{Rh-P}} = 106 – 107$ Hz; dt, $J_{\text{Rh-P}} = 91$ Hz), which indicates that the benzoato-ligand is a stronger donor ligand, similar to the Me- ligand. The appearance of a doublet in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $12(\text{a})$ indicates that the two PMe$_3$ ligands are in the same environment; hence, they are located at the axial positions.
The $^1$H NMR spectrum of 12(a) (Figure 3.49) shows only one multiplet for CH$_2$-C=C at 2.85 ppm revealing that 12(a) is a symmetrical compound, which has been confirmed by X-ray crystallography.

![1H NMR spectrum of 12(a)](image)

**Figure 3.49:** $^1$H NMR spectrum (400 MHz, C$_6$D$_6$) of 12(a).

### 3.2.8.2 Crystallographic data for 10, 11(a), 11(c), 12(a) and 13

The X-ray crystallographic data for 10, 11(a), 11(c), 12(a) and 13 are listed in Table 3.15. Crystals of 10 and 13 were grown in a Young’s tube via slow diffusion of hexane into concentrated C$_6$D$_6$ solutions. Rhodium complex 10 crystallises in the hexagonal space group P6$_3$/m, whereas the di-rhodium complex 13 adopts the monoclinic space group P2$_1$. The molecular structures of 10 and 13 are shown in Figures 3.50 and 3.51, respectively.
**Figure 3.50:** Molecular structure of 10. Hydrogen, C6i, O2i atoms and C6D6 molecule are omitted for clarity (thermal ellipsoids are shown at 50% probability).

**Figure 3.51:** Molecular structure of 13. Hydrogen atoms and C6D6 molecule are omitted for clarity (thermal ellipsoids are shown at 50% probability).
Table 3.15: Crystallographic data for 10, 13, 11(a), 11(c) and 12(a).

<table>
<thead>
<tr>
<th>Compound</th>
<th>10</th>
<th>13</th>
<th>11(a)</th>
<th>11(c)</th>
<th>12(a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>$\text{C}<em>{16}\text{H}</em>{32}\text{O}<em>{2}\text{P}</em>{3}\text{Rh} \cdot \text{C}<em>{6}\text{D}</em>{6}$</td>
<td>$\text{C}<em>{22}\text{H}</em>{58}\text{O}<em>{4}\text{P}</em>{6}\text{Rh}<em>{2} \cdot \text{C}</em>{6}\text{D}_{6}$</td>
<td>$\text{C}<em>{44}\text{H}</em>{54}\text{O}<em>{6}\text{P}</em>{3}\text{Rh} \cdot \text{C}<em>{6}\text{D}</em>{6}$</td>
<td>$\text{C}<em>{40}\text{H}</em>{50}\text{O}<em>{2}\text{P}</em>{3}\text{Rh} \cdot \text{C}<em>{6}\text{D}</em>{6}$</td>
<td>$\text{C}<em>{37}\text{H}</em>{42}\text{O}<em>{2}\text{P}</em>{2}\text{Rh} \cdot \text{C}<em>{6}\text{D}</em>{6}$</td>
</tr>
<tr>
<td>Formula weight</td>
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<td>862.47</td>
<td>843.55</td>
<td>960.86</td>
<td>683.56</td>
</tr>
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<td>Temperature (K)</td>
<td>120(2)</td>
<td>120(2)</td>
<td>120(2)</td>
<td>120(2)</td>
<td>120(2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Hexagonal</td>
<td>Monoclinic</td>
<td>Orthorhombic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$P6_3/m$</td>
<td>$P2_1$</td>
<td>$Pbca$</td>
<td>$P2_1/c$</td>
<td>$P2_1/c$</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>17.5052(2)</td>
<td>9.7664(3)</td>
<td>8.9317(6)</td>
<td>9.0388(3)</td>
<td>20.1880(18)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>17.5052(2)</td>
<td>11.2945(4)</td>
<td>23.2239(18)</td>
<td>18.7389(7)</td>
<td>9.1185(9)</td>
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<tr>
<td>$c$ (Å)</td>
<td>13.6195(2)</td>
<td>19.2319(7)</td>
<td>38.962(2)</td>
<td>28.9001(10)</td>
<td>18.6726(18)</td>
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<td>V (Å$^3$)</td>
<td>3614.31(8)</td>
<td>2071.61(12)</td>
<td>8081.8(9)</td>
<td>4886.0(3)</td>
<td>3435.1(6)</td>
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<td>Z</td>
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<td>2</td>
<td>8</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated) (Mg/m$^3$)</td>
<td>1.401</td>
<td>1.383</td>
<td>1.387</td>
<td>1.306</td>
<td>1.322</td>
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<td>0.707</td>
<td>0.494</td>
<td>0.620</td>
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<tr>
<td>Crystal size (mm$^3$)</td>
<td>0.50 x 0.35 x 0.25</td>
<td>0.25 x 0.15 x 0.02</td>
<td>0.25 x 0.14 x 0.04</td>
<td>0.13 x 0.07 x 0.04</td>
<td>0.50 x 0.22 x 0.03</td>
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<td>2.7 to 29.9</td>
<td>2.50 to 29.94</td>
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<td>2.18 to 29.54</td>
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<td>126368</td>
<td>52305</td>
<td>24951</td>
</tr>
<tr>
<td>Independent reflections</td>
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<td>11961</td>
<td>9742</td>
<td>8603</td>
<td>7113</td>
</tr>
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<td>3660 / 6 / 147</td>
<td>11961 / 1 / 398</td>
<td>9742 / 10 / 476</td>
<td>8603 / 0 / 535</td>
<td>7113 / 15 / 406</td>
</tr>
<tr>
<td>Final R indices [I&gt;2$\sigma$(I)]</td>
<td>$R1 = 0.0282$</td>
<td>$R1 = 0.0305$</td>
<td>$R1 = 0.0375$</td>
<td>$R1 = 0.0594$</td>
<td>$R1 = 0.0458$</td>
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<tr>
<td></td>
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<td>$wR2 = 0.0586$</td>
<td>$wR2 = 0.0866$</td>
<td>$wR2 = 0.1118$</td>
<td>$wR2 = 0.1032$</td>
</tr>
<tr>
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<td>$R1 = 0.0324$</td>
<td>$R1 = 0.0419$</td>
<td>$R1 = 0.0455$</td>
<td>$R1 = 0.1629$</td>
<td>$R1 = 0.0699$</td>
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<td></td>
<td>$wR2 = 0.0731$</td>
<td>$wR2 = 0.0629$</td>
<td>$wR2 = 0.0914$</td>
<td>$wR2 = 0.1420$</td>
<td>$wR2 = 0.1152$</td>
</tr>
</tbody>
</table>
In 10, the Rh-P1 bond length of 2.3002(5) Å is substantially longer than the Rh-P2 bond length of Rh-P2 [2.1935(7) Å]. This confirms that the PMe$_3$ ligand has a stronger \textit{trans}-influence than the oxygen atom. The O1-C6 and O2-C6 bond lengths are 1.261(3) and 1.232(3) Å, respectively, which are significantly different. The Rh-O1 bond length is 2.1339(16) Å. The bond angles of P1-Rh-P2 and O1-Rh-P1 are 93.255(14) and 86.802(14)°, respectively, revealing that the geometry of 10 is distorted square planar. The larger than 90° P1-Rh-P2 bond angle in 10 is parallel to its large $J_{P-P}$ value (48 Hz) in the $^{31}$P{$^{1}$H} NMR, consistent with the correlation between bond angles and coupling constants which were described by Karplus fifty years ago.$^{34, 35}$ All of the PMe$_3$ ligands are rotationally disordered: C1, C2, C3, C4 and C5 with attached hydrogens [and their symmetrical equivalents] occupy positions a (0.85 occupancy) and b (0.15 occupancy). The phenyl group and O1 lie on a mirror plane (together with the Rh and P2 atoms), but C6 and O2 are disordered between two positions related by this plane with equal occupancies.

In 13, the Rh1-P1 and Rh1-P3 bond lengths are 2.2958(8) and 2.2941(8) Å, respectively (which are identical within experimental error), whereas the Rh1-P2 bond length is 2.1984(8) Å. This result is consistent with those in 10, which further confirms that the PMe$_3$ ligand has a stronger \textit{trans}-influence than the \textit{η}$_1$-succinato oxygen atom. The Rh1-O1 and Rh2-O3 bond lengths are statistically identical [2.119(2) and 2.114(2) Å, respectively], and are shorter than the Rh-O1 bond length in 10 [2.1339(16) Å]. Similar to 10, the P1-Rh1-P2 bond angle is larger than 90°, which can be observed from the large $J_{P-P}$ value (45 Hz) in its $^{31}$P{$^{1}$H} NMR spectrum. The P1-Rh1-P2, P1-Rh1-O1, P2-Rh1-P3 and P3-Rh-O1 bond angles are 94.15(3), 85.34(7), 94.35(3) and 85.94(7)°,
respectively, whereas the P5-Rh2-P6, O3-Rh2-P6, P5-Rh2-P4 and O3-Rh2-P4 bond angles are 93.72(3), 84.64(7), 93.83(3) and 88.14(7)°, respectively, confirming that the geometry of 13 is distorted square planar. The C19-C20 and C20-21 bond lengths are 1.519(4) and 1.512(4) Å, respectively, which are typical for single C(sp³)-C(sp³) bonds.

Crystals of 11(a) and 11(c) were grown via slow vapour diffusion of hexane into their respective concentrated THF solutions. Rhodacyclopentadiene 11(a) crystallised in the orthorhombic space group Pbca, whereas 11(c) crystallised in the monoclinic space group P2₁/c. The molecular structures of 11(a) and 11(c) are shown in Figures 3.52 and 3.53, respectively. The crystallographic data are listed in Table 3.15.

Figure 3.52: Molecular structure of 11(a). Hydrogen atoms and the CH₂Cl₂ molecule are omitted for clarity (thermal ellipsoids are shown at 50% probability).
Figure 3.53: Molecular structure of 11(c). Hydrogen atoms and the C₆H₁₄ molecule are omitted for clarity (thermal ellipsoids are shown at 50% probability).

In 11(a) and 11(c), the Rh-P1 bond lengths of 2.3614(6) - 2.359(2) Å are slightly shorter than those of Rh-P2 [2.3739(6) - 2.378(2) Å], but the Rh-P3 bond lengths [2.3235(6) - 2.3215(19) Å] are much shorter than those of Rh-P2. The Rh-O1 bond lengths in 11(a) and 11(c) [2.1992(17) - 2.195(4) Å] are also significantly longer than those in 10 and 13, because there is no α-carbon from the rhodacycle ring in 10 and 13. Similarly, the shorter Rh-C20 bond lengths [2.033(2) - 2.012(7) Å] compared to Rh-C17 [2.071(2) - 2.063(7) Å] also confirm that the PMe₃ ligands have a stronger trans-influence compared to the oxygen atom in the η¹-benzoato-ligand.

The C=C C19-C20 and C17-C18 bond lengths are 1.376(3) - 1.350(9) and 1.369(3) - 1.356(9) Å, but the C18-C19 bond lengths of 1.446(3) - 1.441(9) Å are shorter than a typical C-C single bond length [1.52 Å]. This is due to the fact that they are both sp²-hybridised, with the possibility of increased the double bond character in C18-C19. The C23 atom in 11(a) is disordered between two positions, namely position a (0.75 occupancy) and b (0.25 occupancy).
In 11(a), the C-C≡C-C moiety at C17 is distorted from linearity to roughly the same degree as the analogous one at C20. The C17-C25-C26 and C25-C26-C27 bond angles are 178.3(3)° and 175.8(3)°, whereas the C20-C33-C34 and C33-C34-C35 bond angles are 178.1(3)° and 175.1(3)°. However, in 11(c), the former is distorted slightly more than the latter: C17-C25-C26 [177.1(8)°] and C25-C26-C27 [173.5(8)°] versus C20-C35-C36 [178.5(8)°] and C35-C36-C37 [176.1(8)°].

Single crystals of 12(a) were obtained via slow vapour diffusion of hexane into a concentrated THF solution. It crystallised in the monoclinic space group $P2_1/c$. The molecular structure of 12(a) is shown in Figure 3.54, and its crystallographic data are listed in Table 3.15. The C1-O1 [1.281(5) Å] and C1-O2 [1.291(5) Å] bond lengths are identical within experimental error, which indicates that the electrons are delocalised in the O1-C1-O2 fragment. In addition, the Rh-O1 and Rh-O2 bond lengths are also identical [2.240(2) and 2.241(3) Å, respectively]. The O1-Rh-O2 bond angle is 59.88(10)°, which is similar to the one reported by Werner et al.30 (60.2(1)° for $[\text{Rh}(\eta^2-\text{O}_2\text{CMe})(\text{PiPr}_3)_2]$) but slightly larger than those reported by Matsumoto and Yoshida31 (58.5(2)° for $[\text{Rh}(\eta^2-\text{O}_2\text{CMe})(\text{ppy})_2]$) and Merola et al.32 (58.9(3)° for $[\text{RhCp}^\ast(\eta^1-\text{O}_2\text{CPh})(\eta^2-\text{O}_2\text{CPh})]$). The Rh-Cα bond lengths in 12(a) (Rh-C16 [2.017(4) Å] and Rh-C23 [2.019(3) Å]) are generally shorter than those in 11(a) [2.033(2) - 2.071(2) Å] and 11(b) [2.012(7) – 2.063(7) Å]. The C-C≡C-C moiety at C16 is distorted from linearity slightly more than the one at C23 by comparing the bond angles of C16-C15-C14 [171.8(4)°] and C15-C14-C32 [176.9(5)°] to C23-C24-C25 [173.8(4)°] and C24-25-26 [177.4(4)°]. The two PMe₃ ligands are disordered: the P1Me₃ ligand is disordered between positions a and b with equal occupancies, whereas at the P2Me₃ ligand, all of the
methyl groups are disordered between positions a and b with occupancies of 0.85 and 0.15, respectively. In addition, the C19 and C20 atoms in the cyclohexyl ring are also disordered between positions a and b with equal occupancies.

![Molecular structure](image)

**Figure 3.54:** Molecular structure of 12(a). Disorder is shown but hydrogen atoms are omitted for clarity (thermal ellipsoids are shown at 50% probability).

### 3.2.8.3 Photophysical studies

Table 3.16 shows a summary of the photophysical data of 11(a) – (c) and 12(a) – (c). The absorption and emission spectra of 11(a) – (c) and 12(a) – (c) are shown in Figures 3.55 and 3.56, respectively.

Both electron withdrawing and donating substituents lead to a bathochromic shift on the $\lambda_{\text{max}}$ values of absorption and emission for both the $\eta^1$- and $\eta^2$-benzoato-rhodacyclopentadienes. The rhodacyclopentadienes with the electron withdrawing $R = \text{CO}_2\text{Me}$ substituent absorb and emit at lower wavelengths than those with the electron donating substituent, $R = \text{SMe}$. In addition, the $\lambda_{\text{max}}$ values are shifted to longer wavelengths upon conversion of the $\eta^1$-benzoato-rhodacyclopentadienes to their $\eta^2$-
benzoato analogues. In the absorption spectra, the smallest bathochromic shift is ca. 8 nm, but in the emission spectra, the smallest bathochromic shift is only 5 nm.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \lambda_{\text{max}} ) ABS (nm)</th>
<th>( \varepsilon ) (mol(^{-1}) cm(^{-1}) dm(^3))</th>
<th>( \lambda_{\text{max}} ) EM (nm)</th>
<th>Stokes shift (cm(^{-1}))</th>
<th>( \Phi )</th>
<th>( \tau ) (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11(a), R = H</td>
<td>465</td>
<td>19000</td>
<td>520</td>
<td>2300</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>11(b), R = SMe</td>
<td>477</td>
<td>19000</td>
<td>533</td>
<td>2500</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>11(c), R = CO(_2)Me</td>
<td>503</td>
<td>19000</td>
<td>570</td>
<td>2300</td>
<td>0.07</td>
<td>1.4</td>
</tr>
<tr>
<td>12(a), R = H</td>
<td>474</td>
<td>20000</td>
<td>525</td>
<td>2000</td>
<td>0.007</td>
<td>-</td>
</tr>
<tr>
<td>12(b), R = SMe</td>
<td>485</td>
<td>23000</td>
<td>543</td>
<td>2200</td>
<td>0.004</td>
<td>-</td>
</tr>
<tr>
<td>12(c), R = CO(_2)Me</td>
<td>512</td>
<td>22000</td>
<td>575</td>
<td>2100</td>
<td>0.03</td>
<td>2.4 (56%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.6 (29%)</td>
<td>0.1 (15%)</td>
</tr>
</tbody>
</table>

Note: All of the data (except \( \varepsilon \)) were recorded in degassed toluene solution at room temperature. \( \varepsilon \) values were recorded in non-degassed toluene solution. - No data recorded due to the low emission efficiency.
Figure 3.55: Absorption (top) and emission (bottom) spectra of 11(a) – (c) in toluene.
Figure 3.56: Absorption (top) and emission (bottom) spectra of 12(a) – (c) in toluene.

Based on Figures 3.55 and 3.56, the emission spectra of 11(a), 11(b), 12(a) and 12(b) are not smooth (they contain significant amounts of noise), which is due to the weak emissions from these four compounds, and the few photons generated by these four compounds are not sufficient for the lifetime measurements. The CO$_2$Me-substituted benzoato-rhodacyclopentadienes have stronger emissions compared to those with H- and SMe-substituted analogues. The $\Phi$ values are 0.07 and 0.03 for the CO$_2$Me-substituented $\eta^1$- and $\eta^2$-benzoato-rhodacyclopentadienes, respectively. The lifetime of 11(c) is 1.4 ns;
however, there are three lifetime components in 12(c), which are 2.4 (56%), 0.6 (29%) and 0.1 ns (15%). Of the three lifetime components, the one of 2.4 ns is more likely to be the real lifetime of 12(c), whereas the other two are probably due to impurities such as decomposition components from 12(c), when it is in low-concentration solutions. Again, the nanosecond lifetimes and small Stokes shifts (~2000 cm\(^{-1}\)) for 11(c) and 12(c) indicate that the emissions originated from singlet excited states.

The \( k_f \) values for 11(c) and 12(c) are 5.00 \( \times \) 10\(^7\) and 1.25 \( \times \) 10\(^7\) s\(^{-1}\), respectively, which are relatively smaller than those in TMSE-rhodacyclopentadienes (\( k_f \) values for 7(a), 7(b) and 7(d): 2.75 – 1.89 \( \times \) 10\(^8\) s\(^{-1}\)). This indicates that the non-radiative processes such as IC and ISC in benzoato-rhodacyclopentadienes are more efficient than the radiative ones. Non-radiative decay mechanisms could include rotations of the phenyl ring in the benzoato- ligand. On the other hand, the high-lying Rh filled d-orbitals could facilitate non-emissive MC d \( \rightarrow \) d\(^*\) transitions, which could also be a possible reason for the low \( \Phi_f \) values in the \( \eta^2\)-benzoato-rhodacyclopentadienes.

Absorption and emission spectra of 12(c) were also recorded in non-degassed toluene solution at room temperature (Figure 3.57). The emission spectrum is the same as that in degassed solution (Figure 3.56) indicating that the emission is from fluorescence rather than phosphorescence.
Figure 3.57: Absorption and emission spectra of 12(c) in non-degassed toluene solution.

Comparing their photophysical data to their \(N,N\)-diethylthiocarbamato-rhodacyclopentadiene analogues, which were synthesised by Dr. Andreas Steffen (Table 3.17),\(^{36}\) reveals that the \(\lambda_{\text{max}}\) values in both absorption and emission for the \(N,N\)-diethylthiocarbamato-rhodacyclopentadienes with \(R = \text{H and SMe}\) are similar to those of 12(a) and 12(b). However, for the \(N,N\)-diethylthiocarbamato-rhodacyclopentadiene with \(R = \text{CO}_2\text{Me}\), the \(\lambda_{\text{max}}\) values in absorption and emission are shifted to lower energy by 6 and 11 nm, respectively, compared to 12(c). Moreover, the \(\Phi_t\) values of the \(N,N\)-diethylthiocarbamato-rhodacyclopentadienes are significantly higher than those in \(\eta^2\)-benzoato-analogues.
Table 3.17: Summary of the photophysical data for dithiocarbama
torhodacyclopentadienes.36

$$\text{R = H, SMe, CO}_2\text{Me}$$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$ ABS (nm)</th>
<th>$\varepsilon$ (mol$^{-1}$ cm$^{-1}$ dm$^3$)</th>
<th>$\lambda_{\text{max}}$ EM (nm)</th>
<th>Stokes shift (cm$^{-1}$)</th>
<th>$\Phi$</th>
<th>$\tau$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = H</td>
<td>476</td>
<td>24000</td>
<td>526</td>
<td>2000</td>
<td>0.07</td>
<td>1.0 (13%) 0.4 (87%)</td>
</tr>
<tr>
<td>R = SMe</td>
<td>487</td>
<td>21000</td>
<td>541</td>
<td>2000</td>
<td>0.16</td>
<td>1.1 (72%) 0.7 (28%)</td>
</tr>
<tr>
<td>R = CO$_2$Me</td>
<td>518</td>
<td>19000</td>
<td>586</td>
<td>2200</td>
<td>0.46</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Compared to the TMSE-rhodacyclopentadienes [7(a), 7(b) and 7(d)], the emissions of 12(a) – (c) and the dithiocarbamato-rhodacyclopentadienes are significantly red-shifted but with lower $\Phi$ values. The implication here is that the Rh centre must be involved in the transitions since the photophysical properties of the rhodacyclopentadienes can be altered by changing the ligand sphere. Again, no phosphorescence was observed for the dithiocarbamato-rhodacyclopentadienes at 77 K, although the Rh participates to a certain extent in the transitions of the rhodacyclopentadienes.36

3.2.9 Acetylacetonato- (acac-) rhodacyclopentadienes

3.2.9.1 Synthesis and characterisation

The acetylacetonato- (acac-) ligand has been used in cyclometallated iridium complexes in order to tune their emission colours and $\Phi_p$ values.37 In this work, the acac- ligand was
attached to rhodacyclopentadienes in order to increase the metal character in the frontier orbitals by destabilising the Rh filled d-orbitals. Although the benzoato- and \( N,N \)-diethyldithiocarbamato- ligands have been examined for this purpose, the nanosecond lifetimes and the small Stokes shifts (about 2000 cm\(^{-1} \)) implied that the emissions were purely from the singlet excited states. This is supported by the results from the low-temperature lifetime measurements for the \( N,N \)-diethyldithiocarbamato- analogues, in which no phosphorescence was observed at 77 K. Moreover, the emissions were quenched in 11(a), 11(b), 12(a) and 12(b), which implies that the benzoato- ligand is not generally interesting for photophysical studies of rhodacyclopentadienes.

To synthesise the acac-rhodacyclopentadienes (Figure 3.58), acetylacetone was added to a \([\text{RhMe}(\text{PMe}_3)_4]\) solution in degassed THF. The reaction was stirred for 1 h and the volatiles were removed in vacuo and refilled with fresh solvent three times in order to remove the methane and two equivalents of PMe\(_3\) to afford the \([\text{Rh(acac})(\text{PMe}_3)_2]\) complex, 14.

**Figure 3.58:** Synthetic route to acac-rhodacyclopentadienes and their biphenyl- rhodacyclopentadiene by-products.
The reaction of [Rh(PMe$_3$)$_4$]Cl with Na(acac) in degassed water was also attempted as a potential route to 14, but was not successful as only starting materials were observed in the \textit{in situ} $^{31}$P{\textsuperscript{1}H} NMR spectrum of the reaction. Interestingly, the reaction between [RhMe(PMe$_3$)$_4$] and acetylacetone in degassed THF provides a clean, easy and fast route with quantitative conversion to give 14 in good isolated yield (86%). Similar to 10, the $^{31}$P{\textsuperscript{1}H} NMR spectrum of 14 at room temperature shows a broad signal at 6.92 ppm. At 203 K, a doublet appears at 5.78 ppm with $J_{\text{Rh-P}} = 185$ Hz indicating that there is only one type of PMe$_3$ present in the structure and the Rh oxidation state is +1. The square planar structure with two PMe$_3$ ligands and a chelating acac-ligand was confirmed by X-ray diffraction analysis.

After confirming the structure of 14, it was reacted with one equivalent of the appropriate 1,12-bis($p$-R-phenyl)dodeca-1,3,9,11-tetrayne at 50 °C to form acac-rhodacyclopentadienes [R = H, 15(a); R = SMe, 15(b); R = CO$_2$Me, 15(c)] and their respective isomeric products [R = H, 16(a); R = SMe, 16(b); R = CO$_2$Me, 16(c)]. The formation of the isomeric species was observed in the \textit{in situ} $^{31}$P{\textsuperscript{1}H} NMR spectra (Figure 3.59).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3.59.png}
\caption{\textit{In situ} $^{31}$P{\textsuperscript{1}H} NMR spectrum (81 MHz, C$_6$D$_6$) of 15(a) and the isomeric product, 16(a).}
\end{figure}
The ratios of the isomers to simple acac-rhodacyclopentadiene are dependent on the R group. For example, for 15(a) [R = H], the ratio of isomeric product 16(a) to acac-rhodacyclopentadiene is ca. 1 : 2 (Figure 3.59), whereas for 15(c) [R = CO₂Me], the ratio of 16(c) : 15(c) is 1 : 1. The reaction times are also dependent on the R groups. For example, for R = CO₂Me, the reaction was complete after 3 days, whereas for R = H, the reaction took about 16 days to complete. The pure acac-rhodacyclopentadienes 15(a) - (c) were able to be separated from the mixtures by washing the residues with hexane, as the isomeric products are soluble in hexane. Single crystals of the biphenyl-based rhodacyclopentadiene 16(c) grew in the hexane solution and were analysed by X-ray diffraction, which confirmed its structure. The ¹H NMR spectrum of isolated 16(c) is shown in Figure 3.60. A doublet and a broad singlet appear at the extreme low field chemical shifts at 9.53 (J = 8 Hz) and 9.11 ppm. A singlet from an aromatic proton overlaps with a doublet at 8.05 ppm; therefore, the proton integration for this signal is 3. Unlike other rhodacyclopentadienes, the CH₂-C=C and CH₂ signals from the cyclohexyl moiety in 16(c) are well resolved, which show triplets for CH₂C=C at 3.24 and 2.91 ppm (J = 8 Hz), and quintets for CH₂ at 1.79 and 1.69 ppm (J = 8 Hz).
It is likely that the isomeric products 16(a) and 16(b) from reactions 15(a) and 15(b) are analogous to 16(c), because the chemical shifts and coupling constants of 16(a) and 16(b) in the $^{31}$P[$^1$H] NMR spectra are similar to those in 16(c). The biphenyl-based rhodacyclopentadiene 16(c) is the first example of an isomeric by-product to be observed in our rhodacyclopentadiene syntheses since our first report in 2001.\footnote{\textsuperscript{7}}

\subsection*{3.2.9.2 Crystallographic data for 14, 15(b), 15(c) and 16(c)}

The X-ray crystallographic data for 14, 15(b), 15(c) and 16(c) are listed in Table 3.18. Rhodium complex 14 was recrystallised via slow diffusion of a layer of hexane into a THF solution in a Young’s tube. It crystallised in the tetragonal space group $P4_2_1c$. The molecular structure of 14 is shown in Figure 3.61.
The C10-C9 [1.383(3) Å] and C9-C8 [1.399(3) Å] bond lengths are shorter than typical C-C single bond lengths, which indicates that the electrons are delocalised in the acac-moiety, and have partial C=C bond character. The C10-C9-C8 bond angle is 126.12(15)°, which supports C9 being an sp^2-hybridised carbon. The Rh-P1 and Rh-P2 bond lengths are identical within experimental error [2.1953(5) and 2.1950(5) Å, respectively]. Similarly, the Rh-O1 and Rh-O2 bond lengths are also identical within experimental error [2.0850(11) and 2.0868(10) Å, respectively]. The P1-Rh-P2 [94.716(15)°], P2-Rh-O1 [89.52(3)°], P1-Rh-O2 [87.98(3)°] and O1-Rh-O2 [88.02(4)°] bond angles are all close to 90°, which indicates that the geometry of the Rh is distorted square planar. The P1Me₃ ligand is rotationally disordered between two orientations, a and b, with occupancies refined to 0.747(4) and 0.253(4), respectively.
### Table 3.18: Crystallographic data for 14, 15(b), 15(c) and 16(c).

<table>
<thead>
<tr>
<th>Compound</th>
<th>14</th>
<th>15(b)</th>
<th>15(c)</th>
<th>16(c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{11}H_{25}O_{2}P_{2}Rh</td>
<td>C_{37}H_{47}O_{2}P_{2}RhS</td>
<td>C_{39}H_{47}O_{6}P_{2}Rh</td>
<td>C_{39}H_{47}O_{6}P_{2}Rh</td>
</tr>
<tr>
<td>Formula weight</td>
<td>354.16</td>
<td>752.72</td>
<td>776.62</td>
<td>776.62</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>120(2)</td>
<td>120(2)</td>
<td>120(2)</td>
<td>120(2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Tetragonal</td>
<td>Triclinic</td>
<td>Triclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P4_{2}1/c</td>
<td>P 1</td>
<td>P 1</td>
<td>P2_{1}/c</td>
</tr>
<tr>
<td>a (Å)</td>
<td>18.090(2)</td>
<td>9.7099(8)</td>
<td>9.8978(8)</td>
<td>14.2755(19)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>18.090(2)</td>
<td>9.7832(8)</td>
<td>10.0553(8)</td>
<td>24.309(3)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>10.1741(14)</td>
<td>20.0082(17)</td>
<td>19.9344(16)</td>
<td>10.5470(14)</td>
</tr>
<tr>
<td>α (°)</td>
<td>90.00</td>
<td>97.636(7)</td>
<td>102.462(6)</td>
<td>90.00</td>
</tr>
<tr>
<td>β (°)</td>
<td>90.00</td>
<td>103.479(7)</td>
<td>99.966(6)</td>
<td>99.423(8)</td>
</tr>
<tr>
<td>γ (°)</td>
<td>90.00</td>
<td>96.458(7)</td>
<td>98.427(6)</td>
<td>90.00</td>
</tr>
<tr>
<td>Volume (Å^3)</td>
<td>3329.6(8)</td>
<td>1811.5(3)</td>
<td>1872.8(3)</td>
<td>3610.6(8)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated) (Mg/m^3)</td>
<td>1.413</td>
<td>1.380</td>
<td>1.377</td>
<td>1.429</td>
</tr>
<tr>
<td>Absorption coefficient (mm^{-1})</td>
<td>1.205</td>
<td>0.706</td>
<td>0.586</td>
<td>0.607</td>
</tr>
<tr>
<td>Crystal size (mm^3)</td>
<td>0.45 x 0.40 x 0.32</td>
<td>0.26 x 0.20 x 0.04</td>
<td>0.20 x 0.14 x 0.10</td>
<td>0.27 x 0.25 x 0.17</td>
</tr>
<tr>
<td>Θ range for data collection (°)</td>
<td>2.30 to 29.99</td>
<td>2.21 to 29.95</td>
<td>2.58 to 29.83</td>
<td>2.58 to 29.96</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>33857</td>
<td>25937</td>
<td>18559</td>
<td>42397</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>4820</td>
<td>10123</td>
<td>10253</td>
<td>10309</td>
</tr>
<tr>
<td>Data / Restraints / Parameters</td>
<td>4820 / 0 / 180</td>
<td>10123 / 0 / 431</td>
<td>10253 / 0 / 469</td>
<td>10309 / 0 / 453</td>
</tr>
<tr>
<td>Final R indices [I&gt;2σ(I)]</td>
<td>R_1 = 0.0152, wR_2 = 0.0360</td>
<td>R_1 = 0.0343, wR_2 = 0.0727</td>
<td>R_1 = 0.0455, wR_2 = 0.0922</td>
<td>R_1 = 0.0307, wR_2 = 0.0678</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R_1 = 0.0161, wR_2 = 0.0363</td>
<td>R_1 = 0.0447, wR_2 = 0.0763</td>
<td>R_1 = 0.0686, wR_2 = 0.1008</td>
<td>R_1 = 0.0386, wR_2 = 0.0707</td>
</tr>
</tbody>
</table>

Single crystals of 15(b) and 15(c) were obtained via slow vapour diffusion from hexane into concentrated THF solutions. Both compounds crystallised in the triclinic space group P 1. The molecular structures of 15(b) and 15(c) are shown in Figures 3.62 and 3.63, respectively.
In both compounds, the Rh-O1 and Rh-O2 bond lengths are 2.1513(14) – 2.1279(18) and 2.1383(14) - 2.1567(17) Å, respectively. The Rh-Cα bond lengths of both compounds are in the range 2.0120(19) – 2.0234(19) Å, which is similar to that of 12(a) [2.017(4) - 2.019(3) Å]. The O1-Rh-O2 bond angles are 88.52(6) – 88.34(5)°, which are slightly larger than the one in 14 [88.02(4)°]. Similarly to 14, the C2-C3 [1.401(3) - 1.400(4) Å] and C3-C4 [1.406(3) - 1.400(4) Å] bond lengths in both 15(b) and 15(c) are also shorter than typical C-C single bond length, which indicates that the electrons are delocalised in the acac- moiety. Moreover, the C2-C3-C4 bond angles of 127.7(2) - 127.8(3)° support
C3 being sp\(^2\)-hybridised in both compounds. The P1-Rh-P2 bond angle in \textbf{15(c)} [173.91(3)°] deviates more from linearity than the one in \textbf{15(b)} [175.63(2)°].

In \textbf{15(b)}, the Rh-C14 and Rh-C21 bond lengths are 2.0234(19) and 2.0120(19) Å, respectively, and the C14-Rh-C21 bond angle is 79.37(8)°. The C-C≡C-C moiety at C14 is distorted more from linearity than the one at C21, which can be observed from the comparison of the C14-C30-C31 [173.5(2)°] and C30-C31-C32 [172.3(2)°] bond angles to C21-C22-C23 [178.0(2)°] and C22-C23-C24 [175.6(2)°]. One of the SMe groups is disordered between two opposite orientations, with occupancies of 0.643(5) for orientation \textit{a} and 0.357(5) for orientation \textit{b}.

In \textbf{15(c)}, the Rh-C12 and Rh-C19 bond lengths are 2.012(2) and 2.020(3) Å, respectively, and the C12-Rh-C19 bond angle is 79.07(10)°. The C-C≡C-C moiety at C19 is distorted much more from linearity than the one at C12 by comparison of the C19-C30-C31 [173.2(3)°] and C30-C31-C32 [170.2(3)°] bond angles to C12-C20-C21 [178.9(3)°] and C20-C21-C22a [178.2(5)°] or C20-C21-C22b [174.2(7)°]. One of the benzene rings (and its CO\(_2\)Me group) is disordered between two orientations (\textit{a} and \textit{b}) differing by an in-plane tilt and a 180°-rotation around the C21-C28 bond, with occupancies refined to 0.704(6) and 0.296(6), respectively.

Biphenyl-rhodacyclopentadiene \textbf{16(c)} crystallises in the monoclinic space group \textit{P}2\(_1\)/\textit{c} from a concentrated hexane solution. The molecular structure of \textbf{16(c)} is shown in Figure 3.64. The Rh-O1 and Rh-O2 bond lengths are 2.1540(12) and 2.1529(12) Å (identical within experimental error), respectively. The Rh-Cα bond lengths, namely, Rh-C12 and Rh-C19 are 1.9914(16) and 2.0062(12) Å, respectively, and these two bonds are slightly shorter (ca. 0.014 – 0.020 Å) than those in \textbf{15(b)} and \textbf{15(c)}. This may be because the
electron delocalisation in the rhodacycle ring in 16(c) is slightly greater than that in 15(b) and 15(c). Moreover, the C12-C17 and C18-C19 bond lengths are 1.424(2) and 1.419(2) Å, respectively, and the C17-C18 [1.477(2) Å] bond length is shorter than the typical C(sp³)-C(sp³) bond length [1.52 Å], since they are both sp²-hybridised carbons. The geometry at the Rh centre is distorted octahedral, because the C12-Rh-C19 [80.75(7)°] and O1-Rh-O2 [88.93(5)°] bond angles are smaller than 90°. The C21-C36, C36-C37, C37-C38, C38-C39 and C22-C39 bond lengths are in the range 1.519(3) – 1.529(3) Å, which are typical C(sp³)-C(sp³) bond lengths.

![Molecular structure](image)

Figure 3.64: Molecular structure of 16(c). Hydrogen atoms are omitted for clarity (thermal ellipsoids are shown at 50% probability).

3.2.9.3 Photophysical studies

Table 3.19 gives a summary of the photophysical data obtained for 15(a), 15(b) and 15(c), and their absorption and emission spectra are shown in Figure 3.65. As expected,
the $\lambda_{\text{max}}$ values of both absorption and emission spectra for the complex containing electron withdrawing substituent ($R = \text{CO}_2\text{Me}$) are also more red-shifted compared to that containing the electron donating substituent ($R = \text{SMe}$). The $\lambda_{\text{max}}$ values of absorption and emission for the acac-rhodacyclopentadienes are close to those of the $\eta^2$-benzoato-rhodacyclopentadienes [12(a), 12(b) and 12(c)]. This indicates that the acac- ligand, as a strong $\sigma$- and $\pi$-donor to the Rh centre, is able to reduce the energy gap between the excited states and the ground state of rhodacyclopentadienes.

Table 3.19: The summary of the photophysical data for 15(a) - (c).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$ ABS (nm)</th>
<th>$\epsilon$ (mol$^{-1}$ cm$^{-1}$ dm$^3$)</th>
<th>$\lambda_{\text{max}}$ EM (nm)</th>
<th>Stokes shift (cm$^{-1}$)</th>
<th>$\Phi$</th>
<th>$\tau$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15(a), $R = \text{H}$</td>
<td>470</td>
<td>16000</td>
<td>520</td>
<td>2000</td>
<td>0.04</td>
<td>3.4 (6%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.0 (10%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.2 (84%)</td>
</tr>
<tr>
<td>15(b), $R = \text{SMe}$</td>
<td>481</td>
<td>23000</td>
<td>534</td>
<td>2100</td>
<td>0.13</td>
<td>2.0 (25%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.5 (75%)</td>
</tr>
<tr>
<td>15(c), $R = \text{CO}_2\text{Me}$</td>
<td>514</td>
<td>34000</td>
<td>579</td>
<td>2200</td>
<td>0.50</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Note: All of the data above (except $\epsilon$) were recorded at room temperature in degassed toluene solution. $\epsilon$ values were recorded in non-degassed toluene solutions.
Figure 3.65: Absorption (top) and emission (bottom) spectra of 15(a) – (c) in toluene.

The $\Phi$ values of the acac-rhodacyclopentadienes are higher than those for the $\eta^2$-benzoato-rhodacyclopentadienes, which may be because the acac-ligand is more rigid than the benzoato-ligand. Acac-rhodacyclopentadiene 15(a) ($R = H$) gave the lowest $\Phi$ value ($\Phi = 0.04$), whereas 15(c) ($R = CO_2Me$) gave the highest $\Phi$ value ($\Phi = 0.50$). Again, the nanosecond lifetimes and small Stokes shifts (ca. 2000 cm$^{-1}$) in the acac-rhodacyclopentadienes confirm that the emissions occur from the singlet excited states, and no phosphorescence was observed at room temperature between 400 – 800 nm. One
of the possible explanations for this lack of phosphorescence is that the triplet excited states lie close in energy to the ground state, increasing the Frank-Condon factors.

### 3.2.9.4 Photophysical studies of 16(c)

The photophysical information from isolated 16(c) is very important to compare with the other rhodacyclopentadienes that have been reported so far. Table 3.20 shows the photophysical data for 16(c), its absorption and emission spectra in non-degassed and degassed solutions are shown in Figure 3.66, and the excitation spectrum is shown in Figure 3.67.

#### Table 3.20: Summary of the photophysical data for 16(c).

<table>
<thead>
<tr>
<th>λ ABS (nm)</th>
<th>ε (mol⁻¹ cm⁻¹ dm³)</th>
<th>λ EM (nm)</th>
<th>Stokes shift (cm⁻¹)</th>
<th>Φ</th>
<th>τ @ 394 nm (ns)</th>
<th>τ @ 544 nm (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>330</td>
<td>28000</td>
<td>394</td>
<td>4600</td>
<td>0.03 (Φₜ)</td>
<td>3.0 (31%)</td>
<td>237.6</td>
</tr>
<tr>
<td>372</td>
<td>24000</td>
<td>416</td>
<td>11920</td>
<td>0.05(Φₚ)</td>
<td>0.6 (69%)</td>
<td></td>
</tr>
<tr>
<td>410 (sh)</td>
<td>9000</td>
<td>544</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>587</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: The data above (except ε) were recorded in degassed toluene at room temperature. ε values were recorded in non-degassed toluene solution.
In the non-degassed toluene solution, a fluorescent emission at 394 nm and a weak broad emission band at 574 nm were observed in the spectrum. After the sample was fully degassed, a strong emission was found with $\lambda_{\text{max}}$ at 544 nm. This emission only appears as a weak broad band in the non-degassed solution; therefore, this must be phosphorescent emission that occurs from the triplet excited states because it was
quenched by the triplet oxygen molecules through the process of triplet-triplet annihilation.

**Figure 3.67:** Excitation spectrum of 16(c) with the emission wavelength at 544 nm.

The dual fluorescent and phosphorescent emissions in emission spectrum of the degassed solution are possibly due to the presence of two chromophores in the structure. The emission at 394 nm is due to the organic chromophore, while the emission at 544 nm is possibly due to the biphenyl-rhodacyclopentadiene moiety.

Two lifetime components were recorded for 16(c): the one on the nanosecond timescale was assigned to the emission at 394 nm, while the other one on the 200 microsecond timescale belongs to the emission at 544 nm. The long-lived emission lifetime (237 µs at room temperature) indicates that the emission at 544 nm is possibly due to triplet state ligand-centred (LC) $\pi \rightarrow \pi^*$ transitions. The long-lived emission lifetime at room temperature is unusual in cyclometallated Rh(III) complexes. For example, as mentioned before, $[\text{Rh(bpy)}_3]^{3+}$ was reported as non-emissive at room temperature. Similar to $[\text{Rh(bpy)}_3]^{3+}$, $[\text{Rh(ppy)}_2(\text{bpy})]^{+}$ was also non-emissive at room temperature in EtOH or
MeOH. However, an emission was observed at 77 K, which was assigned to a $\pi \rightarrow \pi^*$ transition with a lifetime of 177 $\mu$s.\textsuperscript{38} Moreover, Lo et al.\textsuperscript{39} reported their cyclometallated Rh\textsuperscript{(III)} diimine complexes e.g. [Rh(pba)$_2$(bpy)]Cl (Hpba = 4-(2-pyridyl)benzaldehyde; bpy = 2,2’-bipyridine) have the room temperature phosphorescence lifetimes of 4.2 – 8.7 $\mu$s. The room temperature lifetime of 16(c) is at least twenty-five times longer than those reported by Lo et al.

In typical phosphorescent rhodium complexes containing cyclometallating ligands, the emissions are usually weak especially at room temperature ($\Phi_p = 0.001 – 0.03$),\textsuperscript{39-41} but the $\Phi_p$ value at room temperature for 16(c) is 0.05.

Compound 16(c) is the only rhodacyclopentadiene that we have found to phosphorescence at room temperature in this work. The photophysical properties of 16(c) have proven that Rh participates in the excited states, as it shows phosphorescent emission. Compared to the other rhodacyclopentadienes in this work, the difference between 16(c) and the others is in the rhodacycle ring: namely that 16(c) contains a biphenyl moiety, where as the others have cyclohexyl loops or phenyl rings. It is possible that the electron delocalisation in the rhodacycle ring in 16(c) is more effective than that in the others. This can be supported by inspection of the Rh-C$\alpha$ bond lengths which are shorter in 16(c) [1.9914(16) – 2.0062(16) Å] than in 15(b) [2.012(19) – 2.0234(19) Å] and 15(c) [2.012(2) – 2.020(3) Å]. The effectiveness of the electron delocalisation in the rhodacycle ring is a possible factor, which might determine the amount of Rh participation in the excited states.
3.3 Summary and conclusion

Twenty-six rhodacyclopentadienes with different types of ligands were synthesised and characterised. Many of their structures have also been confirmed from single-crystal X-ray diffraction data. The photophysical data for these rhodacyclopentadienes were collected and the general results are as follows:

(i) nanosecond lifetimes and small Stokes shifts (ca. 2000 cm\(^{-1}\)) indicate that the emissions originate from the singlet excited states;

(ii) no phosphorescence was observed at room temperature in the 400 – 800 nm range in any of the rhodacyclopentadienes [except 16(c)], despite the fact that the Rh centres are involved in the transitions;

(iii) both electron withdrawing and donating R substituents shift the \(\lambda_{\text{max}}\) values of absorption and emission bathochromically;

(iv) those with electron withdrawing R substituents absorb and emit at lower energies and with higher \(\Phi\) values than those with electron donating R substituents; and

(v) the use of TMSE as the \(\sigma\)-donor ligand to the Rh centre gives the highest \(\Phi\) values compared to the other ligands.

Extended phenylene-ethynylene moieties were applied as the R substituents [namely -C≡C-C\(_6\)H\(_4\)-CO\(_2\)(\(n\)-C\(_8\)H\(_{17}\)) and -C≡C-C\(_6\)H\(_4\)-N(\(n\)-C\(_6\)H\(_{13}\))\(_2\)], and the \(\sigma\)-donor ligand (DHAPEPE-). Both types of rhodacyclopentadienes exhibited a decrease of \(\Phi_t\) values, which is possibly due to the poor rigidity of the long alkyl chains. However, the use of extended phenylene-ethynylene as the R substituents in rhodacyclopentadienes shifts the absorption and emission maxima bathochromically.
Replacement of the two phenyl rings at the 3- and 4-positions of the rhodacycle by a
cyclohexyl ring can greatly improve the $\Phi_f$ values of the TMSE-rhodacyclopentadienes.
The TMSE-rhodacyclopentadiene with $R = H$ [7(a)] has been investigated further by
singlet oxygen experiments, low-temperature lifetime measurements, and time resolved-
infrared (TRIR) experiments. The results from these experiments showed that the singlet
excited state decays effectively only by fluorescence and ISC to a triplet excited state,
with no $S_1 \rightarrow S_0$ internal conversion [since $\Phi_\Delta (0.65) + \Phi_f (0.33) \approx 1.00$]. This is because
the fluorescence rate is competitive with the intersystem crossing (ISC) rate as both rates
are of the order of $10^8$ s$^{-1}$. The TRIR results showed 7(a) has a short-lived triplet excited
state lifetime, which is ca. 55 ns. Based on the results of preliminary TD-DFT
calculations that have been performed for 7(d), the $T_1$ state is low in energy, which
results in appreciably large Frank-Condon factors. Therefore, non-radiative processes are
believed to dominate the deactivation of the $T_1$ state, which result in a short triplet state
lifetime.

Benzoato- and acac- ligands were introduced to the Rh centre in an attempt to increase
the rate of ISC by raising the Rh filled d-orbitals, and consequently increasing the Rh
character in the frontier orbitals. The $\lambda_{\text{max}}$ values in absorption and emission of both $\eta^2$-
benzoato- and acac-rhodacyclopentadienes are very similar. The significant bathochromic
shifts of the $\lambda_{\text{max}}$ values in absorption and emission of $\eta^2$-benzoato- and acac-
rhodacyclopentadienes relative to those rhodacyclopentadienes with other ligands such as
TMSE- and DHAPEPE- indicate that the energy gaps between the excited and ground
states are smaller than those in their TMSE- and DHAPEPE- analogues.
The first example of biphenyl-rhodacyclopentadiene formation in our rhodacyclopentadiene syntheses was observed in the preparation of acac-rhodacyclopentadienes. The biphenyl-rhodacyclopentadiene 16(c) shows phosphorescent emission with a \( \lambda_{\text{max}} \) value of 544 nm in degassed solution. The long-lived phosphorescence lifetime (237 \( \mu \)s) confirms that the phosphorescence arises from \(^3\text{LC} \pi \rightarrow \pi^*\) transitions. The \( \Phi \) values for 16(c) are 0.03 for fluorescence and 0.05 for phosphorescence at room temperature.

In conclusion, we have reported different series of rhodacyclopentadienes, which exhibit long-lived fluorescence and slow ISC rates (\( k_{\Delta} \approx k_f \approx 10^8 \text{ s}^{-1} \), especially TMSE-rhodacyclopentadienes), although the Rh centre is involved to a certain extent in the transitions, which is confirmed by the shifts in \( \lambda_{\text{max}} \) values when different ligands are placed on the Rh centres. This indicates that the efficiency of ISC in an organometallic complex is not only dependent on what type of metal is present, but is also dependent on how efficient the SOC effect from the metal is. The results from the singlet oxygen sensitisation and TRIR experiments showed that the triplet excited states are present in the rhodacyclopentadienes, but no phosphorescence [except for 16(c)] was observed at room temperature in the 400 – 800 nm range. A potential reason for this is the \( T_1 \) states lie close in energy to the ground states, which causes a significant overlap between the triplet excited states and upper vibrational levels of the ground states. As a result, the triplet excited states decay via non-emissive processes which are more efficient than emission of a photon (i.e. phosphorescence).
3.4 Experimental

3.4.1 General

All rhodacyclopentadiene syntheses and purifications were performed in a nitrogen-filled Innovative Technology Inc. glovebox unless otherwise noted. [RhCl₃⋅3H₂O] was purchased from Precious Metals Online, Australia, and used without further purification. 1,12-bis(p-trimethylsilylethynylphenyl)dodeca-1,3,9,11-tetrayne was supplied by Liu Chao from the Green Catalyst Institute, Wuhan University, China. HPLC grade solvents (Fisher Scientific and J.T. Baker) were nitrogen saturated and were dried and deoxygenated using an Innovative Technology Inc. Pure-Solv 400 Solvent Purification System, and further deoxygenated using the freeze-pump-thaw method. C₆D₆ was purchased from Cambridge Isotope Laboratories and dried over sodium granules for 72 h, deoxygenated using the freeze-pump-thaw method and vacuum transferred to a sealed vessel.

All NMR spectra recorded at ambient temperature, were obtained using Varian Mercury 400 (¹H: 400 MHz, ³¹P{¹H}: 162 MHz, ¹⁹F{¹H}: 376 MHz), Bruker Avance 400 (¹H: 400 MHz, ³¹P{¹H}: 162 MHz), Varian Inova 500 (¹H: 500 MHz, ³¹P{¹H}: 202 MHz) or Varian DD-700 (¹H: 700 MHz) spectrometers. The ³¹P{¹H} NMR spectra of 1, 10, 13 and 14 at 196 – 203 K were recorded using a Varian Inova 500 spectrometer. ¹H NMR chemical shifts are reported relative to TMS and were referenced via residual proton resonances of the appropriate deuterated solvent (C₆D₆: 7.15 ppm), whereas the ³¹P{¹H} NMR spectra were referenced externally to H₃PO₄ (85%) at 0 ppm.

Elemental analyses were obtained using an Exeter Analytical Inc. CE-440 elemental analyzer in the Department of Chemistry at Durham University. Mass spectrometric
determinations were obtained using either a MALDI ToF Applied Biosystems Voyager-DE STR mass spectrometer or by ES using a Thermo-Finnigan LTQ FT spectrometer operating in positive ion mode. The samples for elemental analysis and mass spectrometric determinations were prepared in the glovebox. IR spectra were recorded as KBr disks using a Perkin-Elmer Spectrum 100 series FT-IR spectrometer.

The crystallographic data collections and structure solutions were carried out by Dr. Andrei S. Batsanov, the Department of Chemistry, Durham University, using a Bruker three-circle diffractometer with a CCD area detector. The structures were solved by direct methods and refined by full-matrix least squares against $F^2$ of all data, using SHELXTL software.

### 3.4.2 Photophysical studies

UV-Vis and fluorescence spectra were recorded in HPLC toluene which was degassed via the freeze-pump-thaw method. All of the UV-Vis absorption spectra and extinction coefficients were measured on a Hewlett-Packard 8453 diode array spectrophotometer using standard 1 cm width quartz cells. Emission spectra were obtained on a Horiba Jobin-Yvon Fluoromax-3 spectrophotometer. The emission spectra were fully corrected using the manufacturer's correction curves for the spectral response of the emission optical components.

Low temperature emission, quantum yield and fluorescence lifetime measurements were recorded using the instruments located in Dr. Andrew Beeby’s laboratory, in the Department of Chemistry, Durham University. The low temperature emission spectrum
of 7(a) was recorded by Dr. Andrew Beeby in an iso-pentane/Et$_2$O/EtOH glass at 77 K. The quantum yield and lifetime measurements as well as the singlet oxygen sensitisation experiments were carried out by Dr. Andreas Steffen from our group. Quantum yields for samples with absorbance at the maximum typically below 0.2 were determined using a Horiba Jobin-Yvon Fluorolog 3-22 Tau-3 spectrophotometer. The method of quantum yield calculation followed that described in the literature.$^{42}$

Fluorescence lifetimes were measured by time-correlated single-photon counting (TCSPC) using a pulsed diode laser 396 nm providing a 1 MHz train of pulses of $< 100$ ps. The fluorescence emission was collected at right angles to the excitation source, with the emission wavelength selected using a monochromator and detected by a single-photon avalanche diode (SPAD). The instrument response function was measured using a dilute LUDOX® suspension as the scattering sample, setting the monochromator at the emission wavelength of the laser, giving an instrument response function (IRF) of 200 ps at 396 nm. The resulting intensity decay was a convolution of the fluorescence decay with the IRF, and iterative reconvolution of the IRF with a decay function and non-linear least-squares analysis were used to analyse the convoluted data.$^{43, 44}$

Singlet oxygen sensitisation experiments for 7(a), 7(b) and 7(d) in aerated solutions were also performed in Dr. Andrew Beeby’s laboratory. The quantum yields of singlet oxygen formation were determined relative to perinaphthanone in toluene ($\Phi_\Delta = 1.0$) using a method described by Nonell and Braslavsky.$^{29}$ The samples and the reference compounds were analysed in the same solvent because of the strong dependence of the radiative and non-radiative rate constants for deactivation of the triplet states on the solvent. The singlet oxygen emission was detected at 1269 nm from solutions in a 1 cm
path length quartz cuvette after being excited at 355 nm by a Q-switched Nd:YAG laser (Spectra Physics, Quanta Ray GCR-150-10) with a 10 Hz repetition rate. The emission was collected at 90° to the excitation beam by a liquid nitrogen cooled germanium photodiode (North Coast E0-817P) after passing through an interference filter centred at 1270 nm. The photodiode output was amplified and AC coupled to a digital oscilloscope which digitised and averaged the transients. The averaged data were then analysed using the Microsoft Excel package.

Time-resolved infrared (TRIR) measurements for 7(a) were performed in Prof. Michael George’s laboratory, School of Chemistry in the University of Nottingham. The concentration of 7(a) was approximately 10^{-3} M in all the TRIR experiments. A brief explanation of the measurement technique was reported in the supporting information in reference 36.

3.4.3. Preparation of tetrakis(trimethylphosphine)methylrhodium

Rhodium cyclooctadiene chloride dimer\textsuperscript{45} 

[\text{RhCl}_3\cdot3\text{H}_2\text{O}] (10.00 g, 37.98 mmol) was added to a 500 mL round bottom flask which had been evacuated and refilled 3 times with \text{N}_2. Degassed spectroscopic grade ethanol (120 mL) and degassed distilled water (50 mL) were transferred to the flask via cannula and the solution was stirred rapidly. 1,5-Cyclooctadiene (COD, in liquid form, density = 0.882 g/mL) (10 mL, 81.53 mmol) was added dropwise to the solution via dropping funnel and the reaction was heated at 60 °C for 24 h under \text{N}_2. The product, [\text{RhCl(COD)}]_2, was precipitated as a yellow solid, and was collected by filtration, washed
with degassed EtOH (20 mL), followed by degassed Et₂O (30 mL), dried *in vacuo* and stored under N₂. Yield: 17.60 g, 94%. ¹H NMR (400 MHz, C₆D₆) δ: 4.27 (s, 4H, olefin COD), 2.02 (m, 4H, CH₂, COD), 1.26 (m, 4H, CH₂, COD).

[Tetrakis(trimethylphosphine)rhodium]chloride, [Rh(PMe₃)₄]Cl¹⁹

[RhCl(COD)]₂ (3.215 g, 6.53 mmol) was added under N₂ to degassed THF (100 mL) in a 500 mL round bottom flask and the solution was stirred rapidly. PMe₃ (6.73 mL, 65.30 mmol) was dissolved in THF (20 mL) and added dropwise to the solution using a dropping funnel. The reaction was heated at 60 °C for 3 h. An orange precipitate, [Rh(PMe₃)₄]Cl, formed as addition continued and the solution turned yellow. The product, [Rh(PMe₃)₄]Cl, was collected by filtration, washed with degassed Et₂O (50 mL), dried *in vacuo* and stored under N₂. Yield: 2.60 g, 90%. ¹H NMR (400 MHz, D₂O) δ: 1.34 (s, 36H, PMe₃). ³¹P{¹H} NMR (162 MHz, D₂O) δ: -15.46 (d, Jₐₙₚ = 125 Hz, 4P).

1 – Tetrakis(trimethylphosphine)methylrhodium, [RhMe(PMe₃)₄]¹⁹

In a nitrogen-filled glovebox, [Rh(PMe₃)₄]Cl (2.50 g, 5.65 mmol) was added to a flask that contained 50 mL of degassed THF and the suspension was stirred rapidly. MeLi (1.6 M in Et₂O, 4.59 mL, 7.34 mmol) diluted with ca. 5 mL of degassed Et₂O was added dropwise to the solution using a dropping funnel. The reaction was stirred for 3 h; the solution turned yellow and white LiCl precipitated. The solution was filtered through a small bed of celite and the solvent was removed *in vacuo* to give [RhMe(PMe₃)₄] as a yellow crystalline solid. Yield: 2.01 g, 84%. ¹H NMR (400 MHz, C₆D₆) δ: 1.16 (s, 36H, PMe₃), 0.01 (d, J = 4 Hz, 3H, CH₃). ³¹P{¹H} NMR (202 MHz, 196 K, 10% C₆D₆ in THF)
δ: -0.52 (dq, $J_{\text{Rh-P}} = 105$ Hz, $J_{\text{P-P}} = 40$ Hz, 1P), -22.68 (dd, $J_{\text{Rh-P}} = 158$ Hz, $J_{\text{P-P}} = 40$ Hz, 3P). Anal. Calcd. for C$_{13}$H$_{39}$P$_4$Rh: C, 36.98; H, 9.31. Found: C, 37.30; H, 9.12%.

3.4.4 Preparation of 4-[p-(N,N-di-n-hexylamino)phenylethynyl]phenylethynylrhodacyclopentadienes

3(a) - *mer,cis*-tris(trimethylphosphine)-4-[p-(N,N-di-n-hexylamino)phenylethynyl]phenylethynyl-2,5-bis(phenylethynyl)-3,4-bis(phenyl)rhodacyclopenta-2,4-diene [20]

The compound 4-(4-ethynylphenylethynyl)-N,N-di-n-hexylaniline (EPEDHA) (0.0181 g, 0.047 mmol) in THF (1 mL) was added dropwise to a 28 mL vial that contained a stirred solution of [RhMe(PMe$_3$)$_4$] (0.0198 g, 0.047 mmol) in THF (1 mL), and the resulting solution was stirred for 15 min. A solution of 1,4-diphenylbuta-1,3-diyne (0.0190 g, 0.094 mmol) in THF (1 mL) was added, the solution was stirred for 5 min and the solvent was removed *in vacuo*. THF (2 mL) was added to the vial, the solution was stirred for 5 min and the solvent was removed *in vacuo* again. This cycle was repeated one more time and then THF (2 mL) was added and the solution was stirred for 24 h. The solvent was removed *in vacuo* and the compound was washed with hexane, and dried *in vacuo* yielding crude 3(a), which was recrystallised from C$_6$D$_6$ and hexane to give a yellow solid. Yield: 0.045 g, 85%. $^1$H NMR (500 MHz, C$_6$D$_6$) δ: 7.67 (d, $J = 8$ Hz, 2H,
CH$_{arom}$, 7.66 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 7.54 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 7.44 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 7.43 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 7.34 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 7.24 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 7.19 (t, $J = 8$ Hz, 2H, CH$_{arom}$), 7.17 (t, $J = 8$ Hz, 2H, CH$_{arom}$), 7.06 (t, $J = 8$ Hz, 3H, CH$_{arom}$), 7.02 (m, 1H, CH$_{arom}$), 6.93 (t, $J = 8$ Hz, 3H, CH$_{arom}$), 6.84 (t, $J = 8$ Hz, 3H, CH$_{arom}$), 6.53 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 2.98 (t, $J = 7$ Hz, 4H, N(CH$_2$)$_2$)$_2$, 1.39 (d, $J_{P-H} = 8$ Hz, 9H, PMe$_3$ trans to C$\alpha$), 1.34 (vt, $J_{P-H} = 4$ Hz, 18H, PMe$_3$ trans to PMe$_3$), 1.22 (quint, $J = 7$ Hz, 4H, N(CH$_2$CH$_2$)$_2$), 1.13 (m, 12H, 2 x C$_3$H$_6$), 0.88 (t, $J = 7$ Hz, 6H, 2 x CH$_3$). $^{31}$P{$^1$H} NMR (81 MHz, C$_6$D$_6$) $\delta$: -9.07 (dd, $J_{Rh-P} = 98$ Hz, $J_{P-P} = 31$ Hz, 2P), -21.95 (dt, $J_{Rh-P} = 83$ Hz, $J_{P-P} = 31$ Hz, 1P). Anal. Calcd. for C$_{69}$H$_{81}$NP$_3$Rh: C, 73.98; H, 7.29; N, 1.25. Found: C, 73.44; H, 7.18; N, 1.55%. MS (ES$^+$) $m/z$: 1119 [M$^+$]. IR (KBr) $\nu_{C\equiv C} = 2205, 2159, 2132, 2088$ cm$^{-1}$.

3(b) - **mer,cis-[tris(trimethylphosphine)-4-[p-(N,N-di-n-hexylamino)phenylethynyl]phenylethynyl-2,5-bis(p-methoxyphenylethynyl)-3,4-bis(p-methoxyphenyl)rhodacyclopenta-2,4-diene]**

EPEDHA (0.0181 g, 0.047 mmol) in THF (1 mL) was added dropwise to a 28 mL vial that contained a stirred solution of [RhMe(PMe$_3$)$_4$] (0.0198 g, 0.047 mmol) in THF (1 mL), and the resulting solution was stirred for 15 min. A solution of 1,4-bis(p-methoxyphenyl)buta-1,3-diyne (0.0247 g, 0.094 mmol) in THF (1 mL) was added, the solution was stirred for 5 min, and then the solvent was removed *in vacuo*. THF (2 mL) was added to the vial, the solution was stirred for 5 min and the solvent was removed *in vacuo* again. This cycle was repeated one more time, and then THF (2 mL) was added and the solution was stirred for 48 h. The solvent was removed *in vacuo* and the
compound was washed with hexane, and dried in vacuo yielding crude 3(b), which was purified via recrystallisation from C₆D₆ and hexane to give a yellow solid. Yield: 0.037 g, 64%. ¹H NMR (400 MHz, C₆D₆) δ: 7.68 (d, J = 8 Hz, 2H, CH₆arom), 7.63 (d, J = 8 Hz, 2H, CH₆arom), 7.55 (d, J = 8 Hz, 2H, CH₆arom) 7.50 (d, J = 8 Hz, 2H, CH₆arom), 7.46 (d, J = 8 Hz, 2H, CH₆arom), 7.37 (d, J = 8 Hz, 2H, CH₆arom), 7.26 (d, J = 8 Hz, 2H, CH₆arom), 6.86 (d, J = 8 Hz, 2H, CH₆arom), 6.84 (d, J = 8 Hz, 2H, CH₆arom), 6.69 (d, J = 8 Hz, 2H, CH₆arom), 6.59 (d, J = 8 Hz, 2H, CH₆arom), 6.53 (d, J = 8 Hz, 2H, CH₆arom), 3.28 (s, 3H, OCH₃), 3.27 (s, 3H, OCH₃), 3.22 (s, 3H, OCH₃), 3.13 (s, 3H, OCH₃), 2.98 (t, J = 7 Hz, 4H, N(CH₂)₂), 1.46 (d, Jₚ-H = 7 Hz, 9H, PMe₃ trans to Cα), 1.40 (vt, Jₚ-H = 3 Hz, 18H, PMe₃ trans to PMe₃), 1.22 (quint, J = 8 Hz, 4H, N(CH₂CH₂)₂), 1.11 (m, 12H, 2 x C₃H₆), 0.88 (t, J = 7 Hz, 6H, 2 x CH₃). ³¹P{¹H} NMR (162 MHz, C₆D₆) δ: -8.19 (dd, JₐRh-P = 99 Hz, Jₚ-P = 31 Hz, 2P), -21.90 (dt, JₐRh-P = 82 Hz, Jₚ-P = 31 Hz, 1P). Anal. Calcd. for C₇₃H₈₉NO₄P₃Rh: C, 70.69; H, 7.23; N, 1.13. Found: C, 70.98; H, 7.04; N, 0.93%. MS (ES⁺) m/z: 1239 [M⁺]. IR (KBr) νC≡C = 2204, 2160, 2132, 2085 cm⁻¹.

3(c) - mer,cis-[tris(trimethylphosphine)-4-[p-(N,N-di-n-hexylamino)phenylethynyl]phenylethynyl-2,5-bis(4-trifluoromethylphenylethynyl)-3,4-bis(4-trifluoromethylphenyl)-rhodacyclopenta-2,4-diene]²⁰

EPEDHA (0.0181 g, 0.047 mmol) in THF (1 mL) was added dropwise to a 28 mL vial that contained a stirred solution of [RhMe(PMe₃)₄] (0.0198 g, 0.047 mmol) in THF (1 mL), and the resulting solution was stirred for 15 min. A solution of 1,4-bis(4-trifluoromethylphenyl)buta-1,3-diynye (0.0318 g, 0.094 mmol) in THF (1 mL) was added, the solution was stirred for 5 min and the solvent was removed in vacuo. THF (2 mL)
was added to the vial, the solution was stirred for 5 min and the solvent was removed \textit{in vacuo} again. This cycle was repeated one more time and then THF (2 mL) was added and the solution was stirred for 15 h. The solvent was removed \textit{in vacuo} to give crude 3(c), which was further purified by dissolving it in THF (1 mL) and layering this with hexane (ca. 10 mL) to recrystallise the compound as a yellow solid. Yield: 0.053 g, 81%. 

\[ ^1H \text{NMR (400 MHz, C}_6\text{D}_6 \delta: 7.64 (d, J = 8 Hz, 2H, CH}_{\text{arom}}, 7.63 (d, J = 8 Hz, 2H, CH}_{\text{arom}}, 7.39 (d, J = 8 Hz, 2H, CH}_{\text{arom}}, 7.35 (d, J = 8 Hz, 2H, CH}_{\text{arom}}, 7.34 (d, J = 8 Hz, 2H, CH}_{\text{arom}}, 7.28 (d, J = 8 Hz, 2H, CH}_{\text{arom}}, 7.25 (d, J = 8 Hz, 2H, CH}_{\text{arom}}, 7.23 (d, J = 8 Hz, 2H, CH}_{\text{arom}}, 7.16 (d, J = 8 Hz, 2H, CH}_{\text{arom}}, 7.12 (d, J = 8 Hz, 2H, CH}_{\text{arom}}, 6.96 (d, J = 8 Hz, 2H, CH}_{\text{arom}}, 6.53 (d, J = 9 Hz, 2H, CH}_{\text{arom}}, 2.98 (t, J = 7 Hz, 4H, N(CH}_2_2), 1.38 (quint, J = 8 Hz, 4H, N(CH}_2CH}_2), 1.32 (d, J_{P-H} = 8 Hz, 9H, PMe}_3 \text{trans to C}_6), 1.28 (vt, J_{P-H} = 3 Hz, 18H, PMe}_3 \text{trans to PMe}_3), 1.12 (m, 12H, 2 x C}_3H}_6), 0.88 (t, J = 7 Hz, 6H, 2 x CH}_3), ^{31}P\{^1H\} \text{NMR (162 MHz, C}_6\text{D}_6 \delta: -8.98 (dd, J_{Rh-P} = 96 Hz, J_{P-P} = 31 Hz, 2P), -21.58 (dt, J_{Rh-P} = 82 Hz, J_{P-P} = 31 Hz, 1P). ^{19}F\{^1H\} \text{NMR (376 MHz, C}_6\text{D}_6 \delta: -62.29 (s, 3F), -62.31 (s, 3F), -62.61 (s, 3F), -62.68 (s, 3F). Anal. Calcd. for C}_{73}H_{77}F_{12}NP_{3}Rh: C, 62.98; H, 5.57; N, 1.01. Found: C, 62.70; H, 5.68; N, 1.25%. MS (ES^+) m/z: 1391 [M^+]. IR (KBr): \nu_{C=C} = 2205, 2165, 2136, 2091, \nu_{arom} = 1520 \text{ cm}^{-1}. \]

3(d) - \textit{mer,cis-[tris(trimethylphosphine)-4-[p-(N,N-di-n-hexylamino)phenylethynyl]phenylethynyl-2,5-bis(p-carbomethoxyphenyl)-3,4-bis(p-carbomethoxyphenyl)rhodacyclopenta-2,4-diene]}^{20}

EPEDHA (0.0181 g, 0.047 mmol) in THF (1 mL) was added dropwise to a 28 mL vial that contained a stirred solution of [RhMe(PMe}_3]_4 (0.0198 g, 0.047 mmol) in THF (1
mL) and the resulting solution was stirred for 15 min. A solution of 1,4-bis(\(p\)-carbomethoxyphenyl)buta-1,3-diyne (0.0299 g, 0.094 mmol) in THF (1 mL) was added, the solution was stirred for 5 min and then the solvent was removed in vacuo. THF (2 mL) was added to the vial, the solution was stirred for 5 min and the solvent was removed in vacuo again. This cycle was repeated one more time and then, THF (2 mL) was added and the solution was stirred for 15 h. The solvent was removed in vacuo and the compound was washed with hexane, and dried in vacuo yielding 3(d), which was recrystallised from C6D6 and hexane. Yield: 0.032 g, 50%. \(^1\)H NMR (400 MHz, C6D6) \(\delta\): 8.18 (d, \(J = 8\) Hz, 2H, CH\textsubscript{arom}), 8.15 (d, \(J = 8\) Hz, 2H, CH\textsubscript{arom}), 8.01 (d, \(J = 8\) Hz, 2H, CH\textsubscript{arom}), 7.93 (d, \(J = 8\) Hz, 2H, CH\textsubscript{arom}), 7.65 (d, \(J = 8\) Hz, 2H, CH\textsubscript{arom}), 7.64 (d, \(J = 8\) Hz, 2H, CH\textsubscript{arom}), 7.49 (d, \(J = 8\) Hz, 2H, CH\textsubscript{arom}), 7.38 (d, \(J = 8\) Hz, 2H, CH\textsubscript{arom}), 7.36 (d, \(J = 8\) Hz, 2H, CH\textsubscript{arom}), 7.29 (d, \(J = 8\) Hz, 2H, CH\textsubscript{arom}), 7.18 (d, \(J = 8\) Hz, 2H, CH\textsubscript{arom}), 6.55 (d, \(J = 8\) Hz, 2H, CH\textsubscript{arom}), 3.45 (s, 3H, COOCH\textsubscript{3}), 3.44 (s, 3H, COOCH\textsubscript{3}), 3.43 (s, 3H, COOCH\textsubscript{3}), 3.35 (s, 3H, COOCH\textsubscript{3}), 3.00 (t, \(J = 7\) Hz, 4H, N(CH\textsubscript{2})\textsubscript{2}), 1.40 (quint, \(J = 8\) Hz, 4H, N(CH\textsubscript{2})\textsubscript{2}), 1.40 (quint, \(J = 8\) Hz, 4H, N(CH\textsubscript{2})\textsubscript{2}), 1.32 (d, \(J_{\text{P-H}} = 8\) Hz, 9H, PMe\textsubscript{3} trans to Cα), 1.26 (vt, \(J_{\text{P-H}} = 4\) Hz, 18H, PMe\textsubscript{3} trans to PMe\textsubscript{3}), 1.19 (m, 12H, 2 x C\textsubscript{3}H\textsubscript{6}), 0.88 (t, \(J = 7\) Hz, 6H, 2 x CH\textsubscript{3}). \(^{31}\)P\[^1\]H NMR (162 MHz, C6D6) \(\delta\): -9.02 (dd, \(J_{\text{Rh-P}} = 99\) Hz, \(J_{\text{P-P}} = 31\) Hz, 2P), -22.75 (dt, \(J_{\text{Rh-P}} = 81\) Hz, \(J_{\text{P-P}} = 31\) Hz, 1P). Anal. Calcd. for C\textsubscript{77}H\textsubscript{89}NO\textsubscript{8}P\textsubscript{3}Rh: C, 68.39; H, 6.63; N, 1.04. Found: C, 68.00; H, 6.51; N, 1.28%. MS (ES\(^+\)) \(m/z\): 1352 [M\(^+\)]. IR (KBr) \(\nu_{\text{C=C}} = 2204, 2162, 2134, 2091\), \(\nu_{\text{ester(C=O)}} = 1721\) cm\(^{-1}\).
3.4.5 Preparation of *mer,cis*-tris(trimethylphosphine)methyl-2,5-bis(p-di-N,N-methylaminophenylethynyl)-3,4-(p-di-N,N-methylaminophenyl)rhodacyclo-penta-2,4-diene] (4)

In a N₂-filled glovebox, 1,4-bis(p-di-N,N-methylaminophenyl)buta-1,3-diyne (0.0283 g, 0.098 mmol) and [RhMe(PMe₃)₄] (0.0207 g, 0.049 mmol) were added to THF (3 mL) in a Young’s tube. The resulting solution was stirred for 15 min and the solvent was removed in vacuo. THF (3 mL) was added, the solution was stirred for 15 min, and the solvent was removed in vacuo again. This cycle was repeated one more time, and then THF (3 mL) was added. The Young’s tube was removed from the glovebox and heated at 50 °C for 5 d. The reaction progress was monitored in situ by ³¹P{¹H} NMR spectroscopy until complete conversion to 4 was observed. The THF solvent was removed in vacuo and hexane (1 mL) was added to the residue and then removed in vacuo. This process was repeated two times in order to remove completely any residual THF. The hexane was removed in vacuo yielding 4 as a yellow solid, which was purified via recrystallisation from toluene and hexane. Yield: 0.029 g 64%. ¹H NMR (400 MHz, C₆D₆) δ: 7.68 (d, J = 8 Hz, 2H, CH_arom), 7.59 (d, J = 8 Hz, 2H, CH_arom), 7.52 (d, J = 8 Hz, 2H, CH_arom), 7.39 (d, J = 8 Hz, 2H, CH_arom), 6.67 (d, J = 8 Hz, 2H, CH_arom), 6.66 (d, J = 8 Hz, 2H, CH_arom), 6.50 (d, J = 8 Hz, 2H, CH_arom), 6.43 (d, J = 8 Hz, 2H, CH_arom), 2.50 (s, 6H, N(CH₃)₂), 2.48 (s, 6H, N(CH₃)₂), 2.41 (s, 6H, N(CH₃)₂), 2.36 (s, 6H, N(CH₃)₂), 1.43 (d, Jₚ-H = 8 Hz, 9H, PMe₃ trans to Cα), 1.25 (vt, J₁₋-H = 3 Hz, 18H, PMe₃ trans to PMe₃), 0.15 (dq, J_p₁-H = 2 Hz, 3J_p₁-H = 8 Hz, 3H, CH₃-Rh). ³¹P{¹H} NMR (162 MHz, C₆D₆) δ: -5.66 (dd, J_Rh-P =...
106 Hz, $J_{P-P} = 33$ Hz, 2P), -18.39 (dt, $J_{Rh-P} = 89$ Hz, $J_{P-P} = 33$ Hz, 1P). Anal. Calcd. for C$_{50}$H$_{70}$N$_4$P$_3$Rh: C, 65.07; H, 7.64; N, 6.07. Found: C, 65.09; H, 7.59; N, 5.98%. MS (ES$^+$) $m/z = 907$ [M$^+$ - CH$_3$]. IR (KBr) $\nu_{C-H} = 2903$, 2793, $\nu_{C\equiv C} = 2121$, $\nu_{Ar} = 1516$, 1441 cm$^{-1}$.

### 3.4.6 Preparation of TMSE-rhodacyclopentadienes containing extended phenylene-ethynylene groups

![Diagram](image)

6(a) - mer,cis-[tris(trimethylphosphine)trimethylsilylethynyl-2,5-bis-[4-(4-ethynyl-phenylethynyl)-benzoic acid $n$-octyl ester]-3,4-bis(4-phenylethynylbenzoic acid $n$-octyl ester)rhodacyclopenta-2,4-diene]

Trimethylacetylene (TMSA, 8 $\mu$L, 0.058 mmol) in THF (1 mL) was added dropwise to a 28 mL vial that contained a stirred solution of [RhMe(PMe$_3$)$_4$] (0.0207 g, 0.049 mmol) in THF (1 mL) and the resulting solution was stirred for 5 min to give the 5 in THF solution. A solution of 4,4'-bis-(4-carbo-$n$-octyloxylphenylethynyl)diphenyl-buta-1,3-diyne (0.0701 g, 0.098 mmol) in THF (2 mL) was then added and the reaction was stirred for 5 min, and then the solvent was removed in vacuo. THF (2 mL) was added again, the solution was stirred for 5 min and the solvent was removed in vacuo again. This cycle was repeated one more time, and then THF (3 mL) was added and the solution was stirred for 15 h at room temperature. The solvent was removed in vacuo and the compound was washed with hexane, and dried in vacuo yielding 6(a) as a dark red solid. Yield: 0.068 g,
75%.

$^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$: 8.03 (d, $J = 8$ Hz, 4H, CH$_{arom}$), 8.00 (d, $J = 8$ Hz, 4H, CH$_{arom}$), 7.67 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 7.56 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 7.52 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 7.46 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 7.38 (d, $J = 8$ Hz, 4H, CH$_{arom}$) 7.35 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 7.32 (d, $J = 8$ Hz, 4H, CH$_{arom}$), 4.13 (t, $J = 8$ Hz, 8H, OCH$_2$), 1.47 (m, 8H, OCH$_2$CH$_2$), 1.36 (d, $J_{P-H} = 8$ Hz, 9H, PMe$_3$ trans to C$\alpha$), 1.28 (vt, $J_{P-H} = 3$ Hz, 18H, PMe$_3$ trans to PMe$_3$), 1.19 (m, 40H, CH$_2$), 0.84 (t, $J = 7$ Hz, 12H, 4 x CH$_3$), 0.32 (s, 9H, Si(CH$_3$)$_3$).

$^{31}$P {$^1$H} NMR (162 MHz, C$_6$D$_6$) $\delta$: -9.19 (dd, $J_{Rh-P} = 97$ Hz, $J_{P-P} = 31$ Hz, 2P), -22.93 (dt, $J_{Rh-P} = 82$ Hz, $J_{P-P} = 31$ Hz, 1P).

Anal. Calcd. for C$_{114}$H$_{136}$O$_8$P$_3$RhSi: C, 73.68; H, 7.38. Found: C, 73.82; H, 7.41%.

MS (ES$^+$) m/z: 1858 [M$^+$]. IR (KBr) $\nu_{C-H} = 2952, 2923, 2853, \nu_{C=O} = 1716, 2128, 2022, \nu_{Ar} = 1594$ cm$^{-1}$.

6(b) – mer,cis-[tris(trimethylphosphine)trimethylsilylethynyl-2,5-bis[4-(4-di-N,N-n-hexylaminophenylethynyl)phenylethynyl]-3,4-bis[4-(4-di-N-hexylaminophenyl)ethynyl-phenyl]rhodacyclopenta-2,4-diene]

TMSA (8 $\mu$L, 0.058 mmol) in THF (1 mL) was added dropwise to a 28 mL vial that contained a stirred solution of [RhMe(PMe$_3$)$_4$] (0.0207 g, 0.049 mmol) in THF (1 mL) and the resulting solution was stirred for 5 min to give the 5 in THF solution. A solution of 4,4’-bis-(4-di-N,N-n-hexylaminophenylethynyl)diphenylbuta-1,3-diyne (0.0754 g, 0.098 mmol) in THF (3 mL) was added and the reaction was stirred for 5 min and then the solvent was removed in vacuo. THF (3 mL) was added, the solution was stirred for 5 min and the solvent was removed in vacuo again. This cycle was repeated one more time, and then THF (3 mL) was added and the solution was stirred for 15 h at room
temperature. The solvent was removed in vacuo, washed with hexane, and dried in vacuo yielding 6(b) as a red solid. Yield: 0.057 g, 59%. \(^1\)H NMR (400 MHz, C\(_6\)D\(_6\)) \(\delta\): 7.68 (d, \(J = 8\) Hz, 2H, CH\(_{\text{arom}}\)), 7.63 (d, \(J = 8\) Hz, 2H, CH\(_{\text{arom}}\)), 7.60 (d, \(J = 8\) Hz, 2H, CH\(_{\text{arom}}\)), 7.59 (d, \(J = 8\) Hz, 4H, CH\(_{\text{arom}}\)), 7.55 (d, \(J = 8\) Hz, 2H, CH\(_{\text{arom}}\)), 7.52 (d, \(J = 8\) Hz, 2H, CH\(_{\text{arom}}\)), 7.50 (d, \(J = 8\) Hz, 2H, CH\(_{\text{arom}}\)), 7.42 (d, \(J = 8\) Hz, 2H, CH\(_{\text{arom}}\)), 7.33 (d, \(J = 8\) Hz, 2H, CH\(_{\text{arom}}\)), 7.23 (d, \(J = 8\) Hz, 2H, CH\(_{\text{arom}}\)), 7.15 (d, \(J = 8\) Hz, 2H, CH\(_{\text{arom}}\)), 6.52 (d, \(J = 8\) Hz, 4H, CH\(_{\text{arom}}\)), 6.49 (d, \(J = 8\) Hz, 4H, CH\(_{\text{arom}}\)), 2.95 (t, \(J = 8\) Hz, 16H, 4 x N(CH\(_2\))\(_2\)), 1.38 (d, \(J =\) P-H = 8 Hz, 9H, PMe\(_3\) trans to C-\(\alpha\)), 1.28 (vt, \(J =\) P-H = 3 Hz, 18H, PMe\(_3\) trans to PMe\(_3\)), 1.23 (quint, 16H, 4 x N(CH\(_2\))\(_2\)), 1.11 (m, 48H, CH\(_2\)), 0.88 (t, \(J = 3\) Hz, 24H, 8 x CH\(_3\)), 0.34 (s, 9H, Si(CH\(_3\))\(_3\)). \(^{31}\)P{\(^1\)H} NMR (81 MHz, C\(_6\)D\(_6\)) \(\delta\): -9.06 (dd, \(J_{\text{Rh-P}} = 98\) Hz, \(J_{\text{P-P}} = 31\) Hz, 2P), -23.11 (dt, \(J_{\text{Rh-P}} = 82\) Hz, \(J_{\text{P-P}} = 31\) Hz, 1P). Anal. Calcd. for C\(_{126}\)H\(_{172}\)N\(_4\)P\(_3\)RhSi: C, 76.95; H, 8.82; N, 2.85. Found: C, 76.64; H, 8.71; N, 3.19%. MS (ES\(^+\)) \(m/z\): 1965 [M\(^+\)]. IR (KBr) \(\nu_{\text{C-H}} = 2952, 2923, 2853, \nu_{\text{C=C}} = 2202, 2130, 2020, \nu_{\text{Ar}} = 1607\) cm\(^{-1}\).

3.4.7 Preparation of second-generation TMSE-rhodacyclopentadienes

7(a) – mer,cis-[tris(trimethylphosphine)trimethylsilylthynyl-2,5-bis(phenylethynyl)-3,4-\(\mu\)-tetrathymethylenerhodacyclopenta-2,4-diene]

TMSA (8 \(\mu\)L, 0.058 mmol) in THF (1 mL) was added dropwise to a 28 mL vial that contained a stirred solution of [RhMe(PMe\(_3\))]\(_4\) (0.0207 g, 0.049 mmol) in THF (1 mL)
and the resulting solution was stirred for 5 min. A solution of 1,12-diphenyldodeca-
1,3,9,11-tetrayne (0.0150 g, 0.049 mmol) in THF (1 mL) was added and the reaction was
stirred for 5 min, and then the solvent was removed in vacuo. THF (2 mL) was added, the
solution was stirred for 5 min and the solvent was removed in vacuo again. This cycle
was repeated one more time and then, THF (2 mL) was added and the solution was stirred
for 15 h at room temperature. The THF solvent was removed in vacuo and hexane (1 mL)
was added to the residue and removed in vacuo; this process was repeated two more
times in order to remove completely the residual THF. The hexane was removed in vacuo
giving the product 7(a) as a yellow solid, which was recrystallised from C₆D₆ and
hexane. Yield: 0.021 g, 58%. ¹H NMR (500 MHz, C₆D₆) δ: 7.86 (d, J = 8 Hz, 2H,
CH_{arom}), 7.41 (d, J = 8 Hz, 2H, CH_{arom}), 7.18 (t, J = 8 Hz, 2H, CH_{arom}), 7.13 (t, J = 8 Hz,
3H, CH_{arom}), 7.00 (t, J = 8 Hz, 1H, CH_{arom}), 2.93 (m, 4H, CH₂-C=C), 1.65 (m, 4H, CH₂),
1.36 (d, J_{P-H} = 8 Hz, 9H, PMe₃ trans to Cα), 1.20 (vt, J = 3 Hz, 18H, PMe₃ trans to
PMe₃), 0.33 (s, 9H; Si(CH₃)₃). ³¹P{¹H} NMR (162 MHz, C₆D₆) δ: -7.85 (dd, J_{Rh-P} = 99
Hz, J_{P-P} = 31 Hz, 2P, PMe₃), -22.52 (dt, J_{Rh-P} = 83 Hz, J_{P-P} = 31 Hz, 1P, PMe₃). Anal.
Calcd. for C₃₈H₅₄P₃RhSi: C, 62.12; H, 7.41. Found: C, 62.36; H, 7.25%. MS (MALDI⁺)
m/z = 734 [M⁺], 658 [M⁺ - PMe₃]. IR (KBr) ν_{C≡C} = 2124, 2010, ν_{Ar} = 1590, 1418 cm⁻¹.

7(b)  –  mer,cis-[tris(trimethylphosphine)trimethylsilylethynyl-2,5-bis(p-methylthio
phenylethynyl)-3,4-µ-tetramethylenerhodacyclopenta-2,4-diene]

TMSA (8 µL, 0.058 mmol) in THF (1 mL) was added dropwise to a 28 mL vial that
contained a stirred solution of [RhMe(PMe₃)₄] (0.0207 g, 0.049 mmol) in THF (1 mL)
and the resulting solution was stirred for 5 min. A solution of 1,12-bis(p-
methylthiophenyl)dodeca-1,3,9,11-tetrayne (0.0195 g, 0.049 mmol) in THF (1 mL) was added, the reaction was stirred for 5 min and then the solvent was removed in vacuo. THF (2 mL) was added, the solution was stirred for 5 min and the solvent was removed in vacuo again. This cycle was repeated one more time and then, THF (2 mL) was added and the solution was stirred for 15 h at room temperature. The THF solvent was removed in vacuo, hexane (1 mL) was added to the residue and removed in vacuo, and this process was repeated two more times in order to remove completely the residual THF. The hexane was removed in vacuo giving 7(b) as an orange solid, which was recrystallised from THF and hexane. Yield: 0.024 g, 59%. ¹H NMR (400 MHz, C₆D₆) δ: 7.81 (d, J = 8 Hz, 2H, CH₂-arom), 7.33 (d, J = 8 Hz, 2H, CH₂-arom), 7.22 (d, J = 8 Hz, 2H, CH₂-arom), 7.12 (d, J = 8 Hz, 2H, CH₂-arom), 2.98 (m, 2H, CH₂-C≡C), 2.95 (m, 2H, CH₂-C≡C), 1.97 (s, 3H, SCH₃), 1.94 (s, 3H, SCH₃), 1.69 (m, 4H, CH₂), 1.40 (d, J_P-H = 8 Hz, 9H, PMe₃ trans to Cα), 1.23 (vt, J_P-H = 3 Hz, 18H, PMe₃ trans to PMe₃), 0.37 (s, 9H, Si(CH₃)₃). ³¹P{¹H} NMR (162 MHz, C₆D₆) δ: -7.86 (dd, J_Rh-P = 99 Hz, J_P-P = 11 Hz, 2P), -22.41 (dt, J_Rh-P = 84 Hz, J_P-P = 31 Hz, 1P). Anal. Calcd. for C₄₀H₀₅₈P₃Rh₂S₂Si: C, 58.10; H, 7.07. Found: C, 58.51; H, 7.02%. MS (MALDI⁺) m/z = 826 [M⁺]. IR (KBr) ν_C≡C = 2124, 2011, ν_Ar = 1558, 1487 cm⁻¹.

7(c) – mer,cis-[tris(trimethylphosphine)trimethylsilylethynyl-2,5-bis(p-trimethylsilyl ethynylphenylethynyl)-3,4-µ-tetramethylenrhodacyclopenta-2,4-diene]

TMSA (17.5 µL, 0.123 mmol) in THF (1 mL) was added dropwise to a 28 mL vial that contained a stirred solution of [RhMe(PMe₃)₄] (0.0498 g, 0.118 mmol) in THF (2 mL) and the resulting solution was stirred for 5 min. A solution of 1,12-bis(p-
trimethylsilylethynylphenyl)dodeca-1,3,9,11-tetrayne (0.0589 g, 0.118 mmol) in THF (2 mL) was added, the reaction was stirred for 5 min and then the solvent was removed in vacuo. THF (2 mL) was added, the solution was stirred for 5 min and the solvent was removed in vacuo again. This cycle was repeated one more time and then, THF (2 mL) was added and the solution was stirred for 15 h at room temperature. The THF solvent was removed in vacuo, hexane (2 mL) was added to the residue and removed in vacuo, and this process was repeated two more times in order to remove completely the residual THF. The hexane was removed in vacuo giving 7(c) as an orange solid, which was purified via recrystallisation from THF and hexane. Yield: 0.043 g, 39%. 

1H NMR (400 MHz, C6D6) δ: 7.69 (d, J = 8 Hz, 2H, CHarom), 7.52 (d, J = 8 Hz, 2H, CHarom), 7.48 (d, J = 8 Hz, 2H, CHarom), 7.21 (d, J = 8 Hz, 2H, CHarom), 2.87 (m, 2H, CH2-C=C), 2.82 (m, 2H, CH2-C=C), 1.61 (m, 4H, CH2), 1.26 (d, Jp-H = 8 Hz, 9H, PMe3 trans to Cα), 1.11 (vt, Jp-H = 3 Hz, 18H, PMe3 trans to PMe3), 0.25 (s, 9H, Si(CH3)3), 0.21 (s, 9H, Si(CH3)3), 0.19 (s, 9H, Si(CH3)3). 31P{1H} NMR (162 MHz, C6D6) δ: -8.02 (dd, JRh-P = 99 Hz, Jp-P = 31 Hz, 2P), -22.51 (dt, JRh-P = 83 Hz, Jp-P = 31 Hz, 1P). Anal. Calcd. for C48H70P3RhSi3: C, 62.18; H, 7.61. Found: C, 61.61; H, 7.55%. MS (ES+) m/z = 926 [M+]. IR (KBr) νC-H = 2952, 2907, νC=C = 2125, 2019, νAr = 1592, 1491 cm−1.

7(d) – mer,cis-[tris(trimethylphosphine)trimethylsilylethynyl-2,5-bis(p-carbomethoxy phenylethynyl)-3,4-µ-tetramethylenerhodacyclopenta-2,4-diene]

TMSA (8 µL, 0.058 mmol) in THF (1 mL) was added dropwise to a 28 mL vial that contained a stirred solution of [RhMe(PMe3)4] (0.0207 g, 0.049 mmol) in THF (1 mL) and the resulting solution was stirred for 5 min. A solution of 1,12-bis(p-
carbomethoxyphenyl)dodeca-1,3,9,11-tetrayne (0.0207 g, 0.049 mmol) in THF (1 mL) was added, the reaction was stirred for 5 min and then the solvent was removed in vacuo. THF (2 mL) was added, the solution was stirred for 5 min and the solvent was removed in vacuo again. This cycle was repeated one more time, and then THF (2 mL) was added and the solution was stirred for 15 h at room temperature. The THF solvent was removed in vacuo, hexane (1 mL) was added to the residue and removed in vacuo, and this process was repeated two more times in order to remove completely the residual THF. The hexane was removed in vacuo giving 7(d) as a red solid, which was purified by recrystallisation from THF and hexane. Yield: 0.026 g, 62%. 

$^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$: 8.25 (d, $J = 8$ Hz, 2H, C$_{\text{arom}}$), 8.18 (d, $J = 8$ Hz, 2H, C$_{\text{arom}}$), 7.87 (d, $J = 8$ Hz, 2H, C$_{\text{arom}}$), 7.38 (d, $J = 8$ Hz, 2H, C$_{\text{arom}}$), 3.50 (s, 3H, CO$_2$CH$_3$), 3.45 (s, 3H, CO$_2$CH$_3$), 2.92 (m, 2H, CH$_2$-C=C), 2.88 (m, 2H, CH$_2$-C=C), 1.66 (m, 4H, CH$_2$), 1.32 (d, $J_{P-H} = 8$ Hz, 9H, PMe$_3$ trans to C$_{\alpha}$), 1.17 (vt, $J_{P-H} = 3$ Hz, 18H, PMe$_3$ trans to PMe$_3$), 0.33 (s, 9H, Si(CH$_3$)$_3$). $^{31}$P{$^1$H} NMR (162 MHz, C$_6$D$_6$) $\delta$: -8.05 (dd, $J_{\text{Rh-P}} = 98$ Hz, $J_{P-P} = 31$ Hz, 2P), -22.41 (dt, $J_{\text{Rh-P}} = 83$ Hz, $J_{P-P} = 31$ Hz, 1P). Anal. Calcd. for C$_{42}$H$_{58}$O$_4$P$_3$RhSi: C, 59.29; H, 6.87. Found: C, 59.53; H, 6.96%. MS (MALDI$^+$) m/z = 850 [M$^+$]. IR (KBr) $\nu_{\text{C=C}} = 2121$, 2018, $\nu_{\text{ester(C=O)}} = 1718$, $\nu_{\text{Ar}} = 1596$, 1435 cm$^{-1}$.

7(e) – mer,cis-[tris(trimethylphosphine)trimethylsilyl ethynyl-2,5-bis(p-dimesitylboryl phenylethynyl)-3,4-µ-tetramethylenerhodacyclopenta-2,4-diene]

TMSA (8 µL, 0.058 mmol) in THF (1 mL) was added dropwise to a 28 mL vial that contained a stirred solution of [RhMe(PMe$_3$)$_4$] (0.0207 g, 0.049 mmol) in THF (1 mL) and the resulting solution was stirred for 5 min. A solution of 1,12-bis(p-dimesitylboryl
phenyl)dodeca-1,3,9,11-tetrayne (0.0393 g, 0.049 mmol) in THF (1 mL) was added and the reaction was stirred for 5 min and then the solvent was removed in vacuo. THF (2 mL) was added, the solution was stirred for 5 min and the solvent was removed in vacuo again. This cycle was repeated one more time and then, THF (2 mL) was added and the solution was stirred for 15 h at room temperature. The THF solvent was removed in vacuo, hexane (1 mL) was added to the residue and removed in vacuo, and this process was repeated two more times in order to remove completely the residual THF. The hexane was removed in vacuo giving 7(e) as a maroon solid, which was purified by washing with hexane (3 x 1 mL). Yield: 0.024 g, 40%. $^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$: 7.88 (d, $J$ = 8 Hz, 2H, CH$_{arom}$), 7.79 (d, $J$ = 8 Hz, 2H, CH$_{arom}$), 7.70 (d, $J$ = 8 Hz, 2H, CH$_{arom}$), 7.43 (d, $J$ = 8 Hz, 2H, CH$_{arom}$), 6.82 (s, 4H, CH$_{arom}$), 6.79 (s, 4H, CH$_{arom}$), 2.91 (m, 4H, CH$_2$-C=C), 2.20 (s, 12H, Ar-CH$_3$), 2.18 (s, 24H, Ar-CH$_3$), 1.63 (m, 4H, CH$_2$), 1.37 (d, $J_{p-H}$ = 8 Hz, 9H, PMe$_3$ trans to C), 1.17 (vt, $J_{p-H}$ = 3 Hz, 18H, PMe$_3$ trans to PMe$_3$), 0.28 (s, 9H, Si(CH$_3$)$_3$). $^{31}$P{$^1$H} NMR (162 MHz, C$_6$D$_6$) $\delta$: -8.06 (dd, $J_{Rh-P}$ = 98 Hz, $J_{P-P}$ = 31 Hz, 2P), -22.43 (dt, $J_{Rh-P}$ = 83 Hz, $J_{P-P}$ = 31 Hz, 1P). Anal. Calcd. for C$_{74}$H$_{96}$B$_2$P$_3$RhSi: C, 72.20; H, 7.86%. Found: C, 71.85; H, 8.01%. MS (ES$^+$) $m/z$ = 1230 [M$^+$]. IR (KBr) $\nu$$_{C=C}$ = 2122, 2044, $\nu$$_{Ar}$ = 1586, 1420 cm$^{-1}$.

7(f) – *mer,cis*-[(tris(trimethylphosphine)trimethylsilyl)ethenyl-2,5-bis(p-ethynylphenyl ethenyl)-3,4-$\mu$-tetramethylenerhodacyclopenta-2,4-diene]

A 1.0 M THF solution of (n-Bu$_4$N)F (0.172 mL, 0.172 mmol) was added to a rapidly stirred solution of 7(e) (0.0399 g, 0.043 mmol) in THF (3 mL). The solution was stirred for 15 h at room temperature and then the solvent was removed in vacuo. The residual
solid was dissolved in CH$_2$Cl$_2$ (5 mL) and then the solution was washed with water (5 x 10 mL). The organic layer was separated and dried over MgSO$_4$. The solvent was removed in vacuo to give the product as an orange solid. Yield: 0.016 g, 48%. $^1$H NMR (400 MHz, C$_6$D$_6$) δ: 7.69 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 7.47 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 7.40 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 7.19 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 2.88 (m, 2H, CH$_2$-C=C), 2.84 (m, 2H, CH$_2$-C=C), 2.79 (s, 1H, C≡CH), 2.74 (s, 1H, C≡CH), 1.62 (m, 4H, CH$_2$), 1.27 (d, $J_{P-H} = 8$ Hz, 9H, PMe$_3$ trans to Cα), 1.13 (vt, $J_{P-H} = 4$ Hz, 18H, PMe$_3$ trans to PMe$_3$), 0.28 (s, 9H, Si(CH$_3$)$_3$). $^{31}$P($^1$H) NMR (162 MHz, C$_6$D$_6$) δ: -8.01 (dd, $J_{Rh-P} = 98$ Hz, $J_{P-P} = 31$ Hz, 2P), -22.48 (dt, $J_{Rh-P} = 84$ Hz, $J_{P-P} = 31$ Hz, 1P). Anal. Calcd. for C$_{42}$H$_{54}$P$_3$RhSi: C, 64.44; H, 6.95. Found: C, 64.97; H, 7.19%. MS (ES$^+$) m/z = 782 [M$^+$]. IR (KBr) $\nu_{C-H}$ = 2907, $\nu_{C=C}$ = 2124, 2012, $\nu_{Ar}$ = 1594, 1492 cm$^{-1}$.

3.4.8 Preparation of second-generation Me-rhodacyclopentadienes

R -  mer,cis-[tris(trimethylphosphine)methyl-2,5-bis(phenylethynyl)-3,4-µ-tetramethylnerhodacyclopenta-2,4-diene]

1,12-biphenyldodeca-1,3,9,11-tetrayne (0.0150 g, 0.049 mmol) in THF (1 mL) was added to a stirred solution of [RhMe(PMe$_3$)$_4$] (0.0207 g, 0.049 mmol) in THF (1 mL). The reaction was stirred for 5 min and the solvent was removed in vacuo. THF (2 mL) was added, the solution was stirred for 5 min and the solvent was removed in vacuo
again. This cycle was repeated one more time and then, THF (2 mL) was added and the solution was stirred for 4 h at room temperature. The THF solvent was removed in vacuo, hexane (1 mL) was added to the residue and removed in vacuo, and this process was repeated two more times in order to remove completely the residual THF. The hexane was removed in vacuo giving 8(a) as a yellow-orange solid, which was purified by recrystallisation from THF and hexane. Yield: 0.025 g, 78%. 

\( ^1H \) NMR (400 MHz, C\(_6\)D\(_6\)) \( \delta \): 7.71 (d, \( J = 8 \) Hz, 2H, CH\(_{arom}\)), 7.45 (d, \( J = 8 \) Hz, 2H, CH\(_{arom}\)), 7.12 (t, \( J = 8 \) Hz, 2H, CH\(_{arom}\)), 7.07 (t, \( J = 8 \) Hz, 2H, CH\(_{arom}\)), 6.98 (t, \( J = 8 \) Hz, 1H, CH\(_{arom}\)), 6.94 (t, \( J = 8 \) Hz, 1H, CH\(_{arom}\)), 3.02 (m, 4H, CH\(_2\)-C=C), 1.71 (m, 4H, CH\(_2\)), 1.23 (d, \( J_{P-H} = 7 \) Hz, 9H, PMe\(_3\) trans to C\(_\alpha\)), 1.02 (vt, \( J_{P-H} = 3 \) Hz, 18H, PMe\(_3\) trans to PMe\(_3\)), -0.05 (dq, \( J_{Rh-H} = 2 \) Hz, \( J_{P-P} = 8 \) Hz, 3H, CH\(_3\)-Rh). 

\( ^{31}P\{^1H\} \) NMR (162 MHz, C\(_6\)D\(_6\)) \( \delta \): -5.12 (dd, \( J_{Rh-P} = 106 \) Hz, \( J_{P-P} = 33 \) Hz, 2P), -17.87 (dt, \( J_{Rh-P} = 90 \) Hz, \( J_{P-P} = 33 \) Hz, 1P). Anal. Calcd. for C\(_{34}\)H\(_{48}\)P\(_3\)Rh: C, 62.58; H, 7.41. Found: C, 62.20; H, 7.39%. MS (ES\(^+\)) m/z = 637 [M\(^+\) - CH\(_3\)]. IR (KBr) \( \nu_{C-H} = 2907, \nu_{C=C} = 2114, \nu_{Ar} = 1586, 1416 \text{ cm}^{-1} \).

8(b) – mer,cis-[tris(trimethylphosphine)methyl-2,5-bis(p-methylthiophenylethynyl)-3,4-\( \mu \)-tetramethylenerrhodacyclopenta-2,4-diene]

1,12-bis(p-methylthiophenyl)dodeca-1,3,9,11-tetrayne (0.0195 g, 0.049 mmol) in THF (1 mL) solution was added to a stirred solution of [RhMe(PMe\(_3\))\(_4\)] (0.0207 g, 0.049 mmol) in THF (1 mL). The reaction was stirred for 5 min and the solvent was removed in vacuo. THF (2 mL) was added, the solution was stirred for 5 min and the solvent was removed in vacuo again. This cycle was repeated one more time and then, THF (2 mL) was added and the solution was stirred for 15 h at room temperature. The THF solvent
was removed in vacuo, hexane (1 mL) was added to the residue and removed in vacuo, and this process was repeated two more times in order to remove completely the residual THF. The hexane was removed in vacuo giving 8(b) as an orange solid, which was purified by recrystallisation from THF and hexane. Yield: 0.029 g, 80%. 

$^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$: 7.63 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 7.38 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 7.14 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 7.07 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 3.05 (m, 4H, CH$_2$-C=C), 1.98 (s, 3H, SCH$_3$), 1.93 (s, 3H, SCH$_3$), 1.75 (m, 4H, CH$_2$), 1.28 (d, $J_{P-H} = 7$ Hz, 9H, PMe$_3$ trans to C$_\alpha$), 1.06 (vt, $J_{P-H} = 3$ Hz, 18H, PMe$_3$ trans to PMe$_3$), 0.01 (dq, $^2J_{Rh-H} = 2$ Hz, $^2J_{P-H} = 8$ Hz, 3H, CH$_3$-Rh).

$^{31}$P($^1$H) NMR (162 MHz, C$_6$D$_6$) $\delta$: -5.14 (dd, $^3J_{Rh-P} = 106$ Hz, $^3J_{P-P} = 33$ Hz, 2P), -17.82 (dt, $^5J_{Rh-P} = 90$ Hz, $^5J_{P-P} = 33$ Hz, 1P). Anal. Calcd. for C$_{45}$H$_{52}$P$_3$RhS$_2$: C, 58.06; H, 7.04. Found: C, 58.16; H, 7.05%. MS (ES$^+$) m/z = 744 [M$^+$]. IR (KBr) $\nu_{C-H} = 2909$, $\nu_{C=C} = 2117$, $\nu_{Ar} = 1581, 1428$ cm$^{-1}$.

8(c) – mer,cis-[tris(trimethylphosphine)methyl-2,5-bis(p-carbethoxyphenylethynyl)-3,4-µ-tetramethylethacyclooctadeca-2,4-diene]

1,12-bis(p-carbethoxyphenyl)dodeca-1,3,9,11-tetrayne (0.0207 g, 0.049 mmol) in THF (1 mL) solution was added to a stirred solution of [RhMe(PMe$_3$)$_4$] (0.0207 g, 0.049 mmol) in THF (1 mL). Then, the reaction was stirred for 5 min and the solvent was removed in vacuo. THF (2 mL) was added, the solution was stirred for 5 min and the solvent was removed in vacuo again. This cycle was repeated one more time and then, THF (2 mL) was added and the solution was stirred for 15 h at room temperature. The THF solvent was removed in vacuo, hexane (1 mL) was added to the residue and removed in vacuo, and this process was repeated two more times in order to remove
completely the residual THF. The hexane was removed in vacuo giving 8(c) as a dark-red solid, which was purified by recrystallisation from THF and hexane. Yield: 0.030 g, 80%.

$^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$: 8.19 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 8.13 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 7.69 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 7.43 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 3.50 (s, 3H, CO$_2$CH$_3$), 3.45 (s, 3H, CO$_2$CH$_3$), 2.98 (m, 4H, CH$_2$-C=C), 1.72 (m, 4H, CH$_2$), 1.20 (d, $J_{P-H} = 8$ Hz, 9H, PMe$_3$ trans to C$_\alpha$), 0.99 (vt, $J_{P-H} = 3$ Hz, 18H, PMe$_3$ trans to PMe$_3$), -0.05 (dq, $^2J_{Rh-H} = 2$ Hz, $^3J_{P-H} = 8$ Hz, 3H, CH$_3$-Rh). $^{31}$P{$^1$H} NMR (162 MHz, C$_6$D$_6$) $\delta$: -5.49 (dd, $^2J_{Rh-P} = 105$ Hz, $^3J_{P-P} = 33$ Hz, 2P), -17.95 (dt, $^2J_{Rh-P} = 90$ Hz, $^3J_{P-P} = 33$ Hz, 1P). Anal. Calcd. for C$_{38}$H$_{52}$O$_4$P$_3$Rh: C, 59.38; H, 6.82. Found: C, 59.37; H, 6.80%. MS (ES$^+$) $m/z$ = 752 [M$^+$ - CH$_3$]. IR (KBr) $\nu$$_{C-H}$ = 2912, $\nu$$_{C=C}$ = 2112, $\nu$$_{ester(C=O)}$ = 1712, $\nu$$_{Ar}$ = 1593, 1432 cm$^{-1}$.

3.4.9 Preparation of trans-[bis(trimethylphosphine)-µ-η$^2$-succinato-2,5-bis(p-di-N,N-methylaminophenylethynyl)-3,4-(p-di-N,N-methylaminophenyl)rhodacyclopenta-2,4-diene] dimer [9(b)]

In a N$_2$ filled glovebox, succinic acid (0.0013 g, 0.011 mmol) was added into a stirred toluene solution of 4 (0.0203 g, 0.022 mmol) in a Young’s tube. The Young’s tube was then removed from the glovebox and heated at 50 °C. The progress of the reaction was
monitored by $^{31}$P{$^1$H} NMR spectroscopy using C$_6$D$_6$/THF, and the solvent was removed in vacuo and refilled repeatedly until the in situ $^{31}$P{$^1$H} NMR spectrum showed full conversion to 9(b). The solvent was removed in vacuo, hexane (1 mL) was added to the residue and removed in vacuo, and this process was repeated five more times in order to remove completely the residual toluene. Then, the hexane was removed in vacuo to give a yellow-orange solid. Yield: 0.0162 g, 84%. $^1$H NMR (700 MHz, THF-d$_8$) δ: 7.28 (d, $J = 8$ Hz, 8H, CH$_{arom}$), 7.03 (d, $J = 8$ Hz, 8H, CH$_{arom}$), 6.62 (d, $J = 8$ Hz, 8H, CH$_{arom}$), 6.52 (d, $J = 8$ Hz, 8H, CH$_{arom}$), 2.92 (s, 24H, 4 x N(CH$_3$)$_2$), 2.87 (s, 28H, 4 x N(CH$_3$)$_2$ and 2 x CH$_2$), 1.25 (br, s, 36H, 4 x PMe$_3$). $^{31}$P{$^1$H} NMR (162 MHz, THF-d$_8$) δ: -2.29 (d, $J_{Rh-P} = 116$ Hz, 4P). Anal. Calcd. for C$_{96}$H$_{120}$N$_8$O$_4$P$_4$Rh$_2$: C, 64.79; H, 6.80; N, 6.30. Found: C, 63.61; H, 6.65; N, 6.29%. MS (ES$^+$) $m/z$ = 890 [M + 2H]$^{2+}$, 904 [M$^+$/2 + CH$_2$]. IR (KBr) $\nu_{C-H} = 2904$, $\nu_{C=C} = 2131$, $\nu_{Ar} = 1519$, 1442 cm$^{-1}$.

3.4.10 Preparation of a η$^1$-benzoato-rhodium(I) complex and µ-η$^1$-succinato rhodium(I) dimer

10 – Tris(trimethylphosphine)-η$^1$-benzoato-rhodium(I)

Benzoic acid (0.0116 g, 0.095 mmol) in a THF solution (1 mL) was added into a stirred solution of [RhMe(PMe$_3$)$_4$] (0.0401 g, 0.095 mmol) in THF (1 mL), and the resulting solution was stirred at room temperature for 5 min, after which the solvent was removed in vacuo. THF (2 mL) was added, the solution was stirred for 2 min and the solvent was
removed in vacuo again. This cycle was repeated one more time, and then THF (2 mL) was added. The reaction was stirred at room temperature for 1 h, after which the solvent was removed in vacuo to give 10 as a yellow solid. The product was recrystallised in a Young’s tube via slow diffusion of a layer of hexane into a concentrated THF solution of 10. Yield: 0.038 g, 88%. 1H NMR (400 MHz, C₆D₆) δ: 8.63 (d, J = 8 Hz, 2H, CH₅arom), 7.32 (t, J = 8 Hz, 2H, CH₅arom), 7.22 (t, J = 8 Hz, 1H, CH₅arom), 1.11 (br, s, 18H, PMe₃ trans to PMe₃), 1.01 (br, s, 9H, PMe₃ trans to OCOPh). 31P{1H} NMR (202 MHz, 203 K, 10% C₆D₆ in THF) δ: 3.85 (dt, J_Rh-P = 168 Hz, J_P-P = 48 Hz, 1P), -9.55 (dd, J_Rh-P =139 Hz, J_P-P = 48 Hz, 2P).

**13** – Tris(trimethylphosphine)-µ-η¹-succinato-rhodium(I) dimer

Succinic acid (0.0057 g, 0.048 mmol) in THF (1 mL) was added to a stirred solution of [RhMe(PMe₃)₄] (0.0405 g, 0.096 mmol) in THF (1 mL), and the resulting solution was stirred at room temperature for 5 min, after which the solvent was removed in vacuo. THF (2 mL) was added, the solution was stirred for 2 min and the solvent was removed in vacuo again. This cycle was repeated one more time, and then THF (2 mL) was added. The reaction was stirred at room temperature for 1 h, after which the solvent was removed in vacuo to give 13 as a yellow solid. The product was recrystallised in a Young’s tube via slow diffusion of a layer of hexane into a concentrated THF solution of 13. Yield: 0.035 g, 94%. 1H NMR (200 MHz, C₆D₆) δ: 3.21 (br, s, 4H, 2 x CH₂), 1.12 (br,
s, 54H, 6 x PMe$_3$). $^{31}$P{${}^1$H} NMR (202 MHz, 203 K, 10% C$_6$D$_6$ in THF) $\delta$: 3.41 (dt, $J_{\text{Rh-P}}$ = 168 Hz, $J_{P-P}$ = 45 Hz, 2P), -9.41 (dd, $J_{\text{Rh-P}}$ = 143 Hz, $J_{P-P}$ = 45 Hz, 4P).

### 3.4.11 Preparation of η$^1$- and η$^2$-benzoato-rhodacyclopentadienes

![Diagram of η$^1$- and η$^2$-benzoato-rhodacyclopentadienes](image)

**11(a)** — *mer,cis*-[(tris(trimethylphosphine)-η$^1$-benzoato-2,5-bis(phenylethynyl)-3,4-µ-tetramethylenerrhodacyclopenta-2,4-diene]

The compound 1,12-diphenyldodeca-1,3,9,11-tetrayne (0.0291 g, 0.095 mmol) in THF was added to a stirred THF solution of 10 (0.0430 g, 0.095 mmol), which was obtained via *in situ* reaction of benzoic acid (0.0116 g, 0.095 mmol) and [RhMe(PMe$_3$)$_4$] (0.0401 g, 0.095 mmol). The resulting solution was stirred for 15 h at room temperature to give a mixture of the η$^1$-compound 11(a) and η$^2$-compound 12(a). Compound 11(a) was isolated in pure form via several recrystallisations from THF and hexane. Yield: 0.014 g, 19%. $^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$: 8.55 (d, $J = 8$ Hz, 2H, CH$_{\text{arom}}$), 7.41 (d, $J = 8$ Hz, 2H, CH$_{\text{arom}}$), 7.38 (d, $J = 8$ Hz, 2H, CH$_{\text{arom}}$), 7.27 (t, $J = 8$ Hz, 2H, CH$_{\text{arom}}$), 7.22 (t, $J = 8$ Hz, 2H, CH$_{\text{arom}}$), 7.11 (t, $J = 8$ Hz, 2H, CH$_{\text{arom}}$), 6.96 (m, 3H, CH$_{\text{arom}}$), 2.93 (m, 2H, C=C-CH$_2$), 2.79 (m, 2H, C=C-CH$_2$), 1.63 (m, 4H, CH$_2$), 1.36 (d, $J_{P-H}$ = 8 Hz, 9H, PMe$_3$ trans to Cα), 1.27 (vt, $J_{P-H}$ = 4 Hz, 18H, PMe$_3$ trans to PMe$_3$). $^{31}$P{${}^1$H} NMR (162 MHz, C$_6$D$_6$) $\delta$: -7.52 (dd, $J_{\text{Rh-P}}$ = 107 Hz, $J_{P-P}$ = 31 Hz, 2P), -18.86 (dt, $J_{\text{Rh-P}}$ = 91 Hz, $J_{P-P}$ = 31 Hz, 1P).
Anal. Calcd. for C_{40}H_{50}P_3O_2Rh: C, 63.33; H, 6.64. Found: C, 63.60; H, 6.48%. MS (ES\(^+\)) \(m/z\) = 759 [M + H\(^+\)]. IR (KBr) \(\nu_{C-H}\) = 2909, 2850, \(\nu_{C=C}\) = 2135, \(\nu_{C=O}\) = 1601, \(\nu_{Ar}\) = 1566, 1485 cm\(^{-1}\).

**12(a) - trans-[bis(trimethylphosphine)-η\(^2\)-benzoato-2,5-bis(phenylethynyl)-3,4-µ-tetramethylenerhodacyclopenta-2,4-diene]**

In a N\(_2\) filled glovebox, the remaining mixture of 11(a) and 12(a) was added to toluene (3 mL) in a Young’s tube, which was then sealed, removed from the glovebox and heated at 50 °C. The reaction progress was monitored in situ by \(^{31}\)P\({}^1\)H NMR spectroscopy and the toluene was removed in vacuo and refilled repeatedly until the in situ \(^{31}\)P\({}^1\)H NMR spectrum showed complete conversion to 12(a). The product was washed with hexane (5 x 1 mL) to give 12(a) as a yellow-orange solid. Yield: 0.049 g, 76%. \(^1\)H NMR (400 MHz, C\(_6\)D\(_6\)) \(\delta\): 8.52 (d, \(J = 8\) Hz, 2H, CH\(_{arom}\)), 7.77 (d, \(J = 8\) Hz, 4H, CH\(_{arom}\)), 7.20 (t, \(J = 8\) Hz, 2H, CH\(_{arom}\)), 7.15 (t, \(J = 8\) Hz, 2H, CH\(_{arom}\)), 7.09 (t, \(J = 8\) Hz, 4H, CH\(_{arom}\)), 6.98 (t, \(J = 8\) Hz, 1H, CH\(_{arom}\)), 2.85 (m, 4H, C=C-CH\(_2\)), 1.60 (m, 4H, CH\(_2\)), 1.04 (vt, \(J_{P-H} = 4\) Hz, 18H, 2 x PMe\(_3\)). \(^{31}\)P\({}^1\)H NMR (162 MHz, C\(_6\)D\(_6\)) \(\delta\): -1.04 (d, \(J_{Rh-P} = 115\) Hz, 2P). Anal. Calcd. for C\(_{37}\)H\(_{41}\)O\(_2\)P\(_2\)Rh: C, 65.11; H, 6.05. Found: C, 64.96; H, 6.09%. MS (MALDI\(^+\)) \(m/z\) = 682 [M\(^+\)], 561 [M\(^+\) - O\(_2\)CPh]. IR (KBr) \(\nu_{C-H}\) = 2907, \(\nu_{C=C}\) = 2137, \(\nu_{Ar}\) = 1594 cm\(^{-1}\).

**11(b) - mer,cis-[tris(trimethylphosphine)-η\(^1\)-benzoato-2,5-bis(p-methylthiophenylethynyl)-3,4-µ-tetramethylenerhodacyclopenta-2,4-diene]**

The compound 1,12-bis(p-methylthiophenyl)dodeca-1,3,9,11-tetrayne (0.0379 g, 0.095 mmol) in THF was added to a stirred THF solution of 10 (0.0430 g, 0.095 mmol), which
was obtained via in situ reaction of benzoic acid (0.0116 g, 0.095 mmol) and [RhMe(PMe\(_3\))\(_4\)] (0.0401 g, 0.095 mmol). The resulting solution was stirred for 15 h at room temperature to give a mixture of \(\eta^1\)-compound 11(b) and \(\eta^2\)-compound 12(b). Compound 11(b) was isolated in pure form via several recrystallisations from THF and hexane. Yield: 0.012 g, 15%. \(^1\)H NMR (400 MHz, C\(_6\)D\(_6\)) \(\delta\): 8.55 (d, \(J = 8\) Hz, 2H, CH\(_{\text{arom}}\)), 7.29 (d, \(J = 8\) Hz, 2H, CH\(_{\text{arom}}\)), 7.27 (m, 4H, CH\(_{\text{arom}}\)), 7.20 (t, \(J = 8\) Hz, 1H, CH\(_{\text{arom}}\)), 7.07 (d, \(J = 8\) Hz, 2H, CH\(_{\text{arom}}\)), 6.92 (d, \(J = 8\) Hz, 2H, CH\(_{\text{arom}}\)), 2.94 (m, 2H, C=C-CH\(_2\)), 2.80 (m, 2H, C=C-CH\(_2\)), 1.94 (s, 3H, SCh\(_3\)), 1.87 (s, 3H, SCh\(_3\)), 1.64 (m, 4H, CH\(_2\)), 1.37 (d, \(J_{P-H} = 8\) Hz, 9H, PMe\(_3\) trans to C\(_\alpha\)), 1.29 (vt, \(J_{P-H} = 4\) Hz, 18H, PMe\(_3\) trans to PMe\(_3\)). \(^{31}\)P\(_{\{\text{\scriptsize{}H}\}}\) NMR (162 MHz, C\(_6\)D\(_6\)) \(\delta\): -7.50 (dd, \(J_{\text{Rh-P}} = 106\) Hz, \(J_{P-P} = 30\) Hz, 2P), -18.77 (dt, \(J_{\text{Rh-P}} = 91\) Hz, \(J_{P-P} = 30\) Hz, 1P). Anal. Calcd. for C\(_{42}\)H\(_{54}\)O\(_2\)P\(_3\)RhS\(_2\): C, 59.29; H, 6.40. Found: C, 59.08; H, 6.37%. MS (ES\(^+\)) m/z = 729 [M\(^+\) - O\(_2\)CPh]. IR (KBr) \(\nu_{\text{C-H}} = 2909, 2850, \nu_{\text{C=O}} = 2132, \nu_{\text{C=O}} = 1609, \nu_{\text{Ar}} = 1571, 1486\) cm\(^{-1}\).

12(b) - trans-[bis(trimethylphosphine)-\(\eta^2\)-benzoato-2,5-bis(p-methylthiophenylethynyl)-3,4-\(\mu\)-tetramethylenerhodacyclopenta-2,4-diene]

In a N\(_2\) filled glovebox, the remaining mixture of 11(b) and 12(b) was added to toluene (3 mL) in a Young’s tube, which was then sealed, removed from the glovebox and heated at 50 °C. The reaction progress was monitored in situ by \(^{31}\)P\(_{\{\text{\scriptsize{}H}\}}\) NMR spectroscopy, and the toluene was removed in vacuo and refilled repeatedly until the in situ \(^{31}\)P\(_{\{\text{\scriptsize{}H}\}}\) NMR spectrum showed complete conversion to 12(b). The product was washed with hexane (5 x 1 mL) to give 12(b) as an orange solid. Yield: 0.058 g, 79%. \(^1\)H NMR (700 MHz, C\(_6\)D\(_6\)) \(\delta\): 8.51 (d, \(J = 8\) Hz, 2H, CH\(_{\text{arom}}\)), 7.64 (d, \(J = 8\) Hz, 4H, CH\(_{\text{arom}}\)), 7.22 (t, \(J = 8\) Hz,
2H, CH$_{arom}$), 7.17 (t, $J = 8$ Hz, 1H, CH$_{arom}$), 7.05 (d, $J = 8$ Hz, 4H, CH$_{arom}$), 2.83 (m, 4H, C=C-CH$_2$), 1.90 (s, 6H, 2 x SCH$_3$), 1.61 (m, 4H, CH$_2$), 1.05 (vt, $J_{P-H} = 4$ Hz, 18H, 2 x PMe$_3$). $^{31}$P{$^1$H} NMR (162 MHz, C$_6$D$_6$) $\delta$: -0.91 (d, $J_{Rh-P} = 115$ Hz, 2P). Anal. Calcd. for C$_{39}$H$_{45}$O$_2$P$_2$RhS$_2$: C, 60.46; H, 5.85. Found: C, 60.27; H, 5.95%. MS (MALDI$^+$) $m/z$ = 774 [M$^+$], 653 [M$^+$ - O$_2$CPh]. IR (KBr) $\nu$$_{C-H}$ = 2905, $\nu$$_{C\equiv C}$ = 2134, $\nu$$_{Ar}$ = 1591 cm$^{-1}$.

**11(c) – mer,cis-[tris(trimethylphosphine)-$\eta^1$-benzoato-2,5-bis($p$-carboxymethoxyphenyl ethynyl)-3,4-$\mu$-tetramethylenrhodacyclopenta-2,4-diene]**

The compound 1,12-bis(carboxymethoxyphenyl)dodeca-1,3,9,11-tetrayne (0.0401 g, 0.095 mmol) in THF solution was added to a stirred THF solution of compound **10** (0.0430 g, 0.095 mmol), which was obtained via in situ reaction of benzoic acid (0.0116 g, 0.095 mmol) and [RhMe(PMe$_3$)$_4$] (0.0401 g, 0.095 mmol). The resulting solution was stirred for 15 h at room temperature to give a mixture of $\eta^1$-compound **11(c)** and $\eta^2$-compound **12(c)**. Compound **11(c)** was isolated in pure form via several recrystallisations from THF and hexane. Yield: 0.013 g, 16%. $^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$: 8.50 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 8.14 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 7.97 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 7.35 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 7.31 (d, $J = 8$ Hz, 2H, CH$_{arom}$), 7.26 (t, $J = 8$ Hz, 2H, CH$_{arom}$), 7.18 (t, $J = 8$, 1H, CH$_{arom}$), 3.49 (s, 3H, CO$_2$CH$_3$), 3.41 (s, 3H, CO$_2$CH$_3$), 2.88 (m, 2H, C=C-CH$_2$), 2.75 (m, 2H, C=C-CH$_2$), 1.61 (m, 4H, CH$_2$), 1.30 (d, $J_{P-H} = 8$ Hz, 9H, PMe$_3$ trans to Cα), 1.24 (vt, $J_{P-H} = 4$ Hz, 18H, PMe$_3$ trans to PMe$_3$). $^{31}$P{$^1$H} NMR (162 MHz, C$_6$D$_6$) $\delta$: -7.74 (dd, $J_{Rh-P} = 106$ Hz, $J_{P-P} = 31$ Hz, 2P), -18.82 (dt, $J_{Rh-P} = 91$ Hz, $J_{P-P} = 31$ Hz, 1P). Anal. Calcd. for C$_{44}$H$_{54}$O$_6$P$_3$Rh: C, 60.42; H, 6.22. Found: C, 60.25; H, 6.20%. MS (ES$^+$)
m/z = 874 [M⁺]. IR (KBr) \( \nu_{C-H} = 2912, \nu_{C=C} = 2129, \nu_{\text{ester}(C=O)} = 1718, \nu_{C=O} = 1598, \nu_{Ar} = 1570, 1432 \text{ cm}^{-1} \).

12(c) \(-\text{trans-[bis(trimethylphosphine)-}\eta^2\text{-benzoato-2,5-bis(p-carbomethoxy-phenylethynyl)}-3,4-\mu\text{-tetramethylenerhodacyclopenta-2,4-diene]}\)

In a N₂ filled glovebox, the remaining mixture of 11(c) and 12(c) was added to toluene (3 mL) in a Young’s tube, which was then sealed, removed from the glovebox and heated at 50 °C. The reaction progress was monitored in situ by \(^{31}\text{P}\{^1\text{H}\} \text{NMR spectroscopy}, and the toluene was removed in vacuo and refilled repeatedly until the in situ \(^{31}\text{P}\{^1\text{H}\} \text{NMR spectrum showed complete conversion to 12(c). The product was washed with hexane (5 x 1 mL) to give 12(c) as a dark-red solid. Yield: 0.052 g, 69\%. \(^1\text{H NMR (700 MHz, C}_6\text{D}_6) \delta: 8.48 \text{ (d, } J = 8 \text{ Hz, 2H, CH}_{\text{arom}}, 8.12 \text{ (d, } J = 8 \text{ Hz, 4H, CH}_{\text{arom}}, 7.71 \text{ (d, } J = 8 \text{ Hz, 4H, CH}_{\text{arom}}, 7.21 \text{ (t, } J = 8 \text{ Hz, 2H, CH}_{\text{arom}}, 7.18 \text{ (t, } J = 8 \text{ Hz, 1H, CH}_{\text{arom}}, 3.46 \text{ (s, 6H, 2 x CO}_2\text{CH}_3), 2.80 \text{ (m, 4H, C=C-CH}_2\text{), 1.58 \text{ (m, 4H, CH}_2\text{), 0.99 \text{ (vt, } J_{\text{P-H}} = 4 \text{ Hz, 18H, 2 x PMe}_3).}^{31}\text{P}\{^1\text{H}\} \text{NMR (162 MHz, C}_6\text{D}_6) \delta: -1.15 \text{ (d, } J_{\text{Rh-P}} = 114 \text{ Hz, 2P). Anal. Calcd. for C}_{41}\text{H}_{45}\text{O}_6\text{P}_2\text{Rh: C, 61.66; H, 5.68. Found: C, 61.61; H, 5.79\%. MS (MALDI\(^+\}) m/z = 798 [M^+]}, 677 [M^+ - O_2\text{CPh}]. IR (KBr) \nu_{C-H} = 2905, \nu_{C=C} = 2128, \nu_{\text{ester}(C=O)} = 1717, \nu_{Ar} = 1594 \text{ cm}^{-1} \).
3.4.12 Preparation of bis(trimethylphosphine)-η²-acetylacetonato-rhodium(I) (14)

Acetylacetone (0.0095 g, 0.095 mmol) in THF (1 mL) was added to a stirred solution of [RhMe(PMe₃)₄] (0.0401 g, 0.095 mmol) in THF (1 mL), and the resulting solution was stirred at room temperature for 5 min, after which the solvent was removed in vacuo. THF (2 mL) was added, the solution was stirred for 2 min and the solvent was removed in vacuo again. This cycle was repeated one more time, and then THF (2 mL) was added. The reaction was stirred at room temperature for 1 h, after which the solvent was removed in vacuo to give 14 as a yellow solid. The product was recrystallised in a Young’s tube via slow diffusion of a layer of hexane into a concentrated THF solution of 14. Yield: 0.029 g, 86%. ¹H NMR (400 MHz, C₆D₆) δ: 5.36 (s, 1H, acac-CH), 1.83 (s, 6H, acac-CH₃), 1.13 (s, 18H, 2 x PMe₃). ³¹P{¹H} NMR (202 MHz, 203 K, 10% C₆D₆ in THF) δ: 5.78 (d, J_Rh-P = 185 Hz, 2P). Anal. Calcd. for C₁₁H₂₅P₂O₂Rh: C, 37.30; H, 7.11. Found: C, 37.10; H, 7.38%. MS (ES⁺) m/z = 354 [M⁺].
3.4.13 Preparation of acetylacetonato-rhodacyclopentadienes

![Diagram of acetylacetonato-rhodacyclopentadienes]

15(a) - trans-[bis(trimethylphosphine)-η²-acetylacetonato-2,5-bis(phenylethynyl)-3,4-µ-tetramethylenerhodacyclopenta-2,4-diene]

In a N₂ filled glove box, 1,12-diphenyldodeca-1,3,9,11-tetrayne (0.0291 g, 0.095 mmol) in THF was added to a stirred THF solution of 14 (0.0337 g, 0.095 mmol), which was obtained via in situ reaction of acetylacetone (0.0095 g, 0.095 mmol) and [RhMe(PMe₃)₄] (0.0401 g, 0.095 mmol). The resulting solution was transferred into a Young’s tube, which was then sealed and removed from the glovebox. The reaction was heated for 16 d at 50 °C to give a mixture of 15(a) and its isomeric biphenyl-rhodacyclopentadiene 16(a).

Compound 15(a) was isolated by washing the mixture with hexane (5 x 1 mL) as 16(a) was soluble in hexane. The remaining 15(a) was isolated as a yellow-orange solid. Yield: 0.034 g, 54%. ¹H NMR (400 MHz, C₆D₆) δ: 7.74 (d, J = 8 Hz, 4H, CH arom), 7.13 (t, J = 8 Hz, 4H, CH arom), 6.99 (t, J = 8 Hz, 2H, CH arom), 5.15 (s, 1H, acac-CH), 2.96 (m, 4H, C=C-CH₂), 1.95 (s, 6H, acac-CH₃), 1.68 (m, 4H, CH₂), 0.94 (vt, J_P-H = 4 Hz, 18H, 2 x PMe₃). ³¹P{¹H} NMR (162 MHz, C₆D₆) δ: -0.46 (d, J_Rh-P = 114 Hz, 2P). Anal. Calcd. for C₃₅H₄₃O₂P₂Rh: C, 63.64; H, 6.56. Found: C, 63.80; H, 6.46%. MS (ES⁺) m/z = 660 [M⁺], 561 [M⁺ - acac]. IR (KBr) v_C-H = 2908, v_C≡C = 2139, v_Ar = 1588, 1426 cm⁻¹.

16(a): ³¹P{¹H} NMR (81 MHz, C₆D₆) δ: -1.18 (d, J_Rh-P = 115 Hz, 2P).
**15(b) - trans-[bis(trimethylphosphine)-η²-acetylacetonato-2,5-bis(p-methylthiophenyl ethynyl)-3,4-µ-tetramethylnerhodacyclopenta-2,4-diene]**

In a N₂ filled glove box, 1,12-bis(methylthiophenyl)dodeca-1,3,9,11-tetrayne (0.0379 g, 0.095 mmol) in THF was added to a stirred THF solution of 14 (0.0337 g, 0.095 mmol), which was obtained via in situ reaction of acetylacetone (0.0095 g, 0.095 mmol) and [RhMe(PMe₃)₄] (0.0401 g, 0.095 mmol). The resulting solution was transferred into a Young’s tube, which was then sealed and removed from the glovebox. The reaction was heated for 7 d at 50 °C to give a mixture of 15(b) and its isomeric biphenyl-rhodacyclopentadiene 16(b). Compound 15(b) was isolated by washing the mixture with hexane (5 x 1 mL) as 16(b) is soluble in hexane. Compound 15(b) was recrystallised from THF and hexane and isolated as an orange solid. Yield: 0.024 g, 34%. ¹H NMR (400 MHz, C₆D₆) δ: 7.62 (d, J = 8 Hz, 4H, CH₆arom), 7.08 (d, J = 8 Hz, 4H, CH₆arom), 5.17 (s, 1H, acac-CH), 2.96 (m, 4H, C=C-CH₃), 1.97 (s, 6H, acac-CH₃), 1.93 (s, 6H, 2 x SCH₃), 1.69 (m, 4H, CH₂), 0.96 (vt, Jₚ-H = 4 Hz, 18H, 2 x PMe₃). ³¹P{¹H} NMR (162 MHz, C₆D₆) δ: -0.41 (d, Jₚ-Rh = 114 Hz, 2P). Anal. Calcd. for C₃₇H₄₇O₂P₂RhS₂: C, 59.04; H, 6.29. Found: C, 59.60; H, 6.08%. MS (ES⁺) m/z = 752 [M⁺], 676 [M⁺ - PMe₃], 653 [M⁺ - acac]. IR (KBr) ν_C-H = 2910, ν_C=C = 2137, ν_Ar = 1585, 1427 cm⁻¹.

**16(b):** ³¹P{¹H} NMR (162 MHz, C₆D₆) δ: -1.15 (d, Jₚ-Rh = 115 Hz, 2P).

**15(c) - trans-[bis(trimethylphosphine)-η²-acetylacetonato-2,5-bis(p-carbomethoxyphenyl ethynyl)-3,4-µ-tetramethylnerhodacyclopenta-2,4-diene]**

In a N₂ filled glove box, 1,12-bis(carbomethoxyphenyl)dodeca-1,3,9,11-tetrayne (0.0401 g, 0.095 mmol) in THF was added to a stirred THF solution of 14 (0.0337 g,
0.095 mmol), which was obtained via in situ reaction of acetylacetone (0.0095 g, 0.095 mmol) and [RhMe(PMe₃)₄] (0.0401 g, 0.095 mmol). The resulting solution was transferred into a Young’s tube, which was then sealed and removed from the glovebox.

The reaction was heated for 3 d at 50 °C to give a mixture of 15(c) and its isomeric biphenyl-rhodacyclopentadiene 16(c). Compound 15(c) was isolated by washing the mixture with hexane (5 x 1 mL) as 16(c) is soluble in hexane. Compound 15(c) was recrystallised from THF and hexane to give a dark-red solid. Yield: 0.015 g, 20%. ¹H NMR (700 MHz, C₆D₆) δ: 8.13 (d, J = 8 Hz, 4H, CHₐrom), 7.68 (d, J = 8 Hz, 4H, CHₐrom), 5.13 (s, 1H, acac-CH), 3.47 (s, 6H, 2 x CO₂CH₃), 2.91 (m, 4H, C=C-CH₂), 1.91 (s, 6H, acac-CH₃), 1.66 (m, 4H, CH₂), 0.88 (vt, Jₚ-H = 4 Hz, 18H, 2 x PMe₃). ³¹P{¹H} NMR (162 MHz, C₆D₆) δ: -0.56 (d, Jₚ-Rh = 113 Hz, 2P). Anal. Calcd. for C₃₉H₄₇O₆P₂Rh: C, 60.31; H, 6.10. Found: C, 60.15; H, 6.10%. MS (ES⁺) m/z = 776 [M⁺], 700 [M⁺ - PMe₃], 677 [M⁺ - acac]. IR (KBr) νC-H = 2908, νC≡C = 2132, νester(C=O) = 1718, νAr = 1594, 1433 cm⁻¹.

16(c)

Compound 16(c) was separated from 15(c) by washing the mixture with hexane as noted above. The hexane filtrate was kept in a vial, and light-red crystals of 16(c) were formed overnight via slow evaporation. Yield: 0.006 g, 8%. ¹H NMR (400 MHz, C₆D₆) δ: 9.53 (d, J = 8 Hz, 1H, CHₐrom), 9.11 (br, s, 1H, CHₐrom), 8.37 (br, d, J = 8 Hz, 1H, CHₐrom), 8.05 (br, s, 1H, CHₐrom), 8.04 (d, J = 8 Hz, 2H, CHₐrom), 7.56 (d, J = 8 Hz, 2H, CHₐrom), 5.12 (s, 1H, acac-CH), 3.62 (s, 3H, CO₂CH₃), 3.47 (s, 3H, CO₂CH₃), 3.24 (t, J = 8 Hz, 2H, C=C-CH₂), 2.91 (t, J = 8 Hz, 2H, C=C-CH₂), 1.88 (s, 6H, acac-CH₃), 1.79 (quint, J = 8 Hz, 2H, CH₂), 1.69 (quint, J = 8 Hz, 2H, CH₂), 0.56 (vt, Jₚ-H = 3 Hz, 18H, 2
$^{31}$P{\textsuperscript{1}H} NMR (162 MHz, C$_6$D$_6$) $\delta$: -1.16 (d, $J_{\text{Rh-P}} = 113$ Hz, 2P). MS (ES$^+$) $m/z$ = 776 [M$^+$]. IR (KBr) $\nu_{\text{C-H}} = 2908$, $\nu_{\text{C=C}} = 2132$, $\nu_{\text{ester(C=O)}} = 1722$, $\nu_{\text{Ar}} = 1586$, 1433 cm$^{-1}$.

References

Chapter 4

Suggestions for future work
This project has investigated the effect of different ligands (e.g. DHAPEPE-, TMSE-, \( \eta^2 \)-benzoato- and acac-) on the photophysical properties of rhodacyclopentadienes. The TMSE-rhodacyclopentadienes [especially 7(a)] have been investigated further and found that no phosphorescence was observed either at room temperature or 77 K despite the fact that Rh is covalently bound to the organic chromophore. Moreover, some rhodacyclopentadienes, particularly TMSE-rhodacyclopentadienes, exhibit unexpectedly long-lived singlet excited states, fluorescent rates competitive with intersystem crossing rates \( k_f \approx k_\Delta \approx 10^8 \text{ s}^{-1} \) and high \( \Phi_f \) values. On the other hand, the photophysical results for the biphenyl-based rhodacyclopentadiene [16(c), a by-product from the acac-rhodacyclopentadiene synthesis] indicate that the spin-orbit coupling (SOC) effect from the Rh is strong enough to facilitate effective intersystem crossing (ISC) of the singlet excited states to triplet excited states and emit phosphorescence at room temperature. Over the past 50 years, many people have thought that the presence of heavy atoms such as transition metals in the molecule is the main factor to facilitate an effective ISC. However, the photophysical properties of the rhodacyclopentadienes presented in this thesis confirm that the presence of heavy atom is not only the factor required for effective ISC. Indeed, it also depends on how effective the SOC from the heavy atom is in the excited states. Therefore, it will be very interesting to investigate the effectiveness of SOC from heavy atoms in the future, which can be done in two ways:

(i) to study the photophysical properties of other metallacyclopentadienes such as iridacyclopentadienes and platiniacyclopentadienes, which are structurally related to the rhodacyclopentadienes;
(ii) to attach two phenyl rings to the cyclohexyl loop of the rhodacycle ring (Figure 4.1).

Iridacyclopentadienes are suggested because Ir is in the same group with Rh, but Ir has a three times stronger SOC effect than Rh. Therefore, iridacyclopentadienes are expected to be phosphorescent, and no fluorescence is expected to be observed. For the same reasons, platinacyclopentadienes are also interesting because Pt has much stronger SOC effect than Ir and Rh. (SOC constants: \( \text{Rh} = 1259 \text{ \, cm}^{-1}, \) \( \text{Ir} = 3909 \text{ \, cm}^{-1}, \) \( \text{Pt} = 4481 \text{ \, cm}^{-1}. \))

The proposed molecular structure with two phenyl rings attached to the cyclohexyl loop is shown in Figure 4.1. The reason for attaching them is to change the electronic property at the rhodacycle core, which might lead to an increasing of electron delocalisation at the rhodacycle core. Moreover, the presence of the two phenyl rings also increases the rigidity of the rhodacycle; hence the quantum yield values are expected to be increased as well.

![Figure 4.1: Proposed molecular structure of rhodacycle ring with two phenyl rings attached to the cyclohexyl loop.](image)

In addition, we have also demonstrated the deprotection of the C≡C-SiMe\(_3\) groups to produce C≡C-H groups in the TMSE-rhodacyclopentadiene as shown in Figure 3.27. Interestingly, the TMSE- ligand attached to the Rh centre was not affected by the deprotection conditions. Therefore, the two C≡C-H groups at the terminals can be reacted
with other transition metals such as Au\textsuperscript{(I)}, and the changes in the photophysical properties can be investigated. The reason for introducing another metal, such as Au, is to investigate the intra-molecular charge-transfer between Rh and it. In addition, the Au may also increase the SOC effect in the rhodacyclopentadienes, and subsequently may increase the ISC rate.

References: