# Characterisation of Ruthenium – Rhenium Dinuclear Complexes using NMR and HPLC

*Hamid M Younis* [a] *, Nadia Coburn,* [b] *and Johannes G. Vos* [b]*

[a] *Sciences Faculty, Department of Chemistry, Sirte University, Sirte-Libya,*
[b] *SRC for Solar Energy Conversion, School of Chemical Sciences, Dublin City University, Ireland,* [*] .

## *Abstract*

*Many studies have been conducted on substituting ligands to increase photocatalytic activity but an interesting study was conducted again by our group researchon manipulating these properties by structural changes i.e. using different degrees of communication between the metallic sites and the ligands. Enhancement of photocatalytic activity was achieved when the Ru and Re Centres were bound covalently by providing selective excitation and reductive quenching of the Ru excited state to the Re moiety.*

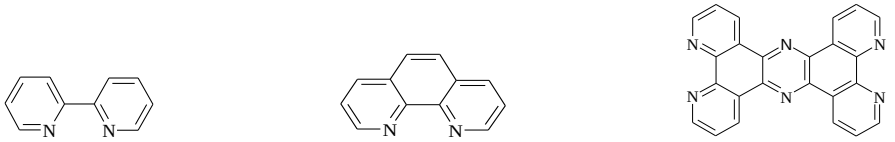
*Photocatalytic studies on a number of dinuclear systems were carried out and the results showed that the photocatalytic response to light was achieved upon addition of the Ru species where it was covalently linked to the Re Centre. The photocatalyic study also indicated that increasing the number of Re Centres attached to the bridging ligand increased the turnover number. This study was influential on the design of the system to be used in the study presented in this work.*

***Key words:*** *Synthesis , Ruthenium , Rhenium Dinuclear, photocatalytic, HPLC.*

## Introduction

The synthesis of dinuclear complexes with the formula $[Ru(bpy)_2(tpphz)Re(CO)_3Cl]$, $[\{Ru(bpy)_2\}_2tpphz]$, $[\{Re(CO)_3Cl\}_2tpphz]$ Where (bpy)= (2,2-bipyridine), and (Tpphz)= (tetrapyrido[3,2-a:2’,3’:3’’,2’’-h:2’’’,3’’’-j]phenazine). Many studies have been conducted on substituting ligands to increase photocatalytic response to light was achieved upon addition of the Ru species where it was covalently linked to the Re Centre. The photocatalyic study also

indicated that increasing the number of Re Centres attached to the bridging ligand increased the turnover number. This study was influential on the design of the system to be used in the study NMR , IR and HPLC. The synthesis and characterization of ruthenium (II) and rhenium (I) mono- and dinuclear complexes containing the symmetric ligand (tpphz) are described. All of the complexes are characterized and examined for their photophysical properties [1]. The structures of the ligand employed and metal complexes synthesized are described in figure 1 and 2.

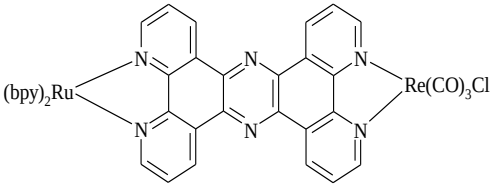


bpy (2,2-bipyridine) Phen (1,10-phenanthroline) Tpphz

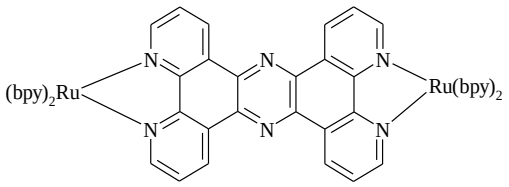

[Ru(bpy)$_2$(1,10-phenanthroline)] [Re(CO)$_3$Cl(1,10 phenanthroline)]


[Ru(bpy)$_2$(tpphz)] [Re(CO)$_3$Cl(tpphz)]

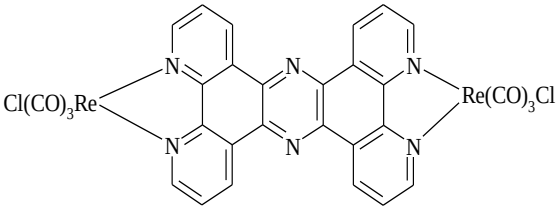
**Figure 1**: Depicts the abbreviations and structures of the ligands (top), and the abbreviations and structures of the mononuclear complexes discussed in [2].




[Ru(bpy)2(tpphz)Re(CO)3Cl]




[{Ru(bpy)2}2tpphz]




[{Re(CO)3Cl}2tpphz]

**Figure 2** Depicts the abbreviations and structures of the dinuclear complexes discussed in [3].

## Instrumental Methods

NMR Spectroscopy.

H NMR spectra were obtained on a Bruker Advance 400 NMR Spectrometer at 400 MHz. Analysis was carried out in deuterated solvents (DMSO, d3- ACN, d3- Acetone and CDCl3) depending on substance solubility. Spectra were calibrated using either the relevant solvent peaks or TMS was added to the NMR tube as an internal reference. Some solutions required sonication for approximately five to ten minutes to ensure a fully dissolved solution due to low compound solubility. Samples containing a rhenium carbonyl species or the ligand tpphz were analyzed immediately in the dark to ensure no photodecomposition.

## Infrared Spectroscopy (IR)

Infrared spectra of compounds in solution were measured using $CH_2Cl_2$ or THF as solvents. A Perkin Elmer 2000 FTIR spectrometer was used and scans were carried out initially in the 4000 $cm^{-1}$ to 600 $cm^{-1}$ range before reducing to the carbonyl stretching frequency 2200 $cm^{-1}$ 1800 $cm^{-1}$ . An average of 25 scans was carried out per sample using an Omni cell with NaCl windows. To obtain a clear spectrum, resolution was set to 4 cm and an interval of 1 cm were used.

**Ultra Violet/Visible Spectroscopy. (UV/Vis)**

UV−Vis absorption spectra were recorded on a Shimadzu 3100 UV-Vis instrument. Sample measurements were carried out using 1 cm quartz cells and a relevant solvent blank. Solvents used for UV-Vis analysis were spectroscopy grade ethanol, DCM or acetonitrile. Cleaning of the quartz cells were carried out using a Kuvettol cleaning solution used as directed or an acid solution of 1:1 (v/v) conc. $H_2SO_4/HNO_3$ to remove any remaining metal residue followed by washing with water. As the latter leads to glass etching and eventually the destruction of the cell it was only used in severe cases.

**High Performance Liquid Chromatography.**

HPLC measurements were performed on a JVA analytical HPLC system consisting of a Varian Prostar HPLC pump using a Partisil P10 SCX-3095 cation exchange column (HiChrom) and a Varian Prostar photodiode array detector. A 20 μL injection loop delivered the sample to the column using typically 0.08 M $LiClO_4$ in $MeCN/H_2O$ (80/20) mobile phase at a flow rate of 2.0 $cm^3$ $min^{-1}$. The chromatogram was monitored at 280 nm and analyzed using Varian ProStar software.

**Synthetic Procedures**

**Ligand Preparation** [4]**:**
1,10-phenanthroline monohydrate (0.0504 mol, 10.00g) was added in small portions to a stirring solution of 60$cm^3$ concentrated sulphuric acid in a 500$cm^3$ round bottom flask equipped with a reflux condenser. When the solid was completely dissolved, sodium bromide (0.0504mol, 5.19g) was added in small portions followed by 30$cm^3$ of 70% $HNO_3$. This was then brought to reflux (110ºC) for six hours and then the temperature was reduced to 95ºC, the reflux condenser removed to allow the bromine vapours to escape and this was left for sixteen hours.

The reaction was then brought to room temperature and poured over 800g of ice and was carefully neutralized to pH 7 with approximately 300$cm^3$ of 10M NaOH. At this point the solution turned a green color with a yellow precipitate. This step was repeated twice. This precipitate was then collected and placed in a round bottom flask and refluxed in 200$cm^3$ of water for 1 hour and the insoluble material was collected by vacuum filtration. This was repeated twice more and then the water was extracted with DCM until the organic layer remained clear. The DCM was then removed by rotary evaporation and an NMR obtained of

the crude material. This was then recrystallized from toluene [6]. Yield: 8.16g, 70% . $^1$H NMR ($d_6$- acetone, 298K) δ 8.99 (d), 8.39 (m), 7.67 (d).

**Tetrapyrido[3,2-a:2',3':3'',2''-h:2''',3'''-j]phenazine (Tpphz)**

1,10-phenanthroline-5,6-dione (0.3045g, 1.5 mmol), sodium hydrosulphite (0.0318g, 0.18 mmol) and ammonium acetate (1.594g, 20.6 mmol) were placed into a 50cm3 round bottom flask which was previously purged with nitrogen. This was slowly heated to 190ºC with constant stirring for two hours. After the reagents have melted the reaction turns a yellow/brown colour. The reaction was then cooled to room temperature and 3cm$^3$ of water was added. The yellow precipitate was then collected under a vacuum, washed with water, methanol and acetone. Yield: 0.1526g, 52.8%. $^1$H NMR ($CDCl_3$ TFA, 298K) δ 10.06(d), 9.47 (m), 8.47 (d).

**Preparation of Mononuclear Complexes**

**[Ru(bpy)$_2$(1,10phenanthroline)]$^{2+}$**

(0.200 g, 3.9 mmol) of [Ru(bpy)$_2$Cl$_2$] and (0.099g, 5.0mmol) of 1,10-phenanthroline were refluxed at 120ºC for 3 hours in 2:1v/v ethanol: water. The reaction was cooled to room temperature and the ethanol removed. 5cm$^3$ of water was added and the product was obtained by the addition of $NH_4PF_6$. The product was stored at +4°C overnight and recrystallized from 2:1 acetone: water. Yield: 0.2232g, 74%

$^1$H NMR (*acetone,* 298K) δ 8.91 (m), 8.88 (m), 8.40 (s), 8.23 (dd), 8.14 (dd), 7.89 (m), 7.58 (m), 7.58 (dd).

**[Ru(bpy)$_2$(phendione)]$^{2+}$ (method 2)**

[Ru(bpy)$_2$Cl$_2$][8], (74 mg, 0.13 mmol) was dissolved in 5cm$^3$ of ethanol. 1,10-phenanthroline-5,6-dione (29 mg, 0.14mmol) was added slowly with constant stirring. This was refluxed for 4 hours at 70ºC. The reaction was then cooled and filtered and saturated ethanolic $KPF_6$ was added. The reaction was then placed at -20ºC overnight and a black solid was obtained. This was recrystallised from 1:1 Acetone: water.

Yield: 44.6mg, 51.6%. $^1$H NMR (*acetone*, 298K) δ: 8.91 (m), 8.88 (m), 8.40 (s), 8.23 (dd), 8.14 (dd), 7.89 (m), 7.58 (m), 7.58 (dd).

**[$Re(CO)_3Cl$ (phenanthroline)]**

20 $cm^3$ of anhydrous toluene was purged for 10 min. $Re(CO)_5Cl$ (0.1 g, 2.76 x $10^{-4}$moles) was weighed out carefully under nitrogen and added to 10$cm^3$ of the toluene. 1,10pnenanthroline (0.0403g, 2.76 x $10^{-4}$ moles) was dissolved in the other 10$cm^3$ of toluene along with a few drops of triflouroacetic acid. The $Re(CO)_5Cl$ was added slowly over a 15min period and then this solution was heated to reflux and left for 3 hours. The reaction had turned a bright yellow colour and was allowed to cool to room temperature and as this occurred a bright yellow precipitate formed. The yellow product was collected by vacuum filtration and to ensure all the product was collected the toluene was evaporated [9]. Yield: 93 mg, 70%. $^1H$ NMR (*acetone,* 298K) δ: 8.84 (dd), 8.41 (m), 8.22 (s), 7.38 (m)

**[$Re(CO)_3Cl$ (tpphz)]**

20$cm^3$ of anhydrous toluene was purged for 10min. $Re(CO)_5Cl$ (0.1g, 2.76x$10^{-4}$moles) was weighed out carefully under nitrogen and added to 10$cm^3$ of the toluene. Tpphz (0.1g, 2.76x$10^{-4}$ moles) was dissolved in the other 10$cm^3$ of toluene along with a few drops of triflouroacetic acid. The $Re(CO)_5Cl$ was added slowly over a 15min period and then this solution was heated to reflux and left for 3 hours. The reaction had turned a bright yellow colour and was allowed to cool to room temperature and as this occurred, a bright yellow precipitate formed. The yellow product was collected by vacuum filtration and to ensure, all of the product was collected, the toluene was evaporated. Yield: 95.3mg, 50%

**Preparation of Dinuclear Complexes**

**$[Ru(bpy)_2(Tpphz)Re(CO)_3Cl]^{2+}$**

$[Re(CO)_3Cl(dione)]$ [10]. (50 mg, 9.69 x $10^{-5}$moles), $[Ru(bpy)_2(dione)]^{2+}$ (91 mg, 9.69 x $10^{-5}$ moles) and ammonium acetate and HS were placed together in a round bottom flask and heated at first until all of the ammonium acetate melted. This was then heated to 100C and left to stir for 5 hours. This was then cooled down and 5 ml of $H_2O$ was added. A yellow precipitate was kept and filtered off. $PF_6$ was then added to the solution and a red precipitate was obtained. NMR see discussion in [11].

**$[Ru(bpy)_2(Tpphz)Re(CO)_3Cl]^{2+}$**

$[Re(CO)_3Cl(Tpphz)]$ (50 mg, 7.236 x $10^{-5}$moles) was dissolved in 2:1(v/v) ethanol: water. $[Ru(bpy)_2Cl_2]$ (42 mg, 7.24 x $10^{-5}$moles) was added to this solution slowly over a twenty minute period. This was left to reflux for six hours and then the ethanol was removed. Any solid was filtered off and the product was precipitated using $PF_6$. Yield: 13.7 mg, 12%. NMR discussion [12].

## Discussion of Experimental Procedures

The Tpphz Ligand was prepared as described by Bolger *et al* [14] by the synthesis of 1,10-phenanthroline-5,6-dione from 1,10-phenanthroline. The reflux was a solventless reaction using the solid with the lowest melting point (ammonium acetate) to form a slurry and then further reaction with the phendione in the presence of a hydrogen donor. This reaction is easily purified by trituration in ethanol and is a relatively easy synthesis to complete. The problem is the tpphz ligand is highly insoluble, so even though the ligand itself is easily obtained using this complex with either metal center as conducted previously became a challenge. There are some reported microwave syntheses[i] which have offered a solution in previous cases but initially it was thought that building the ligand on to the ruthenium and rhenium centers offered an alternative route to using a microwave. To ensure that the addition of the ligand to a metal dichloride would not yield a product a series of micro scale reactions were conducted with a series of solvents (polar, non-polar, chlorinated and unchlorinated) and temperatures, no reaction was found to occur in any case.

### Complex Preparation

A series of routes were taken to prepare the tpphz mononuclear complex, these are best described in Figures 1 – 3. Previous publications agree that the best approach to the formation of the Ru-tpphz-Re dimer is via a Schiff base type of coupling between an aimine and an aldyhyde, Here this is a ruthenium complex containing a phendione ligand reacting with a 1,10-phenanthroline-5,6-diamine ligand. In the beginning this appeared to be a logical route to follow but this was found not to be the case. The preparation of the diamine ligand is complex and often low yielding as an oxime intermediate is required [13]. As the paper reported this synthesis was repeated on both the free ligand and ‘on complex’ with a mixture of products forming often undesired and when the diamine was formed it was in very low yields (5%).

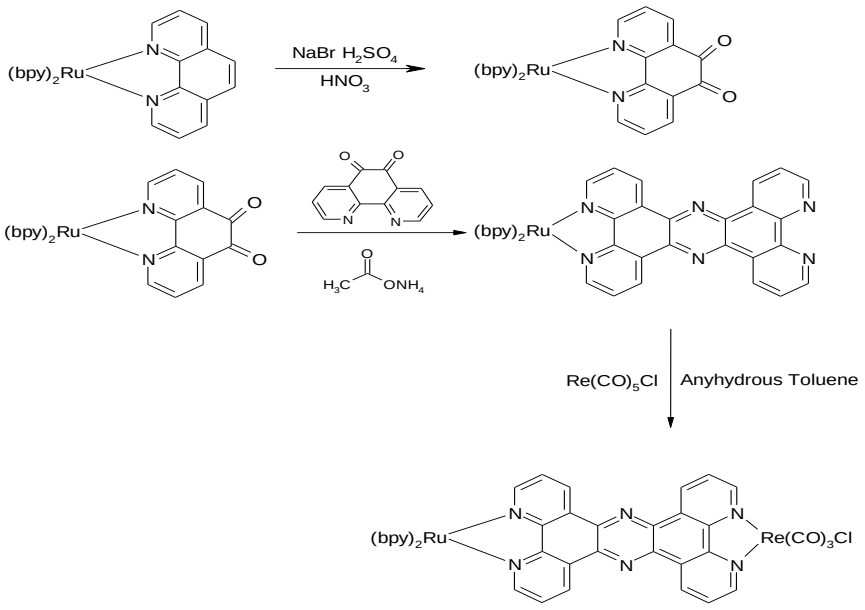



**Figure 3:** Synthetic Route 1 to the formation of the desired heterodimer.

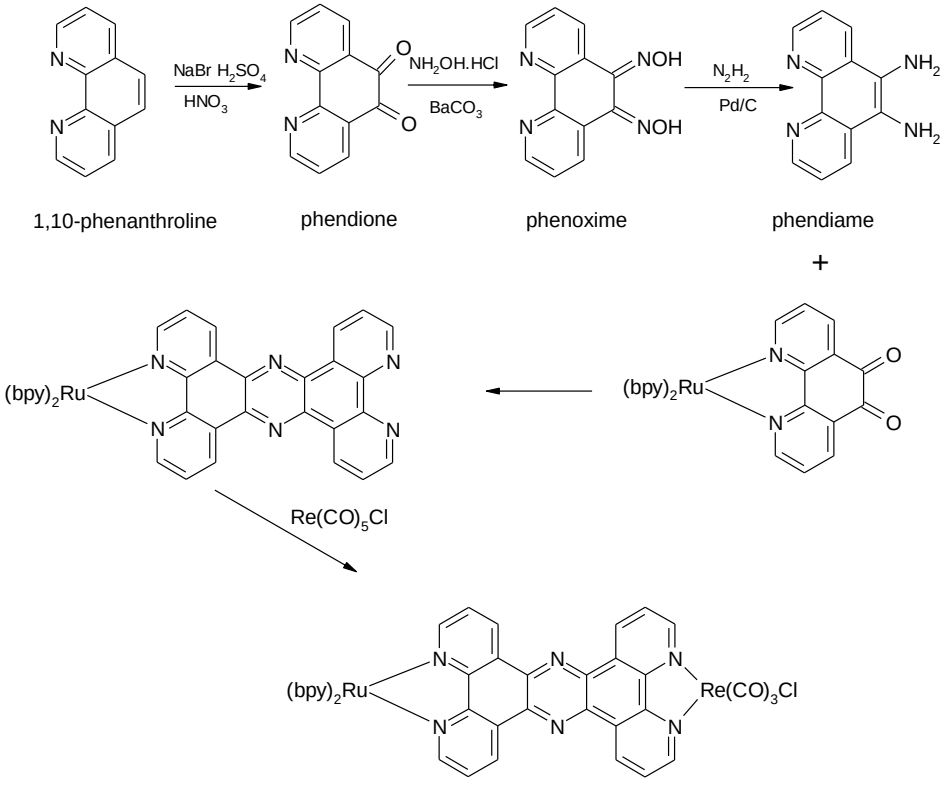



**Figure 4:** Synthetic Route 2 to the formation of the desired heterodimer.

Stepping back from these methods it was decided to return to a condensation type reaction similar to the synthesis of the free ligand. The complexes $[Ru(bpy)_2(phendione)]^{2+}$ and $[Re(CO)_3Cl(phendione)]$ were prepared with the idea of using ammonium acetate and a hydrogen donor to form the desired product. As in previous publications the solvent glacial acetic acid offered a good starting point, but later became problematic as the rhenium complex was found to degrade.

The preparation of the ruthenium dione complex was also interesting as it was found that oxidation of the phenanthroline ligand while bound to the ruthenium gave a higher yield and an overall better reaction than the normal method of complexation.

A second problem with this route is that 3 products are obtained, the desired homonuclear complex (Ru-tpphz-\Re) and two homonuclear complexes (Ru-tpphz-Ru, Re-tpphz-Re). the rhenium homonuclear complex is easily separated as it is neutral and generally crashes out the solvent is neutral, but due to degradation this was hard to obtain.

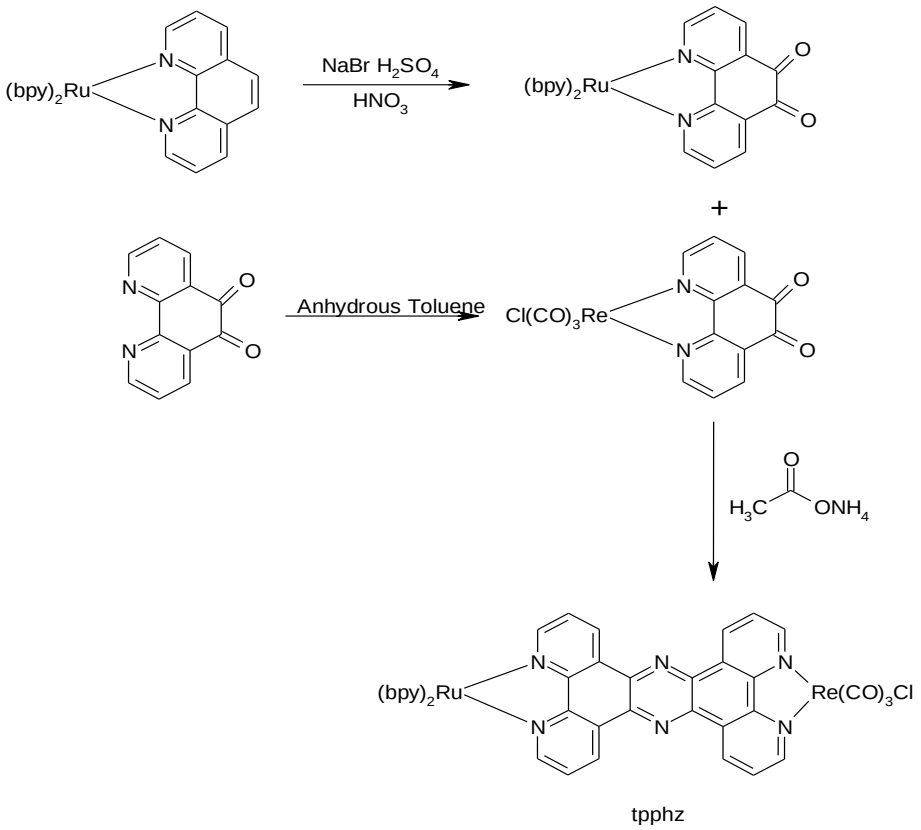



**Figure 5:** Synthetic Route 3 to the formation of the desired heterodimer.

It was then decided to try a solventless reaction using HS as a hydrogen donor as used in the preparation of the free ligand and ammonium acetate to form a slurry. It was found that if left to react for 5 hours the desired product is obtained but again the heterodimer and the Ru homodimer are difficult to separate.

So a final route was devised in which the tpphz ligand itself is dissolved in a small amount of TFA and reacted with $[Re(CO)_5Cl]$ using toluene as a solvent to form the mononuclear complex. As this formed a single mononuclear species it was then easily to attached to the ruthenium metal center using methanol/water as a solvent. Though this has, at this point, only been obtained in a small yield due to time constraints and needs to be repeated on a larger scale.

## Characterisation and Discussion

$^1$H NMR was employed here as mentioned previously, was to determine purity and in the elucidation of structure of both the ligand and metal complexes prepared.

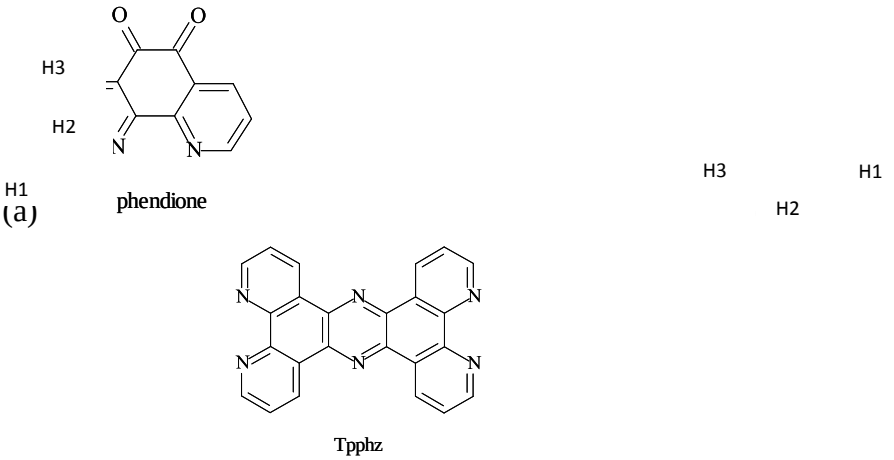



**Figure 6:** Labelling of the phenanthroline based ligands for $^1$HNMR assignment.

**Table 1:** $^1$H NMR data for 1,10-phenanthroline-5,6-dione and Tpphz ligands. a = acetone and b = $CDCl_3$ in the presence of TFA.

| Ligand | $H_1$ (ppm) | $H_2$ (ppm) | $H_3$ (ppm) |
|---|---|---|---|
| Phendione (a) | 8.99 | 7.67 | 8.39 |
| Tpphz (b) | 10.06 | 8.47 | 9.47 |

$^1$H NMR of the ligands are hard to compare, this is due to the insolubility of the tpphz ligand. Comparisons of NMR signals are typically made when analysis is carried out in the same solvent as to ignore solvent effects. Here the analysis was carried out with TMS as a reference and each spectrum was calibrated as such. Even by doing this these NMR values cannot really be compared.

To obtain an NMR of the tpphz ligand was first dissolved in TFA and then placed in $CDCl_3$. This formed more of a suspension then an ideal solution for NMR. This method was tried for the dione ligand, using TFA and $d_6$-acetone but the peaks obtained where undistinguishable. Unfortunately it was also impossible to obtain a decent NMR of the free 1,10-phenanthroline-5,6-dione in $CDCl_3$, which makes a comparison of chemical shift values difficult.

Figure 7 below shows the NMR spectra obtained for both the dione and the tpphz ligands. The presence of a TFA peak is clearly seen at 10.8 ppm. The $H_2$ proton for both ligands appears the furthest upfield. This has been assigned due to the splitting of the peak seen. As the $H_2$ proton in both cases is split by the $H_1$ and the $H_3$ protons.

In the both NMR spectra obtained, only three proton peaks are seen and this is due to the symmetry of the molecules. The dione itself has only 1 plane of symmetry so each peak relates to 2 hydrogens. The tpphz ligand has 2 planes of symmetry, making the hydrogens equivalent therefore only 3 protons again are seen.

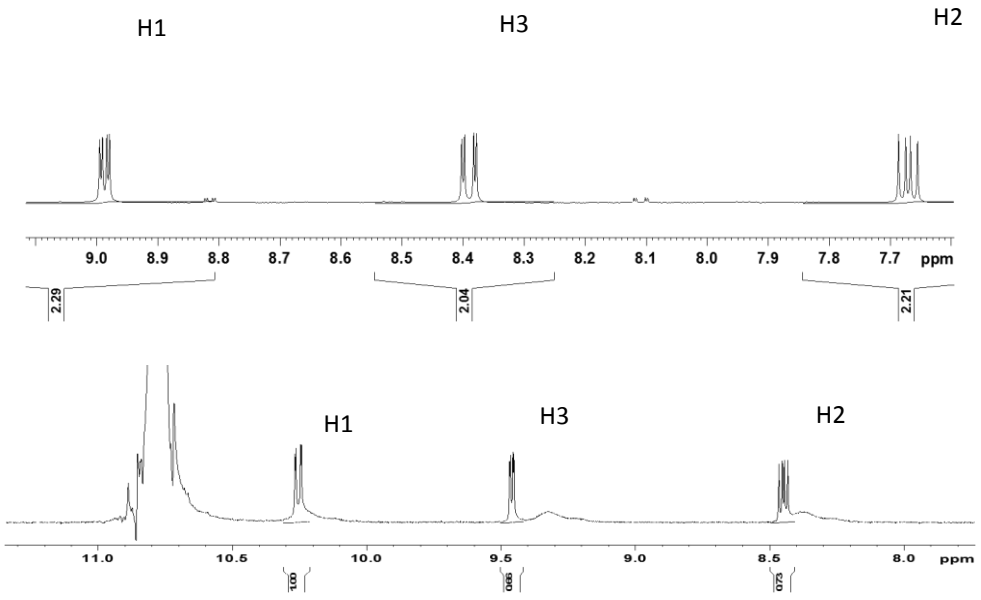



**Figure 7:** $^1$H NMR spectrum for 1,10-phenanthroline-5,6-dione in $d_6$-acetone (above) , and free Tpphz ligand(below) in $CDCl_3$ in the presence of TFA at 298K.

The HNMR analysis of the mononuclear complexes, are thankfully easier to compare. This is due to the increased solubility proprieties of the ligands upon binding. Table 2 below contains the values obtained for the mononuclear complexes prepared in $d_6$-acetone. Here the spectra obtained will be compared to the starting material of the reactions i.e. the phenanthroline complex is compared to that of the dione complex. The ruthenium complexes will be compared and then the rhenium complexes and finally an overall comparison will be made.

**Table 2:** $^1$H NMR data for mononuclear complexes carried out in $d_6$-acetone at 298.

| **Complex** | **H1** | **H2** | **H3** | **H4** |
|---|---|---|---|---|
| $[Ru(bpy)_2Phenanthroline)]^{2+}$ | 8.84 | 7.38 | 8.22 | 8.41 |
| $[Ru(bpy)_2Phendione)]^{2+}$ | 8.58 | 7.61 | 7.98 | - |
| $[Re(CO)_3Cl(Phenanthroline)]$ | 9.41 | 8.85 | 8.03 | 8.22 |
| $[Re(CO)_3Cl(Phendione)]$ | 9.22 | 8.77 | 7.98 | - |

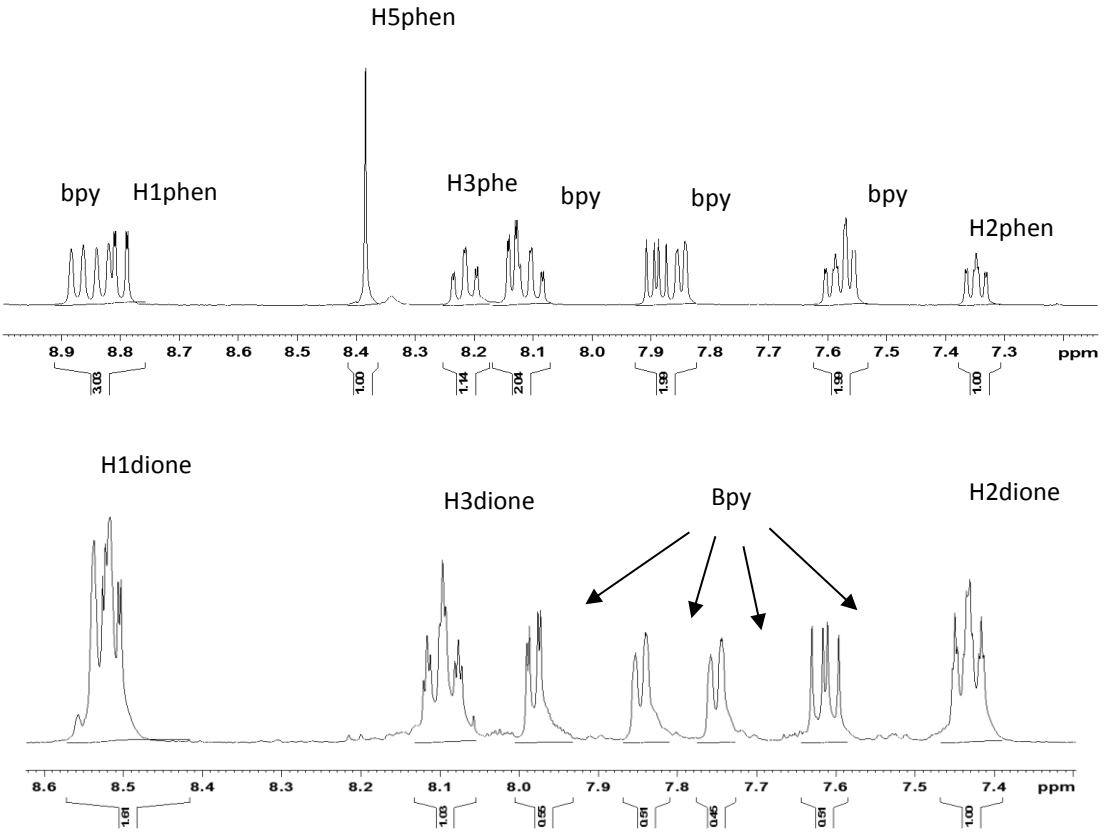
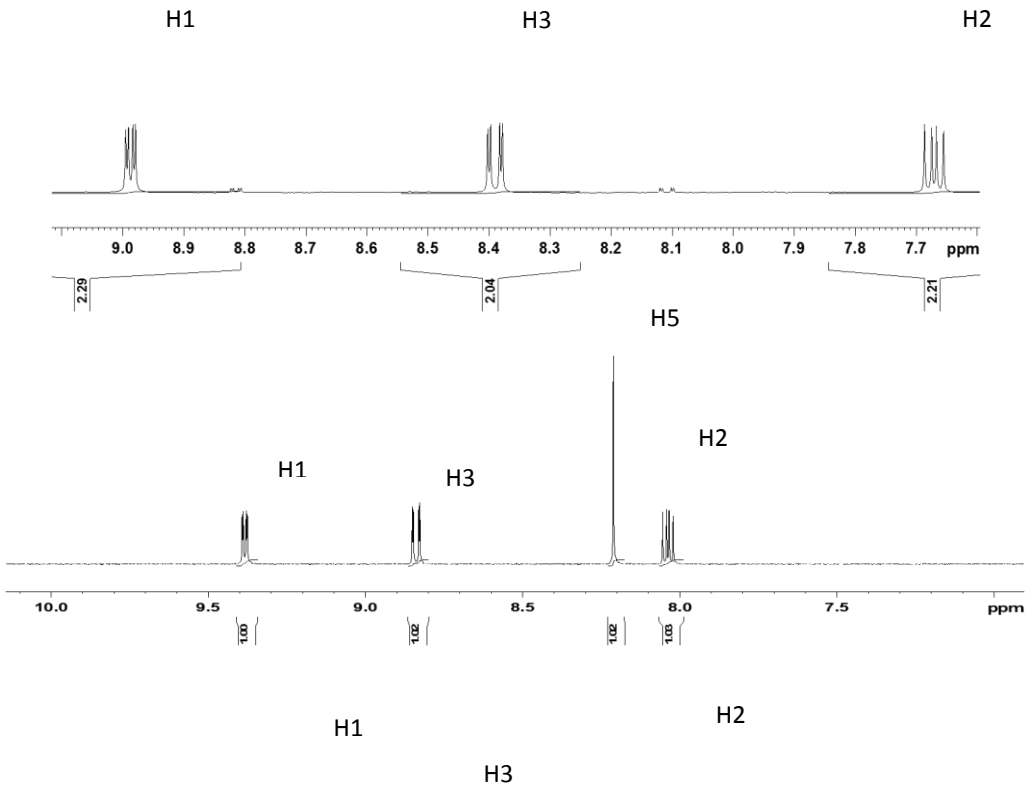



**Figure 8:** $^1$HNMR spectrum for $[Ru(bpy)_2(1,10\text{-phenanthroline}]^{2+}$ and $[Ru(bpy)_2(1,10\text{-phenanthroline-5,6-dione}]^{2+}$ in $d_3$-Acetonitrile at 298K.

Figure 6 above details the spectra obtained for $[Ru(bpy)_2Phenanthroline)]^{2+}$ and $[Ru(bpy)_2Phendione)]^{2+}$ in $d_6$-acetone. There is a clear transformation in moving from the phenanthroline to the dione complex. There is a loss of 2 protons due to the formation of two oxygen double bonds, in the phenanthroline complex these two protons appear as a clear singlet at 8.4 ppm. This peak is clearly absent from the dione complex which is a good indication of the formation of the dione complex. There is also very little shift in the protons of the phenanthroline and the phendione when they are both attached to the Ru metal centre. This is because the effect of binding is the same in both complexes. If a comparison was made between that of the free ligand(e.g. dione) and the complex (e.g. $[Ru(bpy)_2(dione)]^{2+}$) a bigger shift is seen. For example the dione ligand here in acetone these is a shift of the $H_1$ proton (that which is closest to the N) 8.99 to 8.58 ppm. This shift is due to the effect of complexation, i.e. the electron density of the metal centre which has a shielding effect on the hydrogens of the ligand. This effect is much more clearly seen in that of the rhenium complexes, due to the lack of any other protons on the complex other than those of the ligand. A clear shift of 0.2 – 0.4 ppm up field for the ligand protons, is seen upon complication of the dione ligand with the rhenium carbonyl species. This is best explained by the spectra in Figure 10 below.



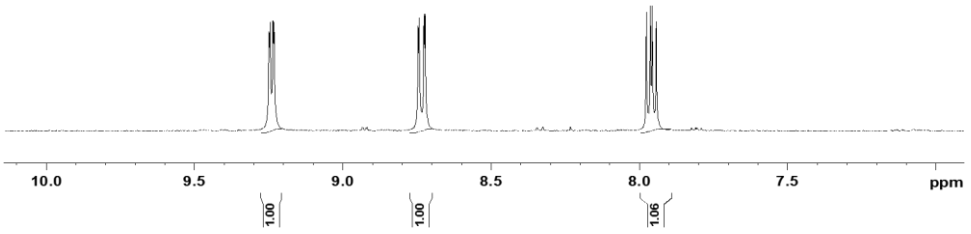



**Figure 10:** $^{1}$H NMR spectrum for 1,10-phenanthroline-5,6-dione,[Re(CO)$_3$(1,10-phenanthroline)Cl] and [Re(CO)$_3$(1,10-phenanthroline-5,6-dione)Cl] in $d_6$-Acetone at 298K.

H NMR itself is not enough in the characterization of the rhenium (I) complexes. This is because no other protons are present in the complex and the effect of the rhenium appears to be a small shift in the NMR spectra. Specific care was taking during the analysis of the NMR spectra in particular the calibration of the spectra, here the solvent peak of the $d_6$-acetone was used, even so a mistake here is easily made. So to verify the formation of the tricarbonyl species infra-red analysis was also carried out during the reactions and when the final product was obtained. This can be better described in [13].

### *$^{1}$H NMR - Dinuclear Complex*

Only one dinuclear complex has been obtained here in enough yield to carry out an NMR analysis and that is of the heterodimer of the tpphz complex. This is seen in Figure 4.8 and was carried out in $d_6$-acetone. Here the protons of the tpphz are no longer equivalent due to the presence of two different metal centres. It was also found difficult to obtain an NMR of this complex, his was not due to solubility problems but the amount obtained during the reaction. There are reports that the NMR changes during different concentrations [13]. This also makes the NMR itself hard to analyses, it would be best to carry out NMR characterization in differing concentrations and solvents. Also a dinuclear complex containing deuterated bipyridine ligands would be very beneficial [15].

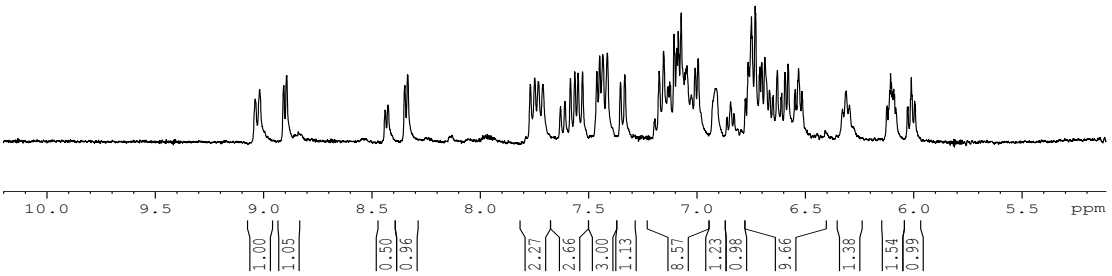



**Figure 11:** $^{1}$HNMR spectrum for$[Ru(bpy)_2(tpphz)Re(CO)_3Cl]$ in $d_6$-Acetone at 298K.

## Infra-red Analysis

The infrared spectra were obtained in solution with NaCl plates and predominantly used in a number of ways [16]. To monitor product formation, and To determine if any unreacted pentacarbonyl remained in the desired product. The infra-red spectra for the tpphz and related reactions were carried out in THF as DCM gave very broad band peaks and sometimes the splitting of the peaks was hard to determine. THF gave sharp peaks for these reactions. Table 3 below contains a summary of the results obtained while Figure 5 and 6 shows typical I.R. spectra obtained for complexes of this type [15].

**Table 3:** Summary of I.R. wavenumbers obtained in THF.

| **Complex** | **$\nu_{(CO)}$ cm$^{-1}$** | | |
|---|---|---|---|
| $[Re(CO)_3Cl(Phenanthroline)]$ | 2020 | 1918 | 1894 |
| $[Re(CO)_3Cl(Phendione)]$ | 2023 | 1923 | 1898 |
| $[Re(CO)_3Cl(Tpphz)]$ | 2022 | 1923 | 1902 |
| $[Ru(bpy)_2tpphzRe(CO)_3Cl]^{2+}$ | 2024 | 1923 | 1900 |

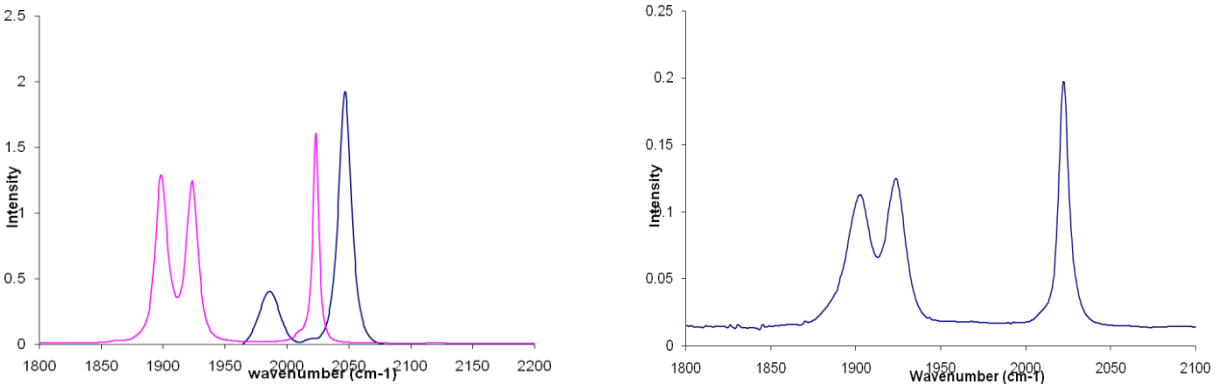



**Figure 12:** I.R. of $[Re(CO)_5Cl]$(blue), $[Re(CO)_3Cl(dione)]$(pink) (a) and $[Re(CO)_3Cl(Tpphz)]$ (b) in THF at 298K.

From the above spectra it is possible to determine that no unreacted pentacarbonyl remained in any of the complexes formed due to the absence of the pentacarbonyl peak at 2046$cm^{-1}$. the first peak in HPLC at 1.69min splits up into two, corresponding to the unreacted bpy and the intermediate species. In Figure 13 (a) the upcoming 3$^{rd}$ peak at retention time 10.44 min corresponds to $[Re(CO)_5Cl]$ H4 proton doublet and δ8.22 multiplet. At 20min for photolysis most of the intermediates get converted into complex II which is evident from HPLC and NMR table 2, as the peaks at δ values 8.41and 8.22 have disappeared on going from 15min to 20min photolysis. At 25min almost all of the bipyridine has reacted and we are left with the final two products. We continued the study up to 1.5 hours which showed that most of the metal got charred at this higher temperature resulting in a decrease of yield to 30% at 1.5hour.

We completely succeeded in eliminating quite a numerous side products in the conventional reaction of Ru-Re metal with bpy by employing a higher temperature resulting in separation of only two products at the end of the reaction clearly proved using the HPLC and NMR data given in Figures 10,11 and 13.

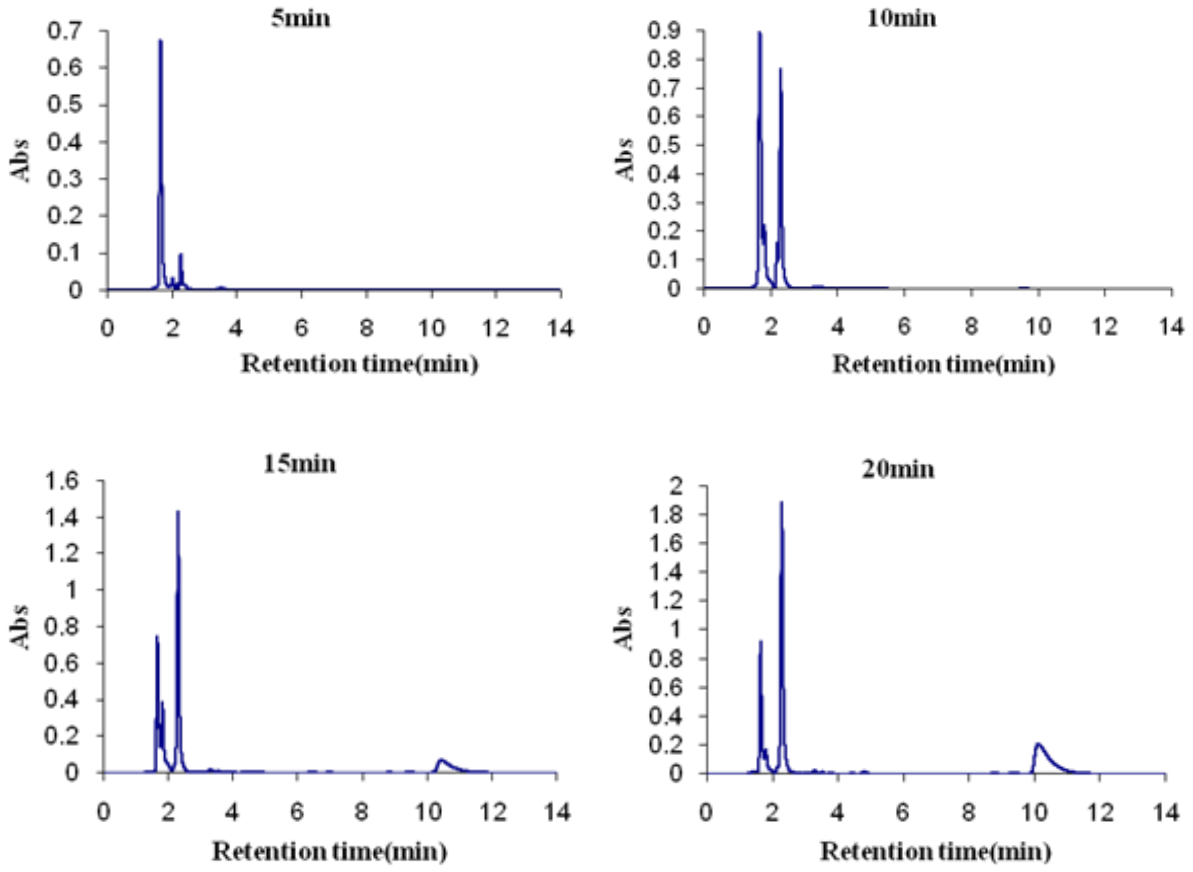



**Figure 13:** HPLC trace for [Ru-Ru](a) , [{Ru-Re](b) , [{Re-Re](c) and photolysis of [Ru-Ru](d) in $CH_3CN$ (mobile phase $CH_3CN$: $H_2O$ with volume ratio 80:20 containing 0.1 M $KNO_3$). Flow rate: 2.0 $cm^3$ $min^{-1}$; detection wavelength at 280 nm.

The stretching obtained in all of the spectra indicates that the fac isomer is obtained for all of the rhenium (I) complexes. This means that the ligands are bound in the equatorial region trans to two carbonyls with a chlorine in the axial position and a CO in final axial position. This is best described in Figure 14.

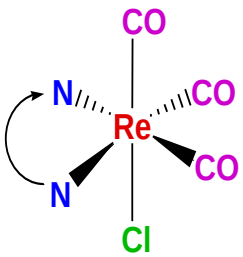



**Figure 14:** Example of coordination of the rhenium tricarbonyl complexes discussed.

Upon bonding, these CO bands move to a lower frequency compared to that of the pentacarbonyl complex. This is due to the presence of back bonding on the Re centre. As the ligand becomes bound to the rhenium metal centre electron density of the rhenium $d_\pi$ orbitals becomes increased and back bonding occurs between these and the CO $\pi^*$ orbitals. This is also an example of the σ-donor ability of the phenanthroline based ligands

## Conclusions

It is very clear that the synthetic routes available for the preparation of $[Ru(bpy)_2(tpphz)Re(CO)_3Cl]^{2+}$ are by no means trivial. Both The NMR and HPLC analysis shows the formation of the dione intermediates for both the Ru and Re complexes. Confirmation of the formation of the tricarbonyl species was carried out using I.R. and HPLC analysis which showed the formation of new peaks with the depletion of the starting material, $[Re(CO)_5Cl]$, at early retention time.

Further synthesis needs to be carried out to increase the yield of the heterodimer the most promising method is that of the reaction of the Re-tpphz monomer with a ruthenium dichloride species. A further study on concentration and NMR results for this complex will also be carried out along with further characterization including, UV-Vis, flouresence and lifetime of the excited state. Elemental analysis needs to be carried out on all of the mentioned complexes along with mass spec.

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