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## Coordination Of 2,6-Bis(8'-Quinoliny)pyridine On Rhenium(i) And Photochemistry Of Cyclopentadienyl Tricarbonyl Molybdenum Dimer With Arene Disulfides

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COORDINATION OF 2,6-BIS(8'-QUINOLINYL)PYRIDINE ON RHENIUM(I)  
AND PHOTOCHEMISTRY OF CYCLOPENTADIENYL TRICARBONYL  
MOLYBDENUM DIMER WITH ARENE DISULFIDES

by

Clayton J. Bosworth

Bachelor of Science, University of North Dakota, 2008

A Thesis

Submitted to the Graduate Faculty

of the

University of North Dakota

In partial fulfillment of the requirements

for the degree of Master of Science

Grand Forks, North Dakota

May

2012

This thesis submitted by Clayton J. Bosworth in partial fulfillment of the requirements for the Degree of Master of Science from the University of North Dakota, has been read by the Faculty Advisory Committee under whom the work has been done and is hereby approved.

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(Chairperson) Sean E. Hightower

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Harmon B. Abrahamson

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Lothar Stahl

This thesis meets the standards for appearance, conforms to the style and format requirements of the Graduate School of the University of North Dakota, and is hereby approved.

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Wayne Swisher Dean of the Graduate School

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April 18, 2012

Date

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Title: Coordination of 2,6-bis(8'-quinolinyl)pyridine on Rhenium(I) and  
Photochemistry of Cyclopentadienyl Tricarbonyl Molybdenum Dimer  
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Department: Chemistry

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## TABLE OF CONTENTS

LIST OF FIGURES .....	viii
LIST OF SCHEMES.....	ix
LIST OF TABLES.....	x
ACKNOWLEDGEMENTS.....	xi
ABSTRACT.....	xii
CHAPTER	
1. INTRODUCTION.....	1
1.1 General Photochemistry.....	1
1.2 Photochemistry of Metal Coordination Compounds.....	3
2. COORDINATION OF 2,6-BIS(8'-QUINOLINYL)PYRIDINE ON RHENIUM(I).....	5
2.1 Introduction.....	5
2.2 Results.....	8

2.2.1 Preparation of Compounds.....	8
2.2.2 Absorption and Emission Studies.....	10
2.2.3 Nuclear Magnetic Resonance Studies.....	13
2.2.4 Infrared Studies.....	15
2.2.5 Mass Spectrometric Studies.....	16
2.2.6 Crystal Structures.....	16
2.2.7 Computational Studies.....	17
2.3 Discussion.....	18
2.3.1 Absorption and Emission Studies.....	18
2.3.2 Nuclear Magnetic Resonance Studies.....	19
2.3.3 Infrared Studies.....	20
2.3.4 Mass Spectrometric Studies.....	21
2.3.5 Crystal Structures.....	22
2.3.6 Computational Studies.....	23
2.4 Experimental Section.....	28

2.4.1 Materials.....	28
2.4.2 Instrumentation.....	28
2.4.3 Synthesis of 2,6-Bis(8'-quinolinyl)pyridine.....	29
2.4.4 Synthesis of <i>fac</i> -Re(bqp- $\kappa^2N$ )(CO) <sub>3</sub> Cl.....	29
2.4.5 Synthesis of <i>fac</i> -[Re(bqp- $\kappa^2N$ )(CO) <sub>3</sub> (NCCH <sub>3</sub> )] [OSO <sub>2</sub> CF <sub>3</sub> ].....	30
2.4.6 Synthesis of <i>fac</i> -[Re(bqp- $\kappa^2N$ )(CO) <sub>3</sub> (NC <sub>5</sub> H <sub>5</sub> )] [OSO <sub>2</sub> CF <sub>3</sub> ].....	31
2.4.7 Synthesis of <i>fac</i> -[Re(bqp- $\kappa^2N$ )(CO) <sub>3</sub> (PPh <sub>3</sub> )] [OSO <sub>2</sub> CF <sub>3</sub> ]..	32
 3. PHOTOCHEMISTRY OF CYCLOPENTADIENYL TRICARBONYL MOLYBDENUM DIMER WITH ARENE DISULFIDES.....	 33
 3.1 Photochemistry of Metal-Metal Bonded Compounds.....	 33
 3.2 Results and Discussion.....	 34
3.2.1 Photoreaction of [Cp(CO) <sub>3</sub> Mo] <sub>2</sub> and ( <i>p</i> -tolylS) <sub>2</sub> .....	34
3.2.2 Photoreaction of [Cp(CO) <sub>3</sub> Mo] <sub>2</sub> and (2-pyS) <sub>2</sub> .....	35
 3.3 Experimental Section.....	 38
3.3.1 Materials.....	38
3.3.2 Instrumentation.....	38

3.3.3 Synthesis of Cp(CO) <sub>3</sub> MoS( <i>p</i> -tolyl).....	38
3.3.4 Synthesis of Cp(CO) <sub>2</sub> MoS(2-pyridyl).....	39
3.3.5 Photochemical Procedure.....	41
3.3.6 Quantitative Photochemistry.....	41

## APPENDICES

A. NMR Spectra.....	43
B. Excited States of Bisquinoliny Pyridine Rhenium(I) Complexes.....	53
C. Mulliken Population Analysis of Re(I) Complexes.....	79
D. Optimized Geometry of Re(I) Complexes.....	85
REFERENCES.....	95



## LIST OF FIGURES

Figure	Page
1. Classification of photochemical processes based on potential energy surfaces.....	2
2. Structures of (a) top left, (b) top right, (c) bottom left, and (d) bottom right.....	6
3. Excited state diagram for typical Ru(II) polypyridine complexes. Dotted lines denote photochemical reactions.....	7
4. Ball and stick Diagram of <i>fac</i> -Re(bqp- $\kappa^2$ N)(CO) <sub>3</sub> Cl ( <b>1</b> ) [left] and <i>fac</i> -[Re(bqp- $\kappa^2$ N)(CO) <sub>3</sub> (NCCH <sub>3</sub> )] <sup>+</sup> ( <b>2</b> ) [right].....	9
5. Ball and Stick Diagram of target products <i>fac</i> -[Re(bqp- $\kappa^2$ N)(CO) <sub>3</sub> (NC <sub>5</sub> H <sub>5</sub> )] <sup>+</sup> ( <b>3</b> ) [left] and <i>fac</i> -[Re(bqp- $\kappa^2$ N)(CO) <sub>3</sub> (PPh <sub>3</sub> )] <sup>+</sup> ( <b>4</b> ) [right].....	10
6. Experimental (–) and calculated spectra (– · · –) in acetonitrile.....	11
7. Room-temperature emission of ( <b>1</b> ) 8.237 × 10 <sup>–5</sup> M, ( <b>2</b> ) 1.129 × 10 <sup>–4</sup> M, ( <b>3</b> ) 6.901 × 10 <sup>–5</sup> M, and ( <b>4</b> ) 5.025 × 10 <sup>–5</sup> M in acetonitrile.....	12
8. IR spectra of the carbonyl stretch region.....	15
9. Crystal structure of <i>fac</i> -[Re(bqp- $\kappa^3$ N)(CO) <sub>3</sub> ] <sup>+</sup> .....	22
10. Schematic diagrams of frontier orbitals for <i>fac</i> -[Re(bqp- $\kappa^3$ N)(CO) <sub>3</sub> ] <sup>+</sup> .....	26

## LIST OF SCHEMES

Scheme	Page
1. Synthesis of 2,6-bis(8'-quinoliny)pyridine (bqp) ligand.....	8
2. Coordination of bqp on Re and reactivity of Re tricarbonyl.....	9
3. Attempted formation of substituted [Re(bqp- $\kappa^2N$ )(CO) <sub>3</sub> L] complexes.....	22
4. Proposed pathway for photochemical reaction of complex 5.....	26

## LIST OF TABLES

Table	Page
1. Absorption Energies (nm), Coefficients ( $M^{-1} \text{ cm}^{-1}$ ), Emissions (nm), and Intensities (a. u.) for Re Complexes.....	11
2. NMR Data with Assignment of Protons.....	14
3. Experimental and Calculated Carbonyl Stretch Frequencies ( $\text{cm}^{-1}$ ).....	16
4. Mass Spectrometric Data for Re Complexes.....	16
5. Singlet Electronic Transitions for Re(I) complexes.....	24
6. Electron Distribution in % of Selected Orbitals of Re(I) Complexes.....	25
7. Calculated Triplet Excited States of Complexes 1–5 in Acetonitrile Based on Lowest Lying Triplet State Geometry.....	27
8. IR Carbonyl Stretching Frequencies for Mo(0) Complexes.....	36
9. NMR Data of Mo(0) complexes and arene disulfides.....	37
10. Molar Extinction Coefficients.....	37

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## ABSTRACT

An ideal photosensitizer should have an excited state with high energy and sufficiently long lifetime to promote electron and/or energy transfer processes. Many *facial*-tricarbonyl Re(I)-diimine complexes have demonstrated sufficiently long lifetimes to photosensitize many reactions. However, these complexes only utilize small portions of the visible spectrum, thereby diminishing their overall effectiveness. Recent work has resulted in opening a synthetic route to the meridionally tris-chelated *mer,cis*-Re(tpy- $\kappa^3N$ )(CO)<sub>2</sub>Cl (tpy = 2,2':6,2-terpyridine) complex which absorbs light throughout the entire visible spectrum. However, as with many other metal-terpyridine complexes, the *mer,cis*-[Re(tpy- $\kappa^3N$ )(CO)<sub>2</sub>L]<sup>n+</sup> (L = NCCH<sub>3</sub>, PPh<sub>3</sub>, NC<sub>5</sub>H<sub>5</sub>, PEt<sub>3</sub>, and Cl; n = 0 or 1) failed to produce emission at room temperature.

The 2,6-bis(8'-quinoliny)pyridine (bqp) ligand has been shown to form meridionally tris-chelated complexes with Ru(II) with observed room temperature emissions on the order of 3  $\mu$ s. Results from our laboratory suggest that the *mer,cis*-Re(bqp- $\kappa^3N$ )(CO)<sub>2</sub>Cl complex is expected to absorb light throughout the entire visible spectrum at molar absorptivities greater than the

*mer,cis*-Re(tpy- $\kappa^3$ N)(CO)<sub>2</sub>Cl. This study details initial coordination studies of the 2,6-bis(8'-quinolinyl)pyridine to Re(I).

The photochemistry of the molybdenum dimer [CpMo(CO)<sub>3</sub>]<sub>2</sub> with organic disulfides were investigated. Broad-band light sources were used for synthesis of the Mo-S containing products. Products were characterized by infrared and <sup>1</sup>H-NMR techniques. Isolation of pure product allowed determination of UV-visible absorption parameters. These parameters were used to determine quantum yields under monochromatic irradiation.

## CHAPTER 1.

### INTRODUCTION

#### 1.1 General Photochemistry

Photochemical processes have been of great interest to scientists since the discovery of photosynthesis. This interest has been around as an organized subfield of chemistry for more than a century. The main concern in photochemistry is the study of electronically excited states of molecules, which provide many unique reactions. These excited states are reached by the energy provided from a photon or quantum of light. The processes induced by the excited states fall into two classes of reactions based on its course along the potential energy surface, adiabatic or diabatic.<sup>1</sup> For an adiabatic reaction, the chemical change occurs on the same continuous potential energy surface, whereas crossing potential surfaces is classified as a diabatic reaction, Figure 1. The photodissociation of small molecules in the vapor state,  $I_2 + h\nu \rightarrow I^* + I$ , and proton transfer in the excited state are two examples of adiabatic processes. For this to happen, the reactants and products need to correlate with one another and the transition state. This means the product will be in an electronic excited state

and detectable by luminescence and/or photochemical properties. However, an intermediate can interfere with the formation of the product. While this form of activation provides different states than thermal activation, the states are not without limitations.<sup>1</sup>

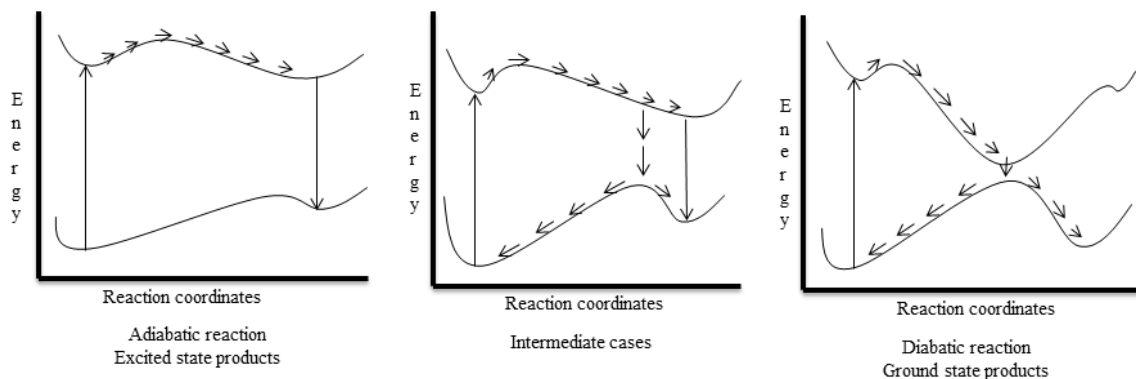


Figure 1. Classification of photochemical processes based on potential energy surfaces (ref. 1).

The first law of photochemistry states that only the light absorbed by a molecule can be effective in producing photochemical change in a molecule.

This law is based on the works of Grotthuss (1817) and Draper (1843).<sup>1b</sup>

The quantum yield is determined from the yield of photochemical product. For the general equation;  $A + h\nu \rightarrow B$ , the quantum yield is defined by

$$\Phi_B = \frac{\text{Molecules of B formed}}{\text{Quanta of light absorbed by A}}$$

The numerator is found by conventional chemical analysis. The denominator is calculated from the measured total energy of the absorbed light of wavelength  $\lambda$  and assuming that each quantum has energy equal to  $h\nu$ .<sup>1,2</sup>

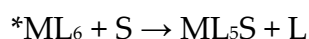


The second law of photochemistry deduced by Stark (1908-1912) and Einstein (1912-13) states the absorption of light by a molecule is a one-quantum process, so the sum of the primary process quantum yields  $\Phi$  must be unity; that is  $\sum \Phi_i = 1.00$ , where  $\Phi_i$  is the quantum yield of the *i*th primary process. These primary processes may include dissociation, phosphorescence, fluorescence, radiationless transitions, isomerization, and all other reaction paths which lead to the destruction or deactivation of the excited molecule.<sup>1b</sup>

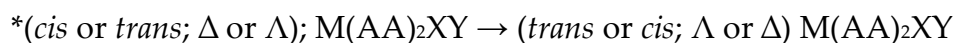
## 1.2 Photochemistry of Metal Coordination Compounds

The use of transition metal complexes in photochemistry has been studied for many years.<sup>3,4</sup> Most transition metal excited states can be easily categorized as two types:<sup>5</sup> ligand field or charge transfer. The difference in the electronic states comes from the composition of the orbitals involved in the transition. For ligand field excited states, both the starting and ending orbitals are predominately metal d-orbital in character. On the other hand, a charge transfer excited state has significant amount ligand contribution to one or the other of the orbitals. The processes generated by these states are as follows:<sup>5</sup>

(1) Substitutional (S = solvent species, L = Ligand)



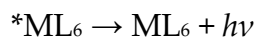
(2) Isomerization (AA = bidentate of two monodentate ligands)



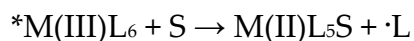
(3) Deactivation



(4) Radiative



(5) Oxidation-reduction ( $\cdot L$  = free radical)



The ligand field states can initiate processes 1–4. A charge transfer excited state can initiate any of the processes.

The main process that will be of interest for the systems in Chapter 2 is oxidation-reduction resulting from a charge-transfer excited state. The light energy absorbed by the compound excites electrons to higher energy states that enable the reduction of molecules like carbon dioxide or water; in the process the metal center is oxidized. The system in Chapter 3 uses a special ligand-field excitation process that relies on two metals.

## CHAPTER 2.

### COORDINATION OF 2,6-BIS(8'-QUINOLINYL)PYRIDINE ON RHENIUM(I)

#### 2.1 Introduction

Some transition metal diimine complexes have shown to be beneficial in electron or energy transfer processes required for photosensitizers.<sup>6-9</sup> An ideal photosensitizer should have an excited state with high energy and sufficiently long lifetime to promote these processes. There has been a lot of focus towards Ru(II) and Os(II)-diimine complexes for these desired processes.<sup>10</sup> The use of *fac*-tricarbonyl Re(I)-diimine complexes have also shown similar results that are desirable for photosensitizing reactions.<sup>10-12</sup> The drawback of these Re(I)-complexes is the limited absorption of the visible spectrum of light, which reduces their overall effectiveness. One way to improve visible absorption has led to the chelation of tridentate amine ligands.<sup>6,10</sup>

A compound that has proven capable of this is *mer,cis*-Re(tpy- $\kappa^3N$ )(CO)<sub>2</sub>Cl (tpy = 2,2':6,2'-terpyridine).<sup>10</sup> However, as with many other metal-terpyridine complexes, the *mer,cis*-[Re(tpy- $\kappa^3N$ )(CO)<sub>2</sub>L]<sup>n+</sup> (L = PPh<sub>3</sub>, NC<sub>5</sub>H<sub>5</sub>, PEt<sub>3</sub>, and Cl; n = 0 or 1) failed to produce emission at room temperature.<sup>13,14</sup> The decay at room-

temperature can be related to the energy gap law.<sup>15</sup> Some strategies used to remedy the failed emission in similar tridentate ruthenium(II) complexes include (a) electron accepting and/or donating substituents,<sup>16-18</sup> (b) ligands with extended  $\pi$ -systems,<sup>18-21</sup> (c) cyclometalating or other strong  $\sigma$ -donor ligands,<sup>18,22-24</sup> and (d) bichromophoric systems<sup>18,25</sup>, Figure 2.

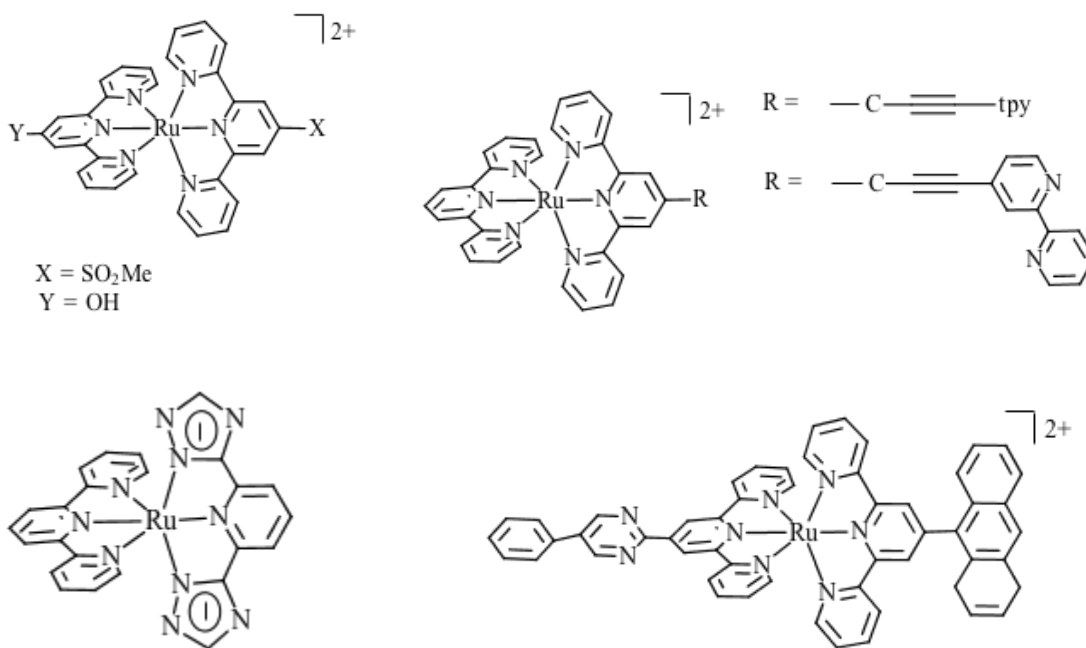


Figure 2. Structures of (a) top left,<sup>26</sup> (b) top right,<sup>28</sup> (c) bottom left,<sup>34</sup> and (d) bottom right.<sup>18</sup>

The 2,6-bis(8'-quinolinyl)pyridine (bqp) ligand has been shown to form meridionally (*mer*) tris-chelated complexes with Ru(II), with observed room temperature emissions on the order of 3  $\mu$ s.<sup>6</sup> Abrahamsson *et al.* suggested the longer lifetimes were observed due to a greater difference of energy between a

triplet metal-to-ligand charge transfer ( $^3\text{MLCT}$ ) and triplet metal-centered states ( $^3\text{MC}$ ), Figure 3. The  $^3\text{MLCT}$  state is the desired excited state, since it generates the energy or electron transfer and the  $^3\text{MC}$  state allows the deactivation of the excited state through nonradiative means or ligand substitution.

To the best knowledge of the writer, there has been no reported attempt to coordinate the relatively new ligand, 2,6-bis(8'-quinolinyl)pyridine, onto rhenium(I). This work investigates methods for coordinating bqp ligand, in addition to accessing the reactivity of  $fac\text{-}[\text{Re}(\text{bqp-}\kappa^2\text{N})(\text{CO})_3\text{L}]^{n+}$  ( $\text{L} = \text{NCCH}_3$ ,  $\text{PPh}_3$ ,  $\text{NC}_5\text{H}_5$ ,  $\text{PEt}_3$ , and  $\text{Cl}$ ;  $n = 0$  or  $1$ ) complexes.

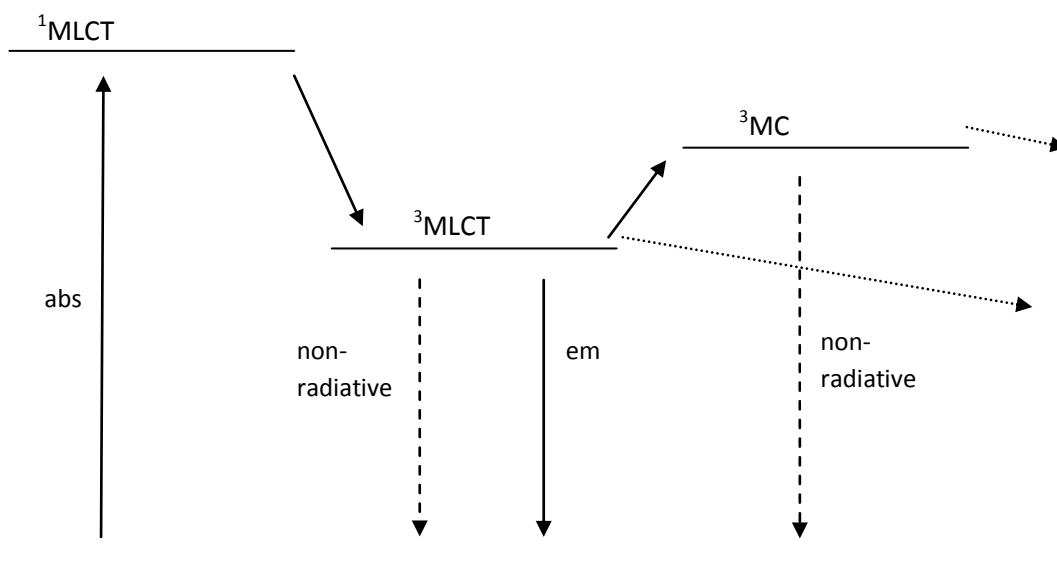


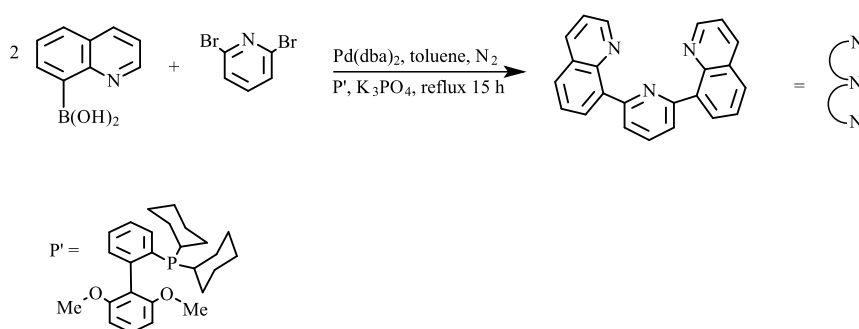
Figure 3. Excited state diagram for typical Ru(II) polypyridine complexes. Dotted lines denote photochemical reactions (refs. 7, 26).

## 2.2 Results

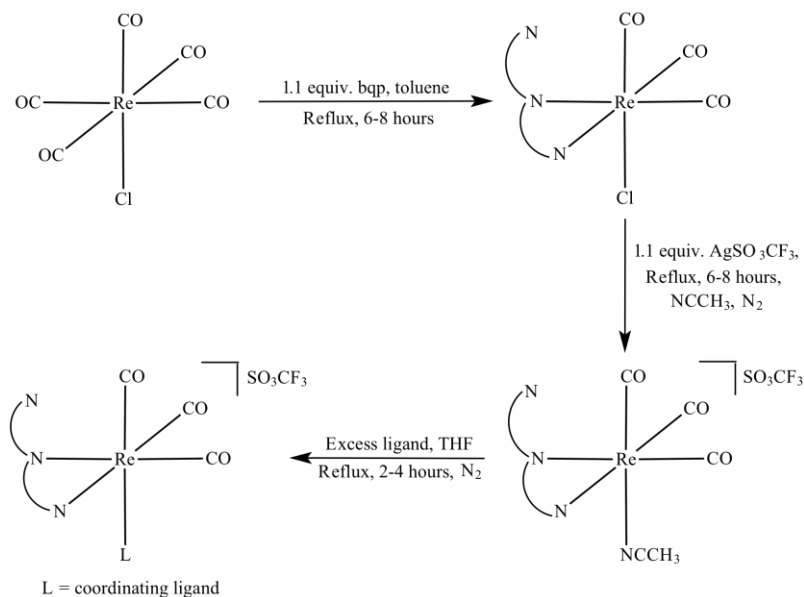
### 2.2.1 Preparation of Compounds

The synthesis of the 2,6-bis(8'-quinolinyl)pyridine (bqp) ligand followed the method reported in the literature (Scheme 1).<sup>6,7</sup> The only change made was a recrystallization of the off-white product from CH<sub>2</sub>Cl<sub>2</sub> with diethyl ether instead of purification by column chromatography. This gave comparable yields and reduced preparation time for the ligand. An outline of the rhenium tricarbonyl synthesis is given in Scheme 2. The approach was to coordinate bqp on Re(CO)<sub>5</sub>Cl by replacing CO as reported previously.<sup>10,11</sup> The removal of chloride from *fac*-Re(bqp-κ<sup>2</sup>N)(CO)<sub>3</sub>Cl (Figure 4) was effected by use of silver triflate, Ag(CF<sub>3</sub>SO<sub>3</sub>), in acetonitrile, yielding *fac*-[Re(bqp-κ<sup>2</sup>N)(CO)<sub>3</sub>(NCCH<sub>3</sub>)] [CF<sub>3</sub>SO<sub>3</sub>] (Figure 4).<sup>11</sup> The silver chloride was easily removed from by filtration.

#### Scheme 1 Synthesis of the 2,6-bis(quinolinyl)pyridine (bqp) ligand



**Scheme 2** Coordination of bqp on Re and reactivity of Re tricarbonyls



L is NC<sub>5</sub>H<sub>5</sub> or PPh<sub>3</sub>

*fac*-[Re(bqp-κ<sup>2</sup>N)(CO)<sub>3</sub>(NCCH<sub>3</sub>)] [CF<sub>3</sub>SO<sub>3</sub>] was stable and was isolated and used in subsequent reactions with coordinating ligands. The approach was to remove acetonitrile from *fac*-[Re(bqp-κ<sup>2</sup>N)(CO)<sub>3</sub>(NCCH<sub>3</sub>)] [CF<sub>3</sub>SO<sub>3</sub>] and replace it with pyridine or triphenylphosphine as previously reported (Figure 5).<sup>10,11,13</sup>

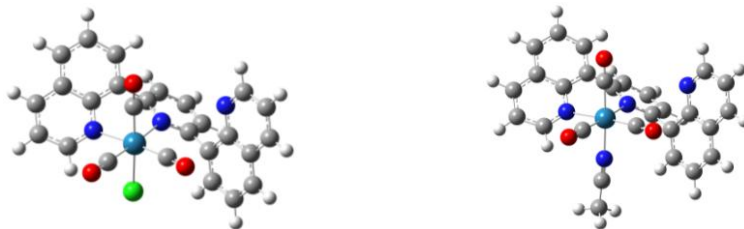


Figure 4. Ball and Stick Diagram of *fac*-Re(bqp-κ<sup>2</sup>N)(CO)<sub>3</sub>Cl (**1**) [left] and *fac*-[Re(bqp-κ<sup>2</sup>N)(CO)<sub>3</sub>(NCCH<sub>3</sub>)]<sup>+</sup> (**2**) [right].

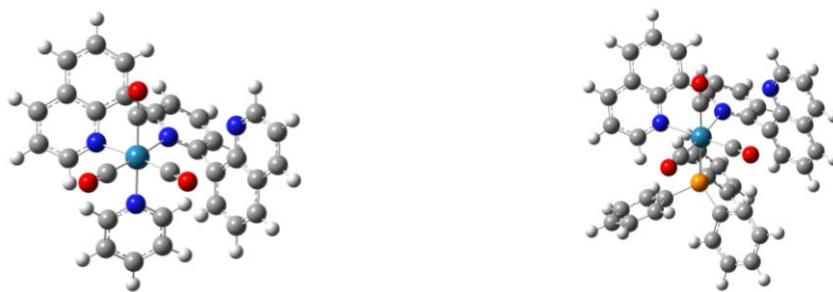


Figure 5. Ball and Stick Diagram of Target Products *fac*-[Re(bqp- $\kappa^2N$ )(CO)<sub>3</sub>(NC<sub>5</sub>H<sub>5</sub>)]<sup>+</sup> (**3**) [left] and *fac*-[Re(bqp- $\kappa^2N$ )(CO)<sub>3</sub>(PPh<sub>3</sub>)]<sup>+</sup> (**4**) [right].

### 2.2.2 Absorption and Emission Studies

Absorption spectra were examined in acetonitrile and are listed in Table 2. Electron transitions are illustrated in Figure 6. The broad, low-energy peak, with extinction coefficients on the order of  $10^2$ – $10^4$ , was assigned as  $d\pi \rightarrow \pi^*$ .<sup>27</sup> The sharp peak at higher energy was assigned as  $\pi \rightarrow \pi^*$ , with extinction coefficients on the order of  $10^5$ – $10^7$ . Extinction coefficients observed for the complexes range from 9691 to 18800  $M^{-1} \text{ cm}^{-1}$  for the  $d\pi \rightarrow \pi^*$  transition. The  $\pi \rightarrow \pi^*$  transition gave extinction coefficients of 12439 to 23310  $M^{-1} \text{ cm}^{-1}$ . Complexes **1** and **2** have a Gaussian shape for the  $d\pi \rightarrow \pi^*$  transitions due to the average absorption transitions. Whereas, complexes **3** and **4** have a shoulder growing in at lower energy on the  $d\pi \rightarrow \pi^*$  peak and are identical to one another.



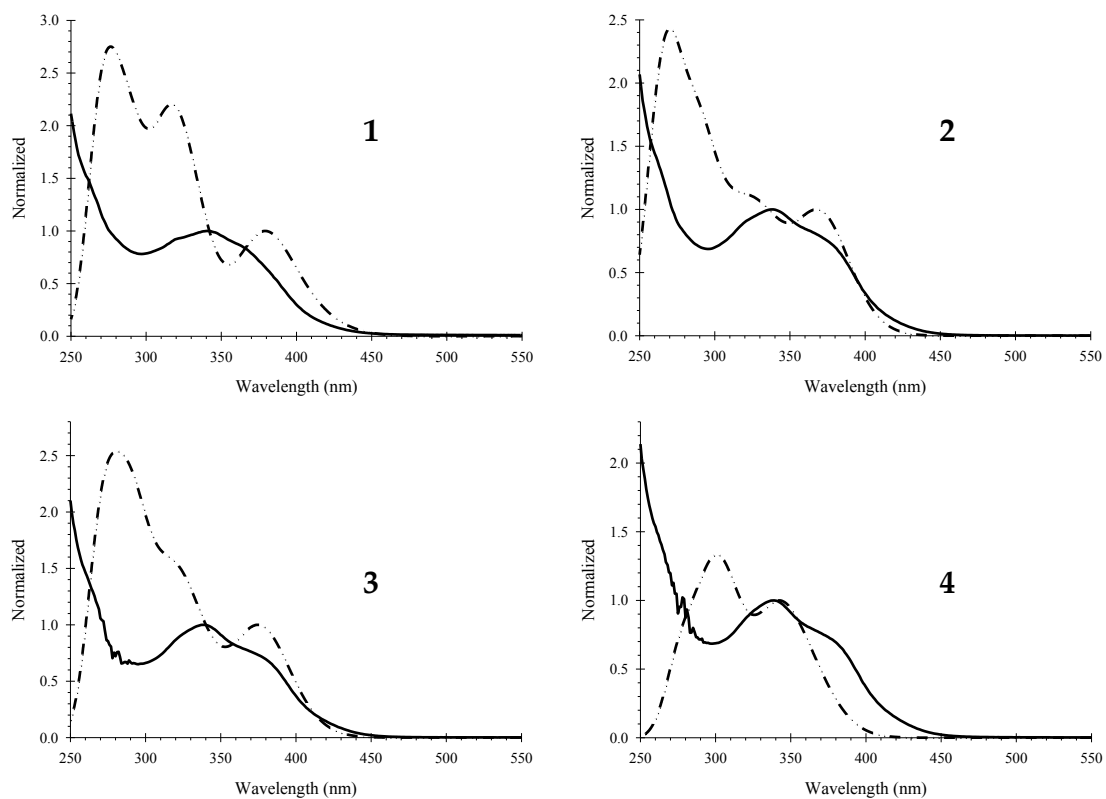


Figure 6. Experimental (—) and calculated spectra (---) in acetonitrile.

Table 1. Absorption Energies (nm), Coefficients ( $M^{-1} \text{ cm}^{-1}$ ), Emissions (nm), and Intensities (a. u.) for Re Complexes

Compound	$\lambda$	$\epsilon$	$\lambda_{\text{ex}}$	$\lambda_{\text{em}}$	I
<b>1</b>	267	17369			
	320	12439			
	338	13746			
	375	9691	370	593.97	39.733
<b>2</b>	267	18631			
	320	14048	315	597.94	27.01
	342	15608			
<b>"3"</b>	375	11612	380	597.94	30.778
	267	17978	290	303.07	13.759
	320	12872		598.97	22.43
	338	14029	338	593.97	52.099
<b>"4"</b>	375	10845	375	597.05	54.112
	267	23310	300	597.94	36.666
	320	16297			
	338	18800	338	597.94	35.225
	375	13676	375	597.94	41.333

The emission spectra were obtained at room temperature in acetonitrile. The emission maxima are presented in Table 1. All complexes showed nonstructured emissions as seen in Figure 7. The room-temperature emission spectra were initially weak in intensity; this was suspected to be due to O<sub>2</sub>-quenching of the excited state energy. Argon was bubbled through the solutions to remove oxygen and intensities were improved. Nonstructured emission was previously observed for rhenium tricarbonyl complexes and was assigned to <sup>3</sup>MLCT-based emission.<sup>38</sup>

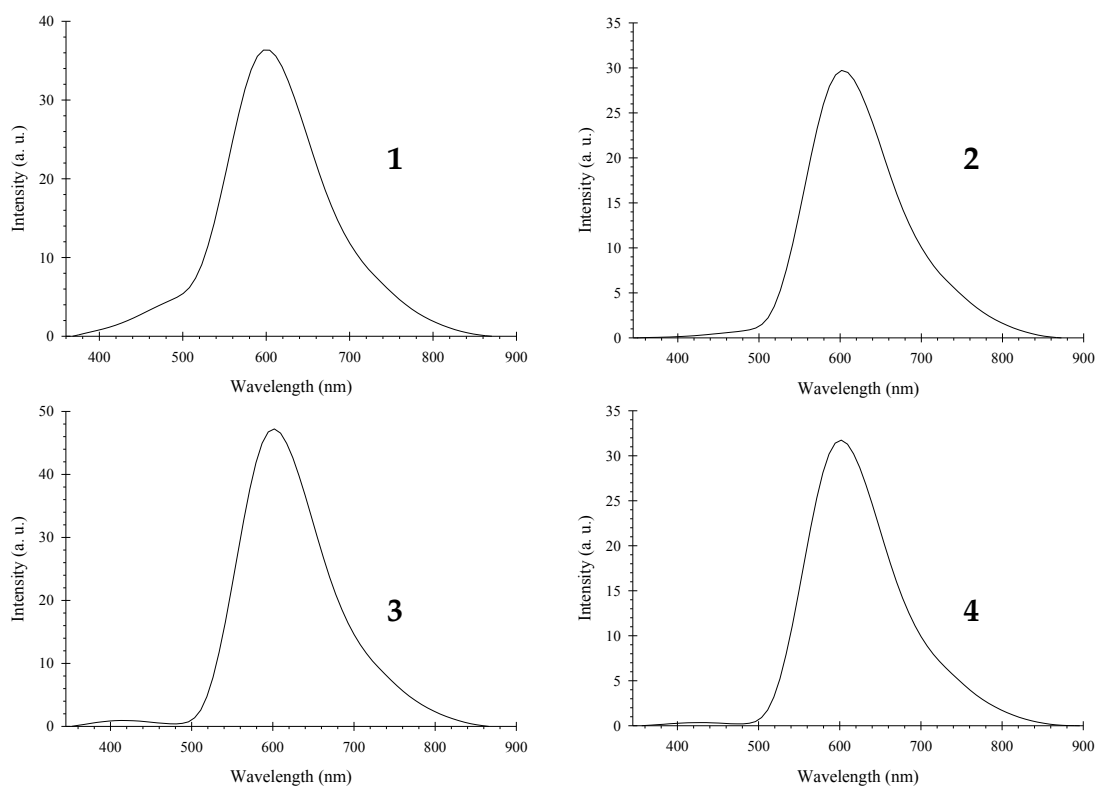


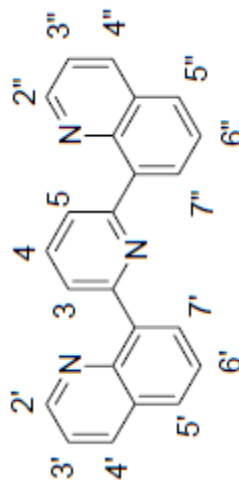
Figure 7. Room-temperature emission of (1)  $8.237 \times 10^{-5}$  M, (2)  $1.129 \times 10^{-4}$  M, (3)  $6.901 \times 10^{-5}$  M, and (4)  $5.025 \times 10^{-5}$  M in acetonitrile.

### 2.2.3 Nuclear Magnetic Resonance Studies

NMR data was collected in CD<sub>2</sub>Cl<sub>2</sub> and presented in Table 3. The spectra are shown in Appendix A. The proton resonances of the pyridine ligand (protons 3, 4, and 5) were found in between those of the quinoline ring (2', 2'', 3', 3'', 4', 4'', 5', 5'', 6', 6'', 7', and 7''). The resonance for all protons are shifted downfield for *fac*-Re(bqp-κ<sup>2</sup>N)(CO)<sub>3</sub>Cl compared with the protons from the free bqp ligand. Replacement of Cl<sup>-</sup> by NCCH<sub>3</sub> causes a further downfield shift of protons 2' and 2'' and protons 3', 3'', 4', 4'', 7', 7'' are shifted slightly upfield. The remaining aromatic proton resonances are not affected. The proton resonance of acetonitrile is shifted downfield when coordinated on rhenium. Attempted replacement of NCCH<sub>3</sub> with NC<sub>5</sub>H<sub>5</sub> or PPh<sub>3</sub> did not causes any change in proton resonance of the bqp ligand and no proton resonance of NC<sub>5</sub>H<sub>5</sub> or PPh<sub>3</sub> was present.

Table 2. NMR Data with Assignment of Protons

Complex	2', 2''	4', 4'', 7', 7''	3, 5	4, 5', 5''	6', 6''	3', 3''	ligand
bqp	8.97, dd, ( $J = 4.1, 1.9$ Hz)	8.26, m	8.12, d, ( $J = 7.8$ Hz)	7.92, m	7.68, dd, ( $J = 8.2, 7.2$ Hz)	7.48, dd, ( $J = 8.3, 4.1$ Hz)	
1	9.68, dd, ( $J = 5.0, 1.6$ Hz)	8.69, dd, ( $J = 8.2, 1.5$ Hz)	8.55, dd, ( $J = 7.2, 1.4$ Hz)	8.25, m	7.98, dd, ( $J = 8.1, 7.4$ Hz)	7.90, m	
2	9.87, dd, ( $J = 5.2, 1.6$ Hz)	8.65, dd, ( $J = 8.2, 1.6$ Hz)	8.54, dd, ( $J = 7.3, 1.4$ Hz)	8.23, m	7.97, m	7.87, d, ( $J = 8.1$ Hz)	2.54, d, ( $J = 11.3$ Hz)
"3"	9.87, dd, ( $J = 5.0, 1.6$ Hz)	8.65, dd, ( $J = 8.3, 1.5$ Hz)	8.54, dd, ( $J = 7.3, 1.4$ Hz)	8.23, m	7.97, m	7.87, d, ( $J = 8.1$ Hz)	
"4"	9.87, dd, ( $J = 5.0, 1.6$ Hz)	8.65, dd, ( $J = 8.3, 1.5$ Hz)	8.54, dd, ( $J = 7.4, 1.4$ Hz)	8.23, m	7.97, m	7.87, d, ( $J = 8.1$ Hz)	



## 2.2.4 Infrared Studies

The energy of the carbonyl stretches for the complexes are shown in Table 4 and the spectra examined in acetonitrile are shown in Figure 8. The symmetry of the carbonyls around the Re(I) center leads to distinct bands in the carbonyl region ( $\nu(\text{CO})$ , 2200-1800  $\text{cm}^{-1}$ ). The *fac*-[Re<sup>I</sup>(L- $\kappa^2$ N)(CO)<sub>3</sub>L']<sup>n+</sup> (where L = 2,2':6,2'-terpyridine, 2,2'-bipyrazine (bpz), or bipyridine (bpy), L' = NCCH<sub>3</sub>, NC<sub>5</sub>H<sub>5</sub>, Cl, or PPh<sub>3</sub>, and n = 0 or 1) complexes typically exhibit three peaks in the carbonyl region.<sup>11,12,27</sup> There were only two carbonyl peaks for all complexes examined here. This was attributed as the two asymmetric IR bands having energies too close together for separation creating a broad Gaussian-shaped peak. The bands for complex 2 shift to higher energy compared to complex 1, while vibrational peaks for complexes 3 and 4 did not change significantly from complex 2.

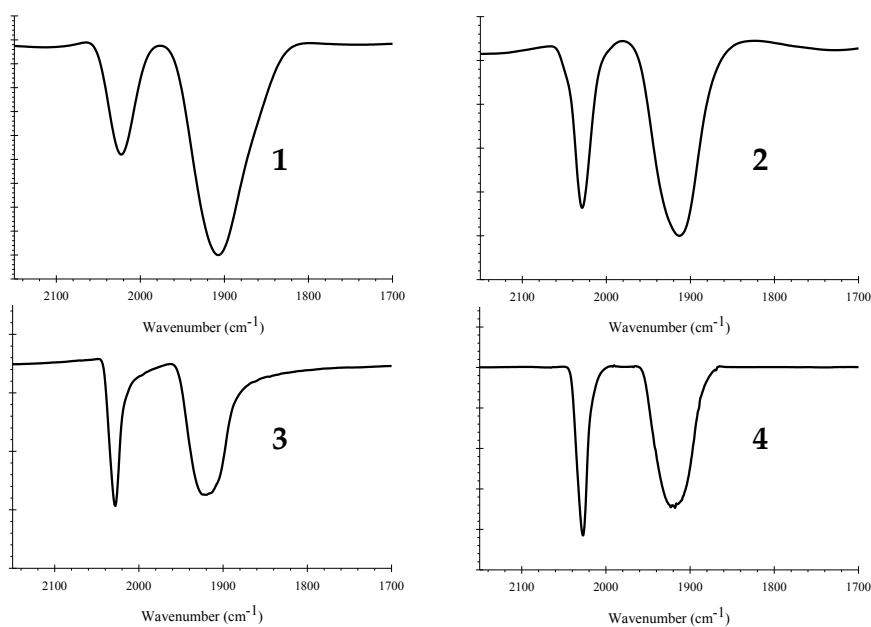


Figure 8. IR spectra of the carbonyl stretch region.

Table 3. Experimental and Calculated Carbonyl Stretch Frequencies (cm<sup>-1</sup>)

	expt'l	calc'd	tpy <sup>21</sup>	bpz <sup>22</sup>	bpy <sup>36</sup>		expt'l	calc'd <sup>a</sup>	bpy <sup>29b</sup>
<b>1</b>	2020	2087.25	2024	2049	2022	<b>3</b>	2028	2097.53	2040
	–	1976.39	1920	1939	sh		1919	1988.42	1950
	1902	1960.43	1898	1915.8	1890		–	1984.21	–
<b>2</b>	2028	2103.33	2040		2026	<b>4</b>	2028	2097.99	
	1918	2000	1941		sh		1923	1999.17	
	–	1994.76	1930		1906		1918	1979.4	

<sup>a</sup>Calculations performed on target compounds

### 2.2.5 Mass Spectrometric Studies

The parent peaks are presented in Table 4. The samples were run as 1 ppm solution in 50% methanol/H<sub>2</sub>O with 10 mM acetic acid as ionization agent and a 250 V fragmentor voltage. The calculated parent peaks were generated via the ChemDoodle computer program.<sup>29</sup>

Table 4. Mass Spectrometric Data

	calc'd	expt'l
<b>1</b>	639.0330	604.0646
<b>2</b>	645.0906	604.0645
<b>3</b>	683.1062	604.0648
<b>4</b>	866.1552	604.0645

### 2.2.6 Crystal Structures

Crystals for complex **2** were grown by slow diffusion of benzene in acetonitrile. The crystals of *fac*-[Re(bqp-κ<sup>3</sup>N)(CO)<sub>3</sub>]<sup>+</sup> were grown by slow diffusion of benzene or diethyl ether in acetonitrile and slow evaporation of CH<sub>2</sub>Cl<sub>2</sub>/CD<sub>2</sub>Cl<sub>2</sub> mixtures.

### 2.2.7 Computational Studies

The singlet ground state geometries of the complexes **1** through **5** were optimized in acetonitrile (CH<sub>3</sub>CN) using Conductor-like Polarizable Continuum Model (CPCM) – Self-Consistent Reaction Field (SCRF)<sup>30</sup> using the B3LPY<sup>31</sup> functional as implemented in the GAUSSIAN 09 program package.<sup>32</sup> The LANL2DZ ECP<sup>33-36</sup> was used for the Re effective core potential (ECP). This ECP effectively puts the all electron 6-311G\* basis set on the valence shell of Re.<sup>37</sup> Mixed basis set calculations using 3-21G\* for H atoms and 6-311G\* for all other atoms were used in order to provide molecular structure and energies of the complexes at a reduced computational cost (Appendix D). All stationary points were characterized by frequency calculations (*i.e.*, the absence of negative frequencies) performed at the same level.

Molecular orbital (MO) compositions and the overlap populations were calculated using the AOMix program<sup>38,39</sup> and the Mullikan scheme.<sup>40-43</sup> Atomic charges were calculated using the Mullikan and natural population analyses<sup>44</sup> (MPA and NPA, respectively) as implemented in GAUSSIAN 09. The analysis of the MO compositions in terms of occupied and unoccupied fragment molecular orbitals (OFOs and UFOs, respectively), construction of orbital interaction diagrams, the charge decomposition analysis (CDA), and the extended charge decomposition analysis (ECDA) were performed using AOMix-CDA.<sup>39,45</sup>

Non-equilibrium TDDFT<sup>46</sup>/CPCM-SCRF calculations were employed to produce a number of singlet excited-states for complexes **1** through **4** and the product *fac*-[Re(bqp- $\kappa^3$ N)(CO)<sub>3</sub>]<sup>+</sup> in CH<sub>3</sub>CN based on the singlet ground-state geometry (Appendix B). The output contained information for the excited state energies and oscillator strengths (*f*) and a list of the excitations that give rise to each excited-state, the orbitals involved, as well as the wave function coefficients of the excitations.

A number of triplet excited states for complexes **1** through **4** and *fac*-[Re(bqp- $\kappa^3$ N)(CO)<sub>3</sub>]<sup>+</sup> were calculated based on the triplet ground-state geometry using non-equilibrium TDDFT<sup>46</sup>/CPCM-SCRF calculations (in CH<sub>3</sub>CN).

## 2.3 Discussion

### 2.3.1 Absorption and Emission Studies

As noted in the Results section, complexes **1–4** showed an intense absorption in the UV, ~230 nm, and a broad, less intense band, 390–420 nm. Complex **2** started to extend further into the visible region, 400–800 nm. The spectra of complexes **3** and **4** were identical. The MLCT absorptions are similar to previously reported bis-chelated diimine Re(I) complexes.<sup>8,23,24</sup> However, the extinction coefficients observed for all Re(bqp- $\kappa^2$ N) complexes here are larger in magnitude than before.<sup>11,12,27,28</sup>



Emission spectra were taken at room-temperature and all complexes showed nonstructured emission with similar energy. These nonstructured emission manifolds were assigned as  $^3\text{MLCT}$  emitters.<sup>28b</sup> With all complexes having similar energies of emission, the coordinated ligand shows little effect on the  $\text{Re}^{\text{I}}(\text{bqp}-\kappa^2\text{N})$  centers.

### 2.3.2 Nuclear Magnetic Resonance Studies

The coordination of the bqp ligand on  $\text{Re}(\text{I})$  was successful, as a downfield shift is seen in the aromatic region of the NMR spectrum. For complex **1**, the electron density present on the bqp ring in the HOMO primarily resides on the 2, 3, and 4 positions on the quinoline rings. Consequently, the influence of acetonitrile coordinated on the metal causes the electron density to shift onto all positions of the quinoline rings. When comparing complex **1** with **2**, it was observed that a small upfield shift in the aromatic region and the downfield shift of coordinated acetonitrile. However, complexes **3** and **4** showed small shifts of aromatic protons when compared to complex **2** and no ligand proton peaks of pyridine, triphenylphosphine, or acetonitrile. Since the hydrogens in the aromatic region are assigned to the bqp ring and acetonitrile is not coordinated anymore, the reactions to coordinate pyridine or triphenylphosphine did not proceed as expected.

### 2.3.3 Infrared Studies

The carbonyl region, 2200–1800  $\text{cm}^{-1}$ , was the focus of IR studies for monitoring the progress of reactions, since the only vibrations present are from carbonyls, and characterizing structures. Rhenium(I) tricarbonyl complexes have exhibited three peaks in this region.<sup>47,48</sup> Group theory analysis assigned these to the  $2A_1 + B_2$  modes.<sup>49-52</sup> The calculations for all complexes show the symmetric and one asymmetric peak involve all three carbonyl groups and the second asymmetric peak involves only the two equatorial carbonyls. The lowest energy vibration is an asymmetric stretch involving all three carbonyl groups. The second lowest vibration involves two carbonyl groups and the highest vibration is the symmetric stretch involving all three carbonyl groups.

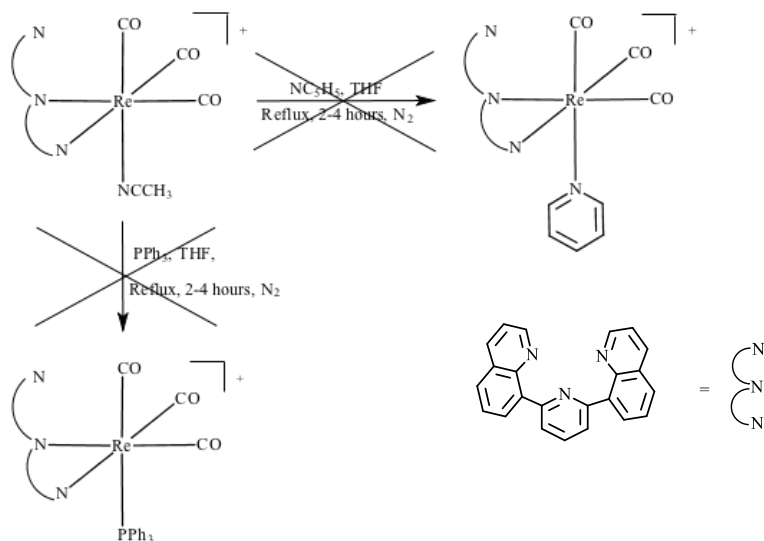
The complexes **1–4** showed only two peaks, one sharp and one broad. The broad peak was reasoned to be the result of the close proximity of the two asymmetric bands causing a broad, Gaussian-shaped peak. As seen in Table 3, complex **1** showed maxima at 2020 and 1902  $\text{cm}^{-1}$ , while complex **2** shifted to higher energy at 2028 and 1918  $\text{cm}^{-1}$ . However, complexes **3** and **4** did not change from the starting material, *fac*-[Re(bqp- $\kappa^2$ N)(CO)<sub>3</sub>(NCCH<sub>3</sub>)]<sup>+</sup>, and were within experimental error. Also shown in Table 3, the carbonyl stretches of similar bis-chelated diimine Re(I) tricarbonyl complexes are presented for

comparison.<sup>10,11,26</sup> A similar shift in vibration energy with ligand replacement of chloride with acetonitrile is seen toward higher energy. This phenomenon is attributed to weakening of the metal backbonding to the carbonyls, when the electron density is increased at the metal center.

#### 2.3.4 Mass Spectrometric Studies

All complexes showed parent peaks at 604 a.u. experimentally. From UV-Vis., IR, and NMR data, complexes **1** and **2** were synthesized successfully. Upon ionization in the MS, the complexes fragment and recombine in varying combinations. For complex **1**, the *fac*-[Re(bqp- $\kappa^3$ N)(CO)<sub>3</sub>]<sup>+</sup> fragment is produced from loss of Cl<sup>-</sup> accounts for a m/z 604 peak. Complex **2** is a charged complex; however, acetonitrile is a very labile ligand quickly giving rise to the fragment with m/z 604. Complexes **3** and **4** are charged also, but their results are inconsistent with the expected m/z for coordination of pyridine (m/z 683) and triphenylphosphine (m/z 866) on Re(I) (Scheme 3). The mass shown for the complexes **3** and **4** is presumed to be *fac*-[Re(bqp- $\kappa^3$ N)(CO)<sub>3</sub>]<sup>+</sup>.

**Scheme 3** Attempted formation of substituted  $[\text{Re}(\text{bqp}-\kappa^2\text{N})(\text{CO})_3\text{L}]$  complexes



### 2.3.5 Crystal Structures

Recently, we were able to grow x-ray quality crystals for the product of the pyridine coordination reaction. Figure 9 shows a trischelated *fac*- $[\text{Re}(\text{bqp}-\kappa^3\text{N})(\text{CO})_3]^+$  complex that may be best described as having trigonal antiprismatic (distorted octahedral) geometry.

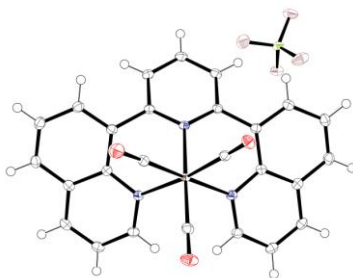


Figure 9. Crystal Structure of *fac*- $[\text{Re}(\text{bqp}-\kappa^3\text{N})(\text{CO})_3]^+$  (5).

### 2.3.6 Computational Studies

Geometry optimization and subsequent frequency calculations provide a convenient starting point in the elucidation of the experimental results. A number of singlet excited-states were computed based on the corresponding optimized singlet ground state geometries for complexes **1** through **5**. The four lowest lying excited-states are listed in Table 6 (while the remainder of the transitions are listed in Appendix B1). Mulliken populations were calculated for the singlet ground-state geometry for complexes **1** through **5** are shown in Table 7. The first four excited states were chosen based on the area of interest, which are the visible and the near-UV regions. Each of the corresponding complexes shows singlet excited-states that are essentially dominated by the frontier molecular orbital region. The HOMO, HOMO-1, and HOMO-2 for complexes **1** and **5** contained 40% or more  $\text{Re}_d$  character. For complexes **2** through **4**, the composition of these orbitals fluctuates between predominantly  $\text{Re}_d$ -based and bqp-based orbitals with notable CO-based contributions. The LUMOs for all complexes are dominated by bqp-based compositions (greater than 80% in all cases). The picture these data portrays is one that is consistent with excitations that are predominantly metal-to-ligand charge transfer (MLCT) or metal-ligand-to-ligand charge transfer (MLLCT). These results are similar to other  $\text{Re}(\text{I})$  diimine complexes<sup>23,37</sup> and a  $\text{Ru}(\text{II})$  triimine complex.<sup>7</sup>

Of particular interest is that complex **5** shows a sizable contribution of CO in the HOMO orbital which is the major contributor to the first excitation (Figure 10). This suggests that removal of electron density from the Re-CO bond could potentially be effected by excitation with light; thereby, labilizing CO to substitution.<sup>53</sup> This could potentially provide a pathway to the meridionally tris-chelated dicarbonyl complex *mer,cis*-Re(bqp-κ<sup>3</sup>N)(CO)<sub>2</sub>(NCCH<sub>3</sub>)<sup>+</sup> shown in Scheme 4. These studies are currently being conducted.

Table 5. Singlet Electronic Transitions for Re(I) complexes

#	λ, nm	f	Assignment MO#→MO#
<b>Complex 1</b>			
1	409.2	0.0110	124→125 (+96%)
2	393.5	0.0102	123→125 (+71%), 122→125 (28%)
3	377.6	0.0843	122→125 (+67%), 123→125 (+25%)
4	335.6	0.0410	121→125 (+94%)
<b>Complex 2</b>			
1	372.2	0.1140	126→127 (+94%)
2	356.9	0.0085	124→127 (+61%), 125→127 (36%)
3	344.5	0.0101	123→127 (+78%), 124→127 (13%), 125→127 (8%)
4	334.8	0.0792	125→127 (+53%), 124→127 (+23%), 123→127 (+19%)
<b>Complex 3</b>			
1	379.8	0.0870	136→137 (+83%), 135→137 (+12%)
2	369.3	0.0334	135→137 (+86%), 136→137 (11%)
3	349.5	0.0072	133→137 (+83%), 134→137 (+15%)
4	337.3	0.0620	134→137 (+79%), 133→137 (15%)
<b>Complex 4</b>			
1	363.9	0.0664	184→185 (+92%)
2	347.1	0.0033	182→185 (+78%), 181→185 (+11%)
3	343.1	0.1044	183→185 (+78%), 181→185 (+11%)
4	338.1	0.0484	181→185 (+46%), 180→185 (+21%), 182→185 (+17%), 183→185 (13%)
<b>Complex 5</b>			
1	395.1	0.1678	115→116 (+93%)
2	384.2	0.0206	115→117 (+84%), 113→116 (+11%)
3	375.9	0.0066	113→116 (+88%), 114→116 (10%)
4	360.4	0.0233	115→117 (+90%)

Table 6. Electron Distribution in % of Selected Orbitals of Re(I) Complexes

Orbital	Re <sub>d</sub>	CO	bqp	L <sup>a</sup>
<b>Complex 1</b>				
121	2	3	95	< 1
122	62	26	11	< 1
123	38	20	3	36
124	42	21	4	32
125	< 1	1	98	< 1
126	< 1	1	98	< 1
<b>Complex 2</b>				
123	42	14	38	6
124	53	18	20	10
125	24	13	60	2
126	21	7	71	1
127	< 1	9	88	< 1
128	< 1	15	83	< 1
<b>Complex 3</b>				
133	64	26	9	< 1
134	32	15	52	< 1
135	61	25	9	5
136	22	8	70	< 1
137	< 1	2	96	< 1
138	< 1	4	9	84
<b>Complex 4</b>				
181	8	3	87	1
183	35	14	25	24
184	32	11	48	9
185	1	10	82	5
186	< 1	19	47	30
<b>Complex 5</b>				
113	51	24	23	NA
114	34	13	53	NA
115	47	18	34	NA
116	< 1	2	96	NA
117	1	1	97	NA

<sup>a</sup>L = Cl<sup>-</sup> (1), NCCH<sub>3</sub> (2), NC<sub>5</sub>H<sub>5</sub> (3), and PPh<sub>3</sub> (4).

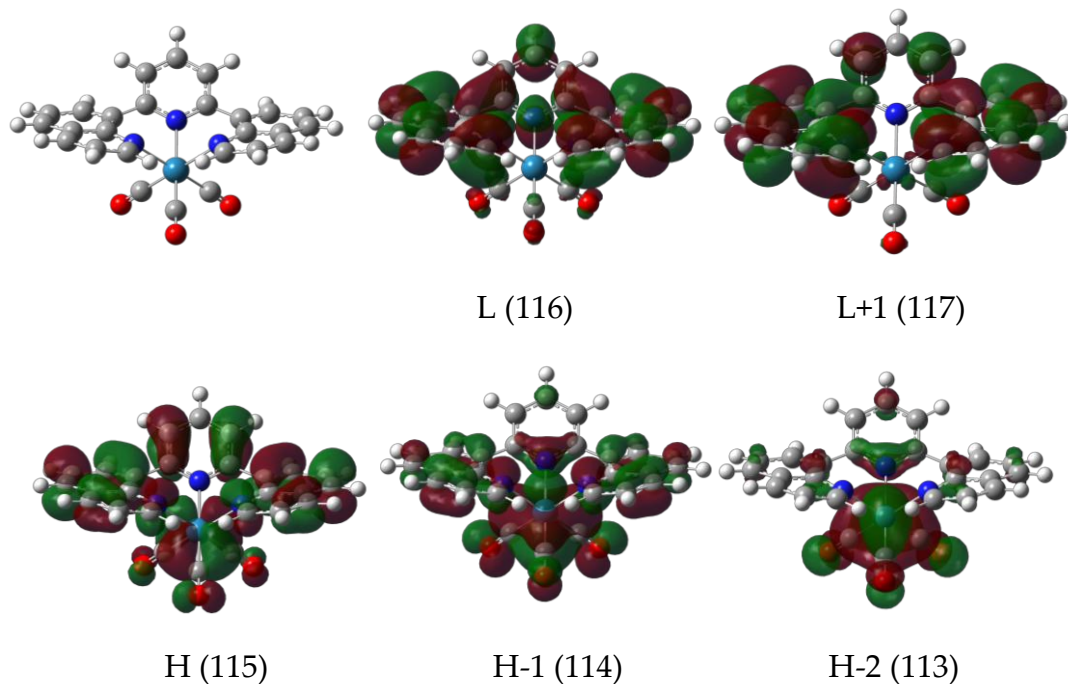
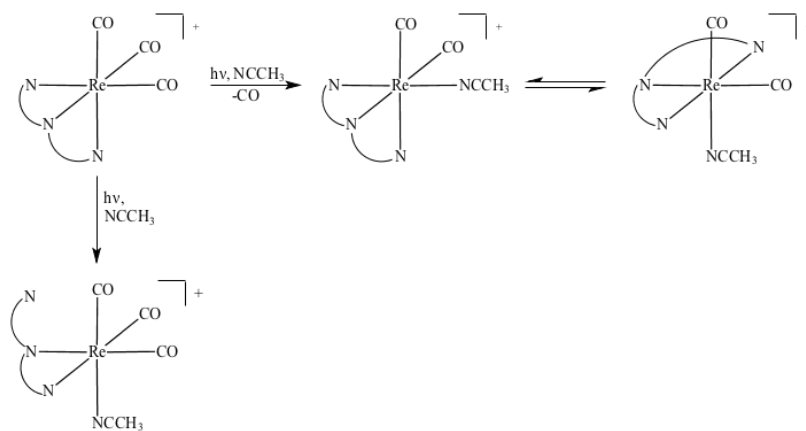


Figure 10. Schematic diagrams of frontier orbitals for *fac*-[Re(bqp- $\kappa^3$ N)(CO) $_3$ ] $^+$  (5).

**Scheme 4** Proposed pathway for photochemical reaction of complex 5



A number of triplet excited states were calculated for complexes 1–5 as well. The four low-lying triplet states are presented in Table 8 (while the remainder of the transitions are listed in Appendix B) since these transitions



occur in the visible region. According to this Kasha's rule, the emitting state will be the zero vibrational level of the lowest excited state.<sup>1</sup> The transitions generated by Gaussian 09 are singlet-triplet excitations. From the nonstructured emission in Figure 7, the relaxation is from a triplet state down to the ground state. Therefore, the emission is expected to exhibit bqp character.

The spatial distributions of the frontier orbitals for the *fac*-[Re(bqp- $\kappa^3$ N)(CO)<sub>3</sub>]<sup>+</sup> complex are shown in Figure 10. As can be seen from the figure, the HOMOs have major contributions from Re<sub>d</sub> (30–50%) and bqp (20–50%). The LUMOs are dominated with bqp-based contribution (>95%).

Table 7. Calculated Triplet Excited States of Complexes 1–5 in Acetonitrile Based on Lowest Lying Triplet State Geometry

State	f	$\Phi_g \rightarrow \Phi_v$	type	$E_{ver}$
Complex 1				
1	0.00	121 → 125, 122 → 125, 123 → 125, 124 → 125	Re <sub>d</sub> , bqp, CO, Cl → bqp	497.14
2	0.00	121 → 127, 121 → 126	bqp → bqp	445.73
3	0.00	124 → 125	Re <sub>d</sub> , CO, Cl → bqp	417.28
4	0.00	123 → 125	Re <sub>d</sub> , Cl, CO → bqp	399.95
Complex 2				
1	0.00	125 → 127, 126 → 127	bqp, Re <sub>d</sub> → bqp, CO	496.03
2	0.00	126 → 128, 127 → 129	bqp → bqp	443.58
3	0.00	122 → 127, 124 → 127, 126 → 127	Re <sub>d</sub> , bqp, CO → bqp	377.52
4	0.00	124 → 127, 123 → 127	Re <sub>d</sub> , bqp, CO → bqp	363.89
Complex 3				
1	0.00	134 → 137, 136 → 137	bqp, Re <sub>d</sub> , CO → bqp	498.26
2	0.00	134 → 140, 136 → 138	bqp, Re <sub>d</sub> , CO → bqp	443.83
3	0.00	135 → 137, 136 → 137, 132 → 137	Re <sub>d</sub> , CO, bqp → bqp	388.54
4	0.00	132 → 137, 136 → 137	bqp, Re <sub>d</sub> → bqp	369.25
Complex 4				
1	0.00	183 → 185, 184 → 185	Re <sub>d</sub> , bqp, PPh <sub>3</sub> → bqp	486.73
2	0.00	184 → 186, 183 → 187	bqp, Re <sub>d</sub> → bqp, CO, PPh <sub>3</sub>	446.61
3	0.00	184 → 185, 182 → 185, 178 → 185	bqp, Re <sub>d</sub> , PPh <sub>3</sub> → bqp	375.72
4	0.00	182 → 185, 182 → 186, 183 → 185	bqp, Re <sub>d</sub> → bqp, CO	364.21
Complex 5				
1	0.00	115 → 116, 111 → 117, 114 → 117	Re <sub>d</sub> , bqp, CO → bqp	514.60
2	0.00	115 → 117, 111 → 116, 114 → 116	Re <sub>d</sub> , bqp, CO → bqp	506.16
3	0.00	114 → 116, 113 → 116	Re <sub>d</sub> , bqp, CO → bqp	396.25
4	0.00	113 → 116, 115 → 117	Re <sub>d</sub> , bqp, CO → bqp	388.09

$E_{ver}$  is the energy of the vertical transition in nm.

## 2.4 Experimental Section

### 2.4.1 Materials

$\text{Re}(\text{CO})_5\text{Cl}$  and triphenylphosphine were purchased from Strem Chemicals Inc. Nitrogen was purchased from AirGas Inc. The 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl was purchased from Sigma-Aldrich. The 2,6-dibromo-pyridine and pyridine were purchased from Alfa Aesar. The bis(dibenzylideneacetone)palladium,  $\text{Pd}(\text{dba})_2$ , was purchased from Tokyo Chemical Industry Co., LTD. The 8-quinoline boronic acid was purchased from Frontier Scientific. Dried solvents (THF and toluene) were distilled over sodium/benzophenone and acetonitrile was distilled over calcium hydride.<sup>54</sup> The other solvents (dichloromethane, 1,2-dichlorobenzene, diethyl ether, and pentane) were used as received from the distributor.

### 2.4.2 Instrumentation

A PerkinElmer Spectrum 400 FT-IR/FT-FIR spectrometer was used for IR spectra taken in NaCl IR cell. A Bruker AVANCE 500 MHz NMR spectrometer was used to record NMR spectra. Absorption measurements were performed in a Varian Cary 50 Bio UV-Visible Spectrophotometer. Emission was analyzed with a Varian Cary Eclipse Fluorescence Spectrophotometer. Mass spectroscopy was performed on an Electrospray Ionization (ESI) with an Agilent Time-of-

Flight MS G1969A Series 6200 in positive ionization mode using 1 ppm of the complexes in a 50% methanol/water (LC/MS) with 10  $\mu$ M of acetic acid (ionization agent).

#### 2.4.3 Synthesis of 2,6-Bis(8'-Quinoliny)Pyridine

An oven-dried flask was charged with 8-quinolineboronic acid (0.413 g, 2.39 mmol), 2,6-dibromo-pyridine (0.265 g, 1.12 mmol), Pd(dba)<sub>2</sub> (0.013 g, 0.023 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (0.019 g, 0.046 mmol) and ground K<sub>3</sub>PO<sub>4</sub> (2.27 g, 10.7 mmol). The flask was evacuated and charged with N<sub>2</sub>. Dry toluene (10 mL) was added via a syringe and the resulting suspension was stirred at 100°C for 15 hours. The mixture was allowed to cool to room temperature, diluted with CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and filtered. The solvent was removed and dissolved in a minimum of CH<sub>2</sub>Cl<sub>2</sub> (3 mL); the resulting solution was clear yellow. Cold hexane was added to the solution while slowly stirring, until an off-white precipitate started to appear. The mixture was placed in the freezer overnight and the solid collected via filtration. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  8.97 (dd, 2H,  $J$  = 4.1, 1.9 Hz), 8.26 (m, 4H), 8.12 (d, 2H,  $J$  = 7.8 Hz), 7.92 (m, 3H), 7.68 (dd, 2H,  $J$  = 8.2, 7.2 Hz), 7.48 (dd, 2H,  $J$  = 8.3, 4.1 Hz).

#### 2.4.4 Synthesis of *fac*-Re(*bqp*- $\kappa^2$ N)(CO)<sub>3</sub>Cl (**1**)

A 300 mL round bottom flask, was charged with Re(CO)<sub>5</sub>Cl (0.1068 g,

0.295 mmol) and 2,6-bis(8'-quinolinyl)-pyridine (0.1146 g, 0.344 mmol); both are white powders. The flask was sealed with a rubber septum. Toluene (100 mL) was added via syringe and the powders dissolved. A condenser was attached and mixture brought to a reflux for 6 hours. The clear mixture turned slightly yellow as reaction progressed. The solution was allowed to cool and approximately half of the solvent removed under reduced pressure. The resulting yellow solid was filtered via Büchner funnel and put in a vial and placed under vacuum for further drying. The filtrate was collected and stored in the freezer overnight. The solvent was removed from the yellow solution via reduced vacuum filtration. The yellow residue was reprecipitated from CH<sub>2</sub>Cl<sub>2</sub> using pentane. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 9.68 (dd, 2H, *J* = 5.0, 1.6 Hz), 8.69 (dd, 4H, *J* = 8.2, 1.5 Hz), 8.55 (dd, 2H, *J* = 7.2, 1.4 Hz), 8.25 (m, 3H), 7.98 (dd, 2H, *J* = 8.1, 7.4 Hz), 7.90 (m, 2H). IR (CH<sub>3</sub>CN): ν (CO) = 1902, and 2020 cm<sup>-1</sup>. TOF-MS: *m/z* 604.0647.

#### 2.4.5 Synthesis of *fac*-[Re(*bqp*-κ<sup>2</sup>N)(CO)<sub>3</sub>(NCCH<sub>3</sub>)] [CF<sub>3</sub>SO<sub>3</sub>] (2)

A 100 mL round bottom flask was charged with *fac*-Re(*bqp*-κ<sup>2</sup>N)(CO)<sub>3</sub>Cl (0.1974 g; 0.309 mmol), AgSO<sub>3</sub>CF<sub>3</sub> (0.0821 g; 0.319 mmol), and a stir bar. The system was purged with N<sub>2</sub> and HPLC grade acetonitrile (50 mL) was added. A water condenser was fitted and water started. While stirring, the mixture was

brought to reflux. After 6 hours, the solution was allowed to cool to room temperature. The solution was then decanted into a celite column (3 cm x 2.5 cm) leaving much of the white AgCl behind. The flask and column were both rinsed with acetonitrile twice. The solvent was then reduced to a minimal volume for the yellow filtrate. By reprecipitating with cold diethyl ether, a yellow solid was produced and filtered.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  9.87 (dd, 2H,  $J = 5.2, 1.6$  Hz), 8.65 (dd, 4H,  $J = 8.2, 1.6$  Hz), 8.54 (dd, 2H,  $J = 7.3, 1.4$  Hz), 8.23 (m, 3H), 7.97 (m, 2H), 7.87 (d, 2H,  $J = 8.1$  Hz), 2.54 (d, 2H,  $J = 11.3$  Hz), 2.47 (m, 1H). IR ( $\text{CH}_3\text{CN}$ ):  $\nu$  (CO) = 1918, and 2028  $\text{cm}^{-1}$ . TOF-MS:  $m/z$  604.0647.

#### 2.4.6 Synthesis of *fac*-[Re(*bqp*- $\kappa^2\text{N}$ )(CO) $_3$ (NC $_5$ H $_5$ )] [CF $_3$ SO $_3$ ] (3)

A 100 mL round bottom flask was charged with *fac*-[Re(*bqp*- $\kappa^2\text{N}$ )(CO) $_3$ (NCCH $_3$ )] [CF $_3$ SO $_3$ ] (0.072 g; 0.0907 mmol), pyridine (0.21 mL, 2.596 mmol), and a stir bar. The materials were dissolved in dry THF (50 mL) and the flask was capped with a water condenser. The system was purged with N $_2$  for 10 minutes. The yellow solution was refluxed for four hours. After cooling to room temperature, a yellow precipitate was observed in the flask. The solid was filtered and stored in a vacuum desiccator overnight; the filtrate was left in the fume hood. The filtrate was concentrated via reduced vacuum and a yellow solid was precipitated by adding cold pentane. The yellow solid was filtered and

stored in a vacuum desiccator overnight.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  9.87 (dd, 2H,  $J = 5.2, 1.6$  Hz), 8.65 (dd, 4H,  $J = 8.2, 1.6$  Hz), 8.54 (dd, 2H,  $J = 7.3, 1.4$  Hz), 8.23 (m, 3H), 7.97 (m, 2H), 7.87 (d, 2H,  $J = 8.1$  Hz). IR ( $\text{CH}_3\text{CN}$ ):  $\nu$  (CO) = 1919 and 2028  $\text{cm}^{-1}$ . TOF-MS:  $m/z$  604.0647.

#### 2.4.7 Synthesis of *fac*-[Re(*bqp*- $\kappa^2\text{N}$ )(CO) $_3$ (PPh $_3$ )] [CF $_3$ SO $_3$ ] (4)

A 100 mL round bottom flask was charged with *fac*-[Re(*bqp*- $\kappa^2\text{N}$ )(CO) $_3$ (NCCH $_3$ )] [CF $_3$ SO $_3$ ] (0.0790 g; 0.0995 mmol), triphenyl phosphine (0.8012 g, 3.055 mmol), and a stir bar. The materials were dissolved in dry THF (50 mL) and the flask was capped with a water condenser. The system was purged with N $_2$  for 10 minutes. The yellow solution was refluxed for four hours. After cooling to room temperature, a yellow precipitate was observed in the flask. The solid was filtered and stored in a vacuum desiccator overnight; the filtrate was left in the fume hood. The filtrate was concentrated via reduced vacuum and a yellow solid was precipitated by adding cold pentane. The yellow solid was filtered and stored in a vacuum desiccator overnight.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  9.87 (dd, 2H,  $J = 5.2, 1.6$  Hz), 8.65 (dd, 4H,  $J = 8.2, 1.6$  Hz), 8.54 (dd, 2H,  $J = 7.3, 1.4$  Hz), 8.23 (m, 3H), 7.97 (m, 2H), 7.87 (d, 2H,  $J = 8.1$  Hz). IR ( $\text{CH}_3\text{CN}$ ):  $\nu$  (CO) = 1918, 1923, and 2028  $\text{cm}^{-1}$ . TOF-MS:  $m/z$  604.0647.

## CHAPTER 3.

### PHOTOCHEMISTRY OF CYCLOPENTADIENYL TRICARBONYL MOLYBDENUM WITH ARENE DISULFIDES

#### 3.1 Photochemistry of Metal-Metal Bonded Compounds

The main result of photoexcitation of metal-metal bonded complexes is homolysis<sup>55</sup> of the M-M bond. However, this does not detract from other possible pathways. These include one-electron oxidation,<sup>56</sup> halogen abstraction,<sup>4</sup> radical coupling,<sup>4,57,58</sup> radical trapping,<sup>4b</sup> and ligand substitution.<sup>59</sup>

The photochemistry of Group VI dimers,  $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]_2$  (M = Cr, Mo, W) has been heavily studied.<sup>3,60-63</sup> Metal dimers of tungsten and molybdenum have shown mechanisms of CO-loss and homolytic dimer cleavage intermediates through flash photolysis.<sup>62</sup>

The tungsten dimer,  $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3]_2$ , has been investigated as a possible catalyst for desulfurization of fuel stocks. Its photoreaction with disulfides has also been investigated.<sup>63-65</sup> However, the research of the molybdenum analog is not as well pioneered. Davidson and Sharp<sup>3</sup> investigated metal trifluoromethylthio-derivatives of many transition metals. They showed that reactions were possible with photolysis of the disulfides and low oxidation

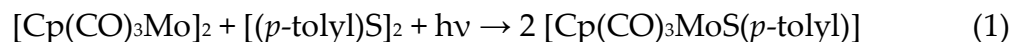
state metal complexes of the nature,  $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]_2$  (M = Mo, W) and  $\text{M}(\text{CO})_5$  (M = Fe).

### 3.2 Results and Discussion

This is a study of the photoreaction of the molybdenum dimer,  $[\text{Cp}(\text{CO})_3\text{Mo}]_2$ , with a variety of arene disulfides. It is an extension of the work done by Daniel Weinmann for his dissertation<sup>64</sup>, where he studied the photoreaction of the analogous  $[\text{Cp}(\text{CO})_3\text{W}]_2$  with disulfides and thiols. Watkins and George<sup>60</sup> also have prepared some of the projected products of my work by thermal routes and IR and <sup>1</sup>H-NMR spectroscopic values were compared with their results.

#### 3.2.1 Photoreaction of $[\text{Cp}(\text{CO})_3\text{Mo}]_2$ and $(p\text{-tolylS})_2$

My project began with the reaction as follows:



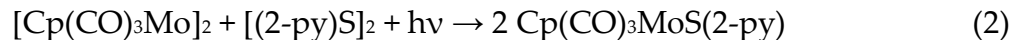
Not all starting metal dimer was consumed with extended 60W visible light irradiation of 40 hours. Therefore, a column separation was needed in order to isolate the product. An initial adsorption column of alumina in a disposable pipet showed good separation, but a larger column size provided less separation. The target product of  $\text{Cp}(\text{CO})_3\text{MoS}(p\text{-tolyl})$ , was identified by IR and <sup>1</sup>H-NMR spectroscopies. Initial comparison of NMR data with those of Watkins and George showed similar peaks at 5.26 ppm for the cyclopentadienyl ligand



and 7.88 ppm for the tolyl ligand.<sup>60</sup> As seen in Appendix A, the proton NMR shows two singlet peaks (4.78 and 5.05 ppm). The first peak is presumably generated by the cyclopentadienyl rings of the target product, Cp(CO)<sub>3</sub>MoS(*p*-tolyl). The singlet at 5.05 ppm is presumed to be caused by the Cp ring of an easily formed dimer, [Cp(CO)<sub>3</sub>MoS(*p*-tolyl)]<sub>2</sub>. Weinmann and Abrahamson<sup>66</sup> saw a similar result from a tungsten analog.

### 3.2.2 Photoreaction of [Cp(CO)<sub>3</sub>Mo]<sub>2</sub> and (2-*py*S)<sub>2</sub>

Due to poor column separation of the tolyl compound above, the disulfide was altered to study its reactivity. The choice was for 2,2'-dipyridyl disulfide for replacement in the reaction, as shown in equation 2.



Irradiation of the reaction mixture was done with a 60 W desk lamp or broadband UV light. The desk lamp took an extended period of irradiation (29 hours) to achieve appreciable conversion, but the UV light was found to convert 90% of the metal dimer, as monitored by its IR band at 2011 cm<sup>-1</sup>, in 3–4 hours of irradiation. The reaction was monitored with IR spectroscopy for peaks as shown in Table 8. After reaction, the mixture was evaporated via dynamic vacuum.

Table 8. IR Stretching for Mo(0) Complexes

Compound	IR Stretch (cm <sup>-1</sup> )
[CpMo(CO) <sub>3</sub> ] <sub>2</sub>	2015; 1956; 1912
CpMo(CO) <sub>3</sub> Spy	2037; 1960; 1873

The mixture was dissolved in 75:25 hexane/toluene solvent and introduced onto an alumina adsorption column. The molybdenum dimer was eluted off as a purple band along with unreacted disulfide. The product was eluted with toluene as an orange band and classified with <sup>1</sup>H-NMR techniques, as shown in Table 9.

While the tricarbonyl Cp(CO)<sub>3</sub>MoS(2-py) was the expected product complex based on the analogous tungsten chemistry,<sup>63</sup> it was suggested by IR frequencies in the carbonyl range that the dicarbonyl compound was readily formed with carbonyl loss. The dicarbonyl complex was then considered since its stability seemed adequate with the nitrogen of the pyridyl ligand presumably taking up the available coordination site formed on loss of CO, as in the analogous tungsten case.<sup>63</sup> The UV-vis spectroscopy was used to monitor the quantitative photochemistry and the wavelengths of interest are presented in Table 10. The quantum yield of appearance was 1.95, averaged from five trials.

Table 9. NMR Data of Mo(0) complexes and disulfides

	Proton		Cp
	Aromatic		
(Spy) <sub>2</sub>	8.16, m	7.37, dd, (J = 8.2, 1.0 Hz)	6.77, td, (J = 7.8, 1.9 Hz)
(CpMo(CO) <sub>3</sub> ) <sub>2</sub>			6.34, ddd, (J = 7.4, 4.7, 1.0 Hz)
CpMo(CO) <sub>2</sub> Spy	7.39, dt, (J = 5.6, 1.3 Hz)	6.50, ddd, (J = 8.7, 7.4, 1.6 Hz)	6.27, dt, (J = 8.4, 1.1 Hz)
CpMo(CO) <sub>3</sub> Stolyl			5.98, ddd, (J = 7.0, 5.7, 1.2 Hz)
			4.68, s
			4.78, s

Table 10. Molar extinction coefficients ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)

Wavelength (nm)	366	390 <sup>a</sup>	417 <sup>b</sup>	512 <sup>a</sup>	546
[CpMo(CO) <sub>3</sub> ] <sub>2</sub>	6513	20213	5373	1965	1597
[CpMo(CO) <sub>2</sub> S(py)]	2235	3216	4019	485	307

<sup>a</sup>Peaks made by metal dimer. <sup>b</sup> Peak made by product.

### 3.3 Experimental Section

#### 3.3.1 Materials

All materials were used as received unless otherwise stated.

Molybdenum dimer was purchased from Sigma Aldrich Co. Pre-purified nitrogen was purchased from AirGas Co. and passed through oxygen scrubbing and drying columns before entering the system. All NMR spectra were taken in  $C_6D_6$  purchased from Sigma Aldrich Co.

#### 3.3.2 Instrumentation

A PerkinElmer Spectrum 400 FT-IR/FT-FIR spectrometer was used for IR spectra taken in an NaCl IR cell sealed with serum caps. An ordinary 60-watt desk lamp was used for visible light irradiation. A Bruker AVANCE 500 MHz NMR spectrometer was used to record NMR spectra. Extinction coefficient measurements were performed using a Shimadzu UV-2501PC UV-Vis Recording Spectrometer in a quartz "H cell" cuvette for inert atmosphere.

#### 3.3.3 Synthesis of $Cp(CO)_3MoS(p\text{-tolyl})$

A nitrogen-purged THF solution of 0.300 g of  $[Cp(CO)_3Mo]_2$  and 0.308 g  $[(p\text{-tolyl})S]_2$  was made in a two neck 50 mL round bottom flask with a gas inlet. The resulting purple mixture was irradiated with visible light from a 60 W desk lamp for one hour and an IR spectrum was taken. Only starting material was seen, so the irradiation was continued for 20 hours. A slight orange color was

present with some orange residue. The mixture was irradiated for an additional 20 hours but no further change was apparent by IR spectroscopy.

A column separation was attempted with a pipet filled with alumina adsorption powder. A 1–2 mL portion of the reaction mixture was introduced to the column and starting material was separated with toluene elution. It was visible as a purple band, with an orange band eluting slowly behind. The orange band was then eluted with THF. The resulting solution was a transparent yellow/orange color. Proton NMR spectra showed not enough material present for characterization. In an attempt to enlarge the separation column, the elution was not as clean due to the introduction technique used.

A second attempt at the irradiation produced the same results up to the elution. Therefore, the purple solution was removed from the orange powder via cannula. The orange powder was dissolved in  $C_6D_6$  and  $^1H$ -NMR spectra were taken. A second attempt with a more concentrated sample was done.

#### *3.3.4 Synthesis of $[Cp(CO)_2MoS(2\text{-pyridyl})]$*

Metal dimer,  $[Cp(CO)_3Mo]_2$ , weighing 0.330 g (0.673 mmole) was degassed and back filled with  $N_2$  with 0.148 g (0.672 mmole) of dipyridyl disulfide in a 50 mL round bottom flask fitted with an air-free adaptor and a magnetic stirrer. The solids were allowed to dissolve in 30 mL of dried, oxygen-free THF giving a maroon colored solution; a small aliquot was removed to get a baseline IR

spectra. A 60 W desk lamp was placed 20 cm away and turned on. An IR spectrum was taken periodically to follow the reaction and irradiation was stopped after 6 hours when the Mo dimer peak at  $2011\text{ cm}^{-1}$  was approximately 10% of the initial strength. The solution appeared to contain an orange hue. The solvent was removed via dynamic vacuum and left behind an orange powder.

An initial column of alumina adsorption was constructed using a disposable pipet. A 5 mL volume of 1:1 hexane/toluene was used to dissolve some powder and was introduced to the column. A pink/purple band of unreacted metal dimer was eluted first using 1:1 hexane/toluene. An orange band of the product slowly moved down the column and was removed with THF. The product solution was dried and IR and  $^1\text{H-NMR}$  were done to determine purity. A larger 30 cm long column, 2-cm diameter 1-m long fritted glass tube, was made with hexane packed alumina adsorption and the remaining orange product was dissolved in 1:1 hexane/toluene in two 10–15 mL portions. A small pink band of metal dimer was removed first and the orange band of the product was removed with toluene. Proton NMR showed some disulfide still present, so a second column was constructed. A new solvent mixture, 75:25 hexane/toluene, was used to dissolve and elute starting material and slow down the progression of the product band. Trace amounts of disulfide were still present in an NMR spectrum. Therefore, the dried orange powder was washed

with hexane. The hexane was removed via syringe and an NMR was taken of the powder left behind and removed. This shown a majority of disulfide was removed with some product.  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.39 (dt, 1H,  $J = 5.6, 1.3$  Hz), 6.50 (ddd, 1H,  $J = 8.7, 7.4$  Hz), 6.27 (dt, 1H,  $J = 8.4, 1.1$  Hz), 5.98 (ddd, 1H,  $J = 7.0, 5.7, 1.2$  Hz), 4.84 (s, 5H).

### 3.3.5 Photochemical Procedure

The irradiation source was green light with a wavelength of 546 nm produced by a medium pressure mercury arc lamp and band-pass filter. The reactions were monitored by UV-Vis spectroscopy. Quantum yields were measured in 4 mL solution of the reactants in a 1 cm cell length cuvette with an attached tube and were degassed by three freeze-pump-thaw cycles. The intensity of the light was measured by ferrioxalate actinometry using Weinmann's adaptation<sup>64</sup> of procedures of Hatchard and Parker.<sup>67</sup>

### 3.3.6 Quantitative Photochemistry

A solution of 0.0102 g of Mo dimer and 0.0044 g of  $[\text{S}(\text{py})]_2$  was mixed with 60 mL of dried toluene and stored in the dark. A 1.5 mL aliquot of the solution was transferred into an H-tube custom glassware and diluted with 5 mL of dried toluene. The mixture was freeze-degassed-thawed three times and irradiated with light. The first trials were irradiated with UV light for 15–30 minutes but the time scale was shorted to 5–10 minutes due to complete

conversion with the longer times. Since the initial product is the tricarbonyl, we wanted to see how long it took for the dicarbonyl to form. Therefore, trials were irradiated and measurements were taken, and the solution was allowed to rest in the dark with periodic monitoring by UV-vis spectroscopy. The transformation seemed to take place with a 24 hour resting after irradiation.

The irradiation wavelengths of 366 and 546 nm were monitored and the longer wavelength was chosen since the light source was available for immediate use. The absorption readings were then administered to a calculation for quantum yields designed by Weinmann.<sup>64</sup> The first calculation attempt suffered from inaccuracies due to high absorption at 390 nm, prompting a second attempt with a lowered concentration.



Appendix A

NMR spectra

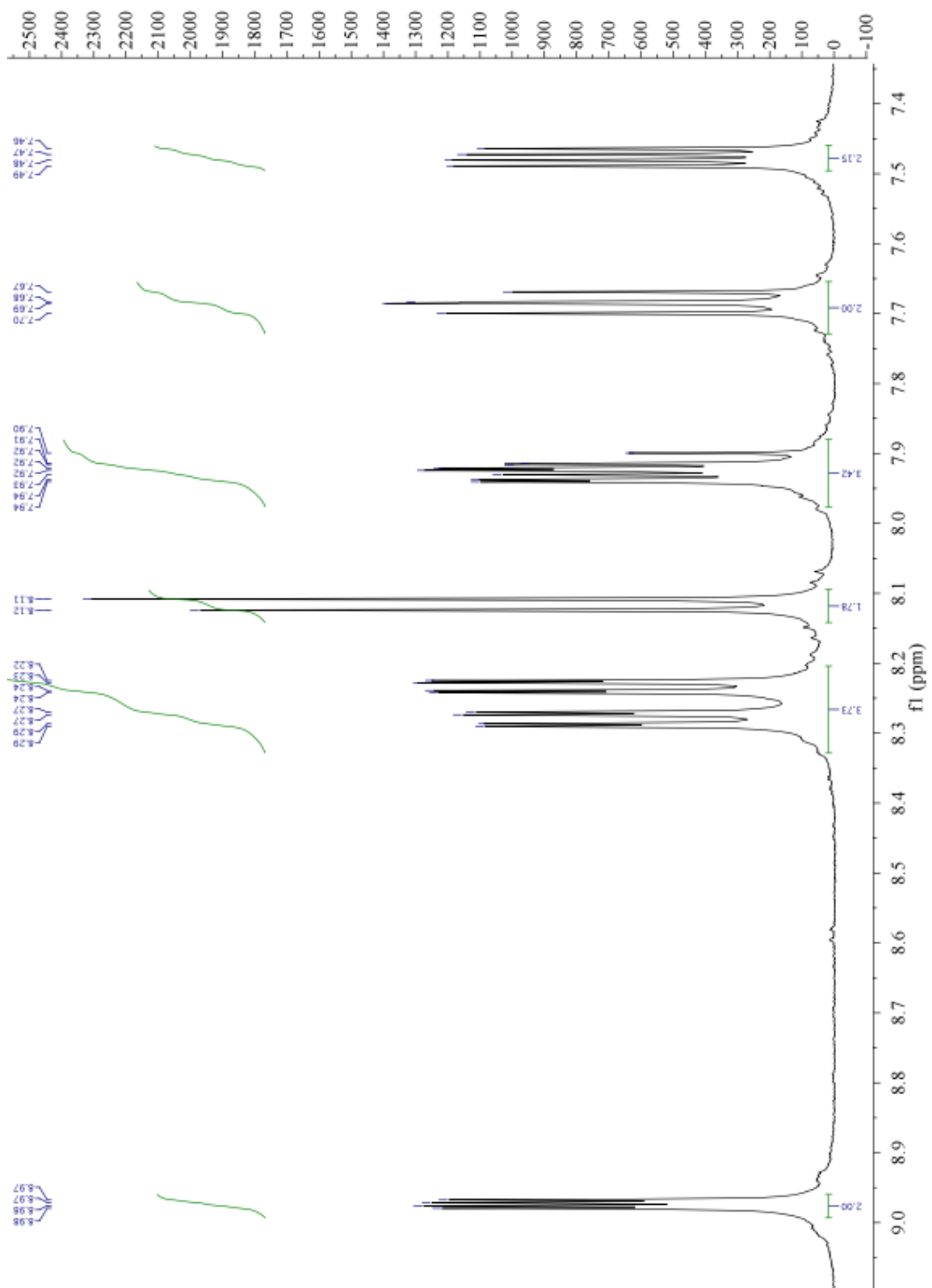


Figure 11.  $^1\text{H-NMR}$  spectrum of 2,6-bis(8'-quinolinyl)pyridine. (The solvent is  $\text{CD}_2\text{Cl}_2$ )

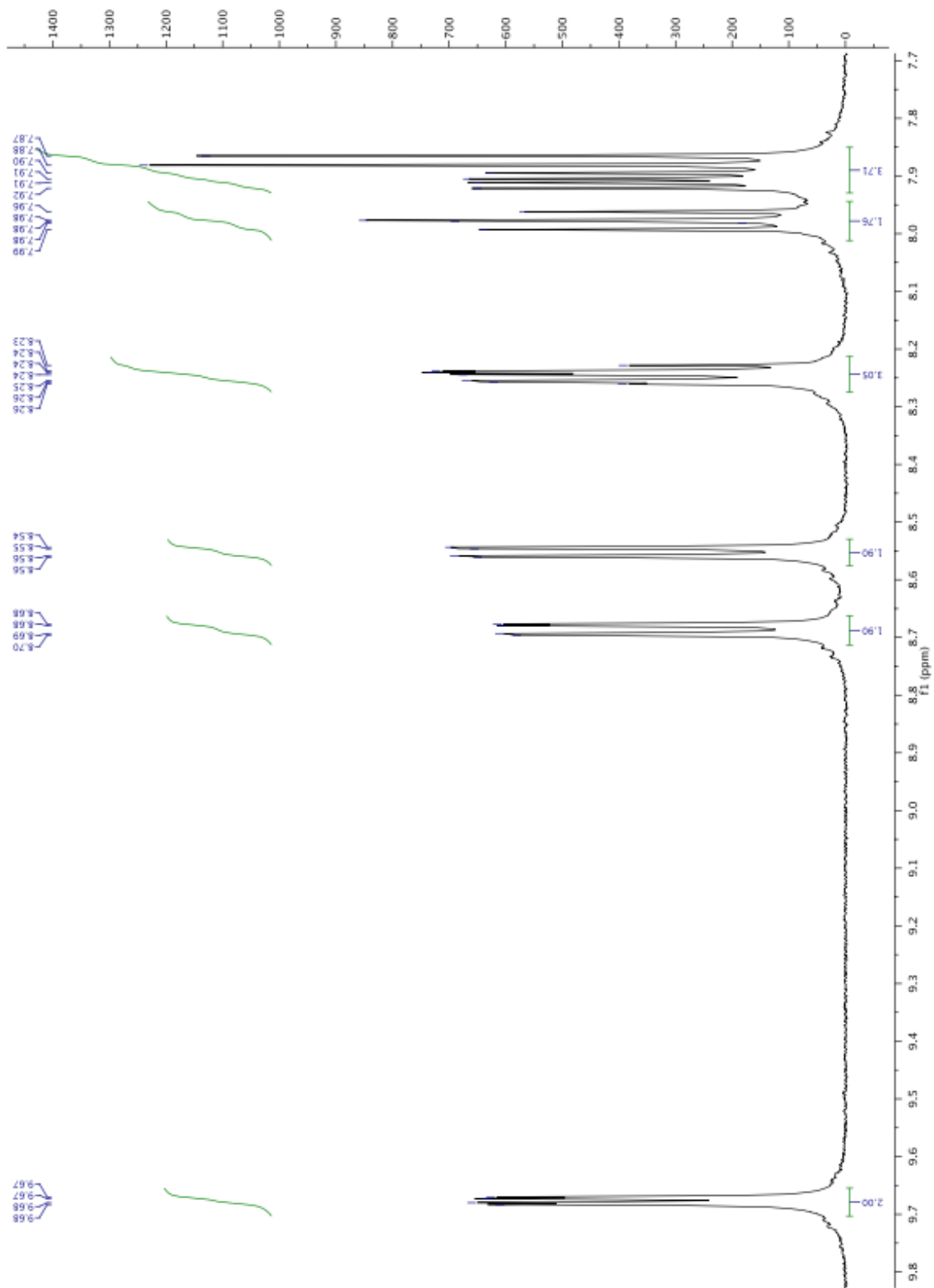


Figure 12.  $^1\text{H-NMR}$  spectrum of  $\text{fac-Re}(\text{bqp-}\kappa^2\text{N})(\text{CO})_3\text{Cl}$ . (The solvent is  $\text{CD}_2\text{Cl}_2$ )

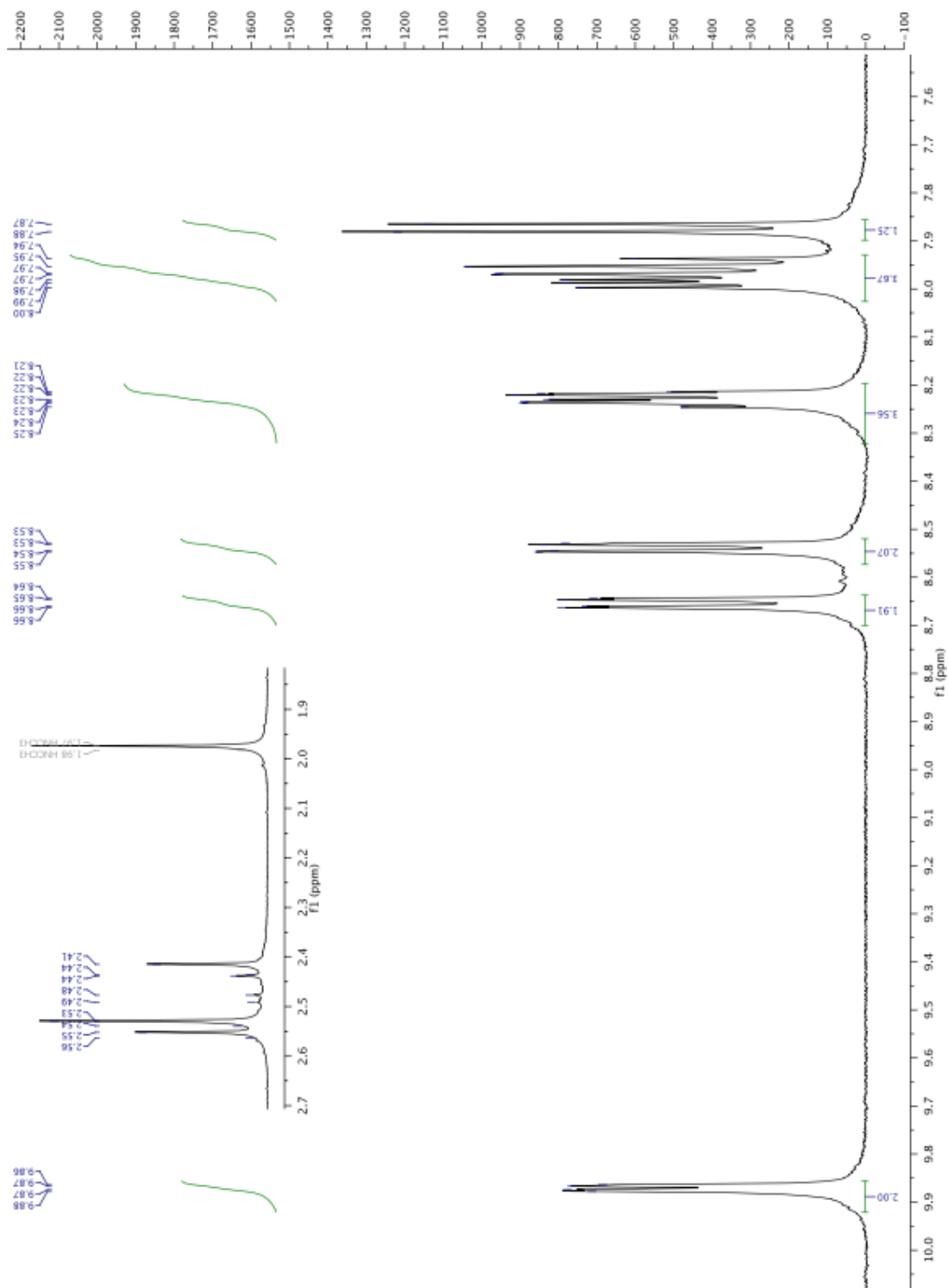


Figure 13.  $^1\text{H-NMR}$  spectrum of  $\text{fac-}[\text{Re}(\text{bqp-}\kappa^2\text{N})(\text{CO})_3(\text{NCCH}_3)]^+$ . (The solvent is  $\text{CD}_2\text{Cl}_2$ )

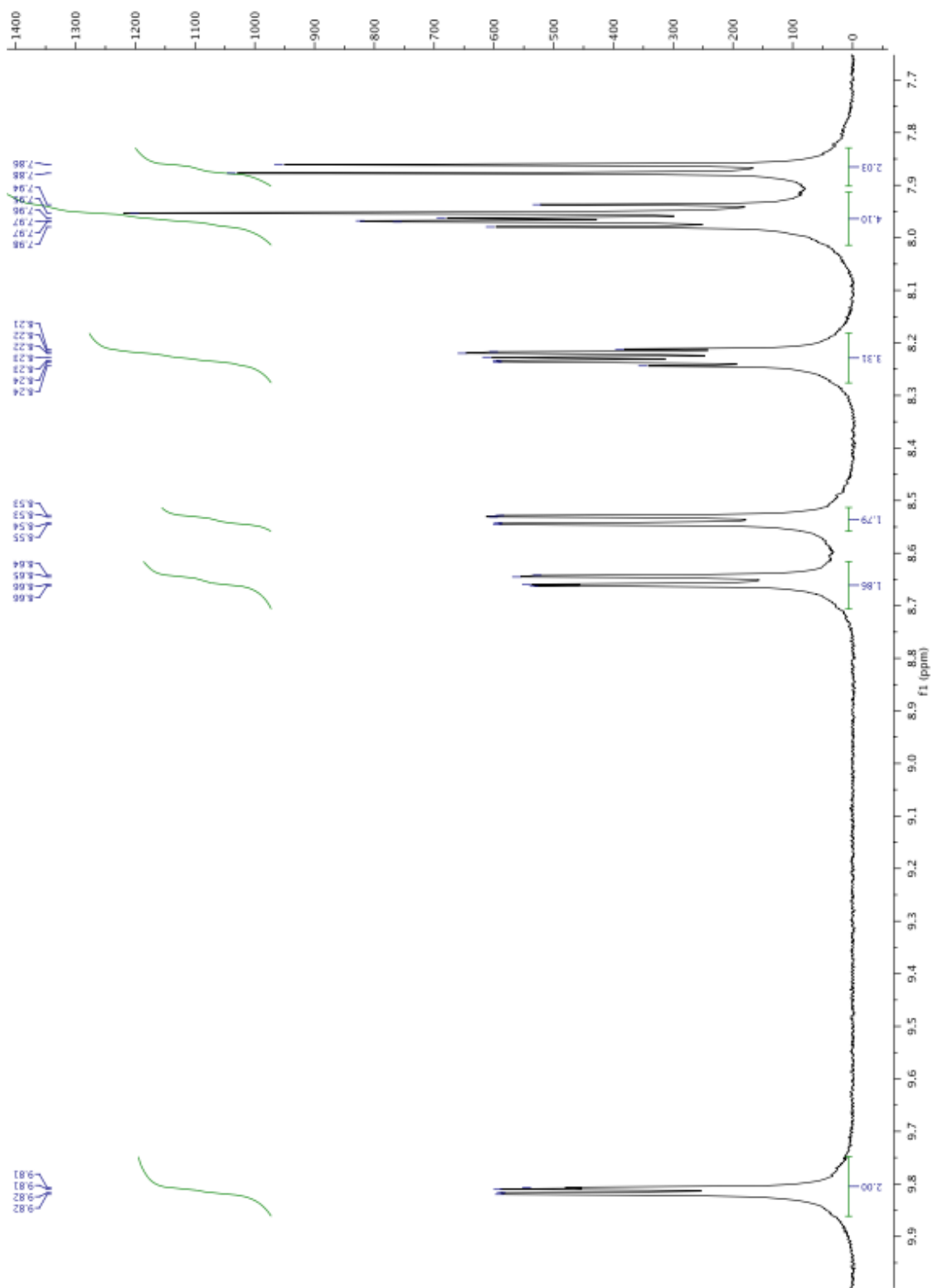


Figure 14.  $^1\text{H-NMR}$  spectrum of  $\text{fac-}[\text{Re}(\text{bqp-}\kappa^3\text{N})(\text{CO})_3]^+$ . (The solvent is  $\text{CD}_2\text{Cl}_2$ )

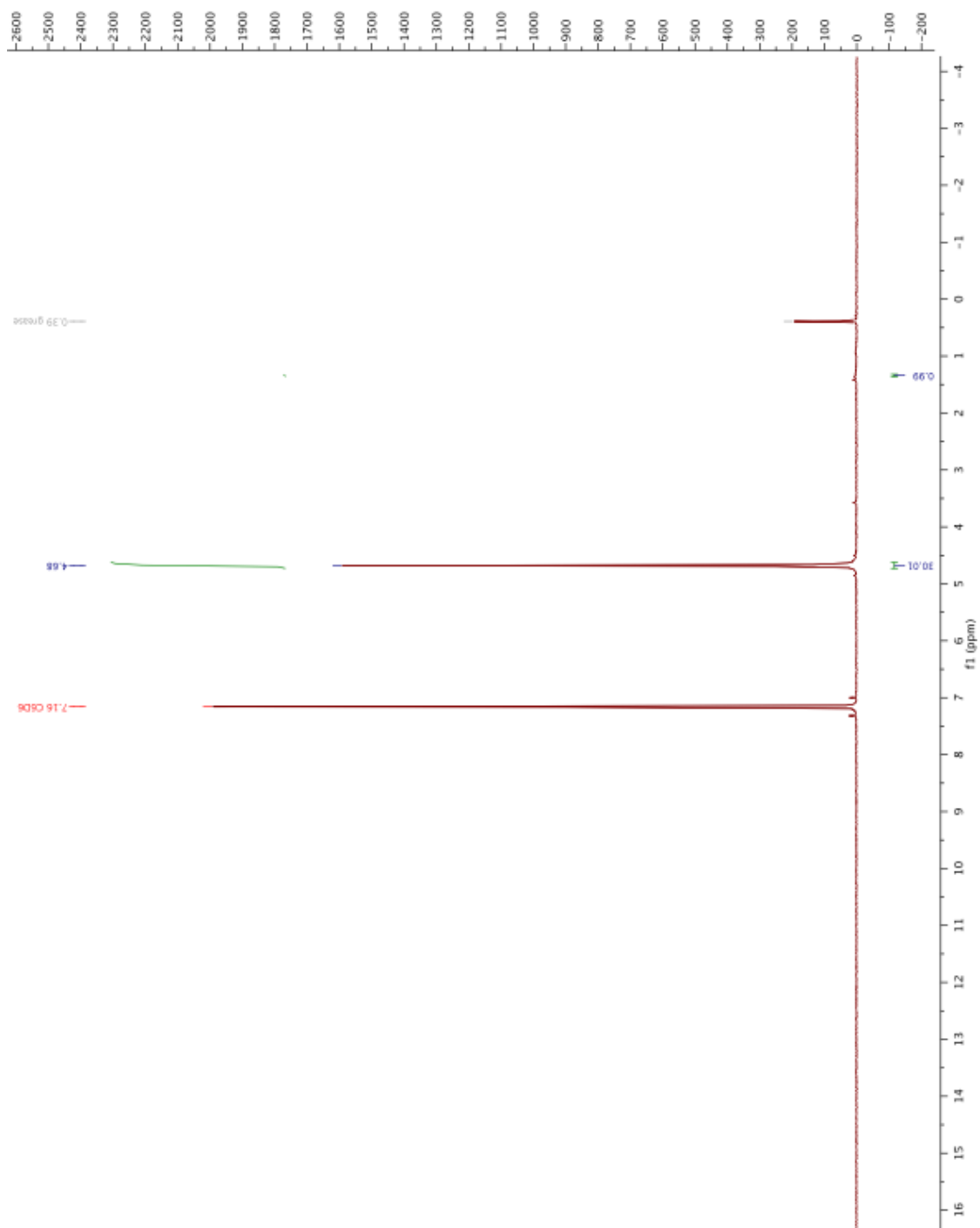


Figure 15.  $^1\text{H-NMR}$  spectrum of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$ . (The solvent is  $\text{C}_6\text{D}_6$ )

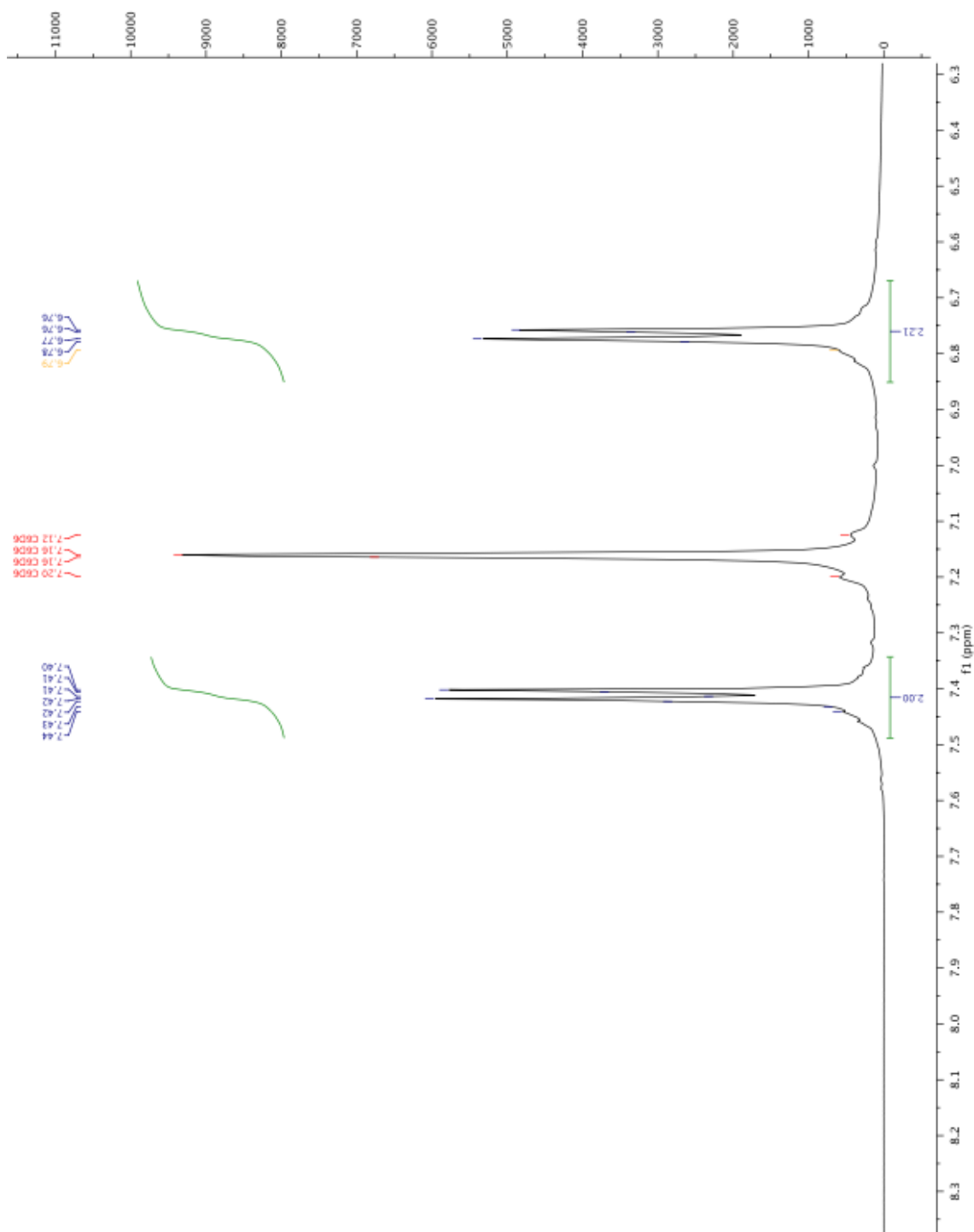


Figure 16.  $^1\text{H-NMR}$  spectrum of  $(p\text{-tolyl})_2$ . (The solvent is  $\text{C}_6\text{D}_6$ )

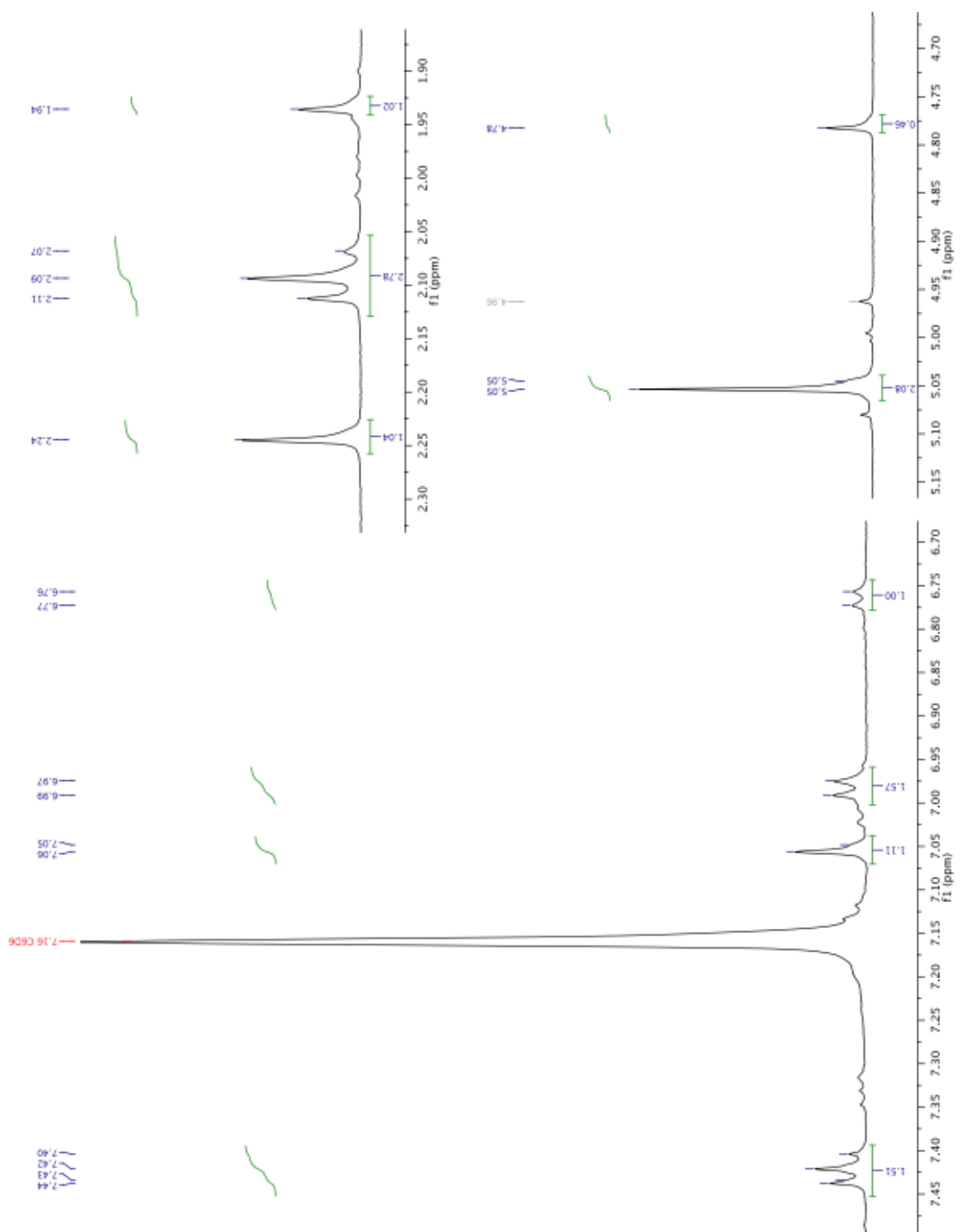


Figure 17.  $^1\text{H-NMR}$  spectrum of  $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3(p\text{-tolylS})$ . (The solvent is  $\text{C}_6\text{D}_6$ )



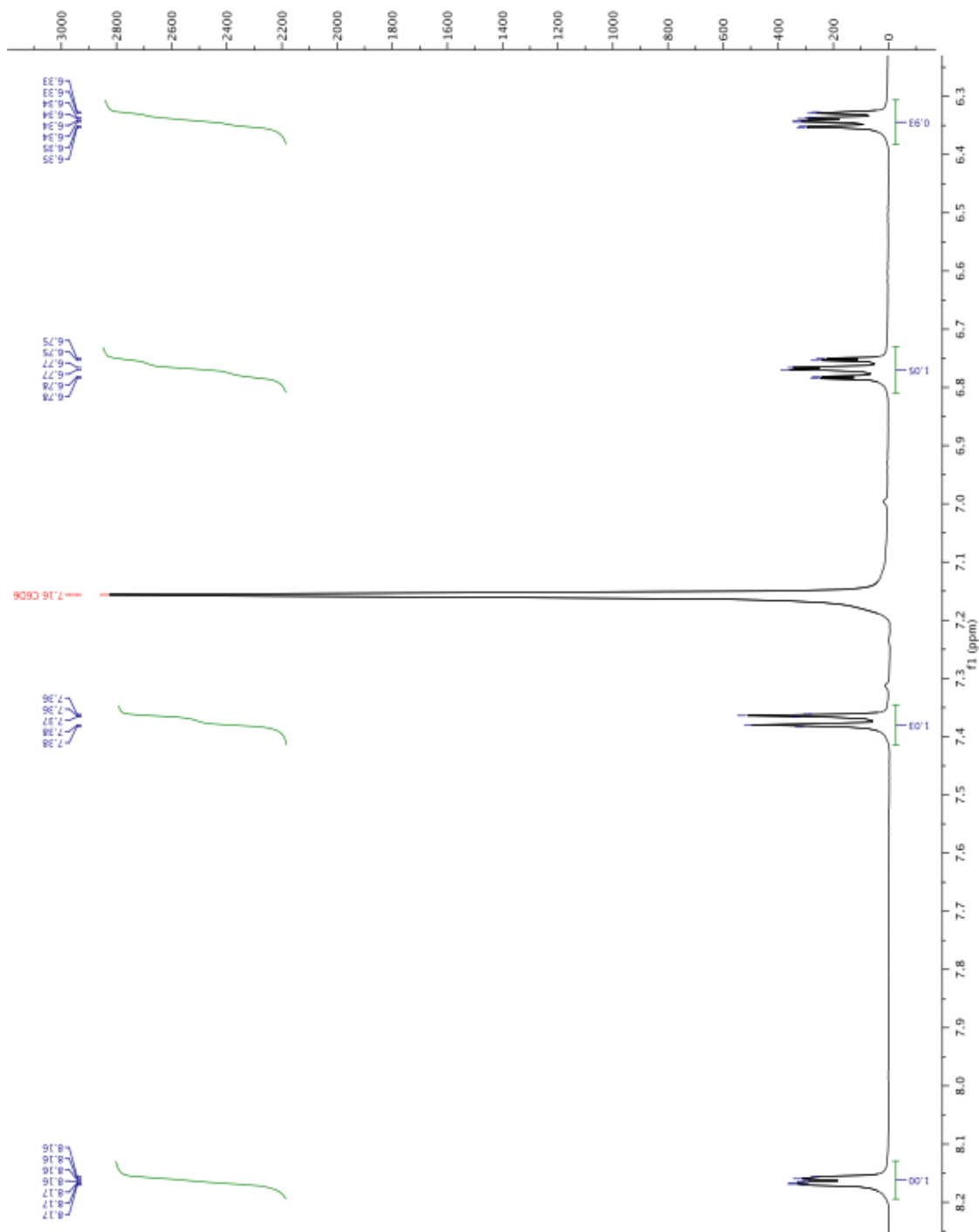


Figure 18.  $^1\text{H-NMR}$  spectrum of  $(2\text{-pyS})_2$ . (The solvent is  $\text{C}_6\text{D}_6$ )

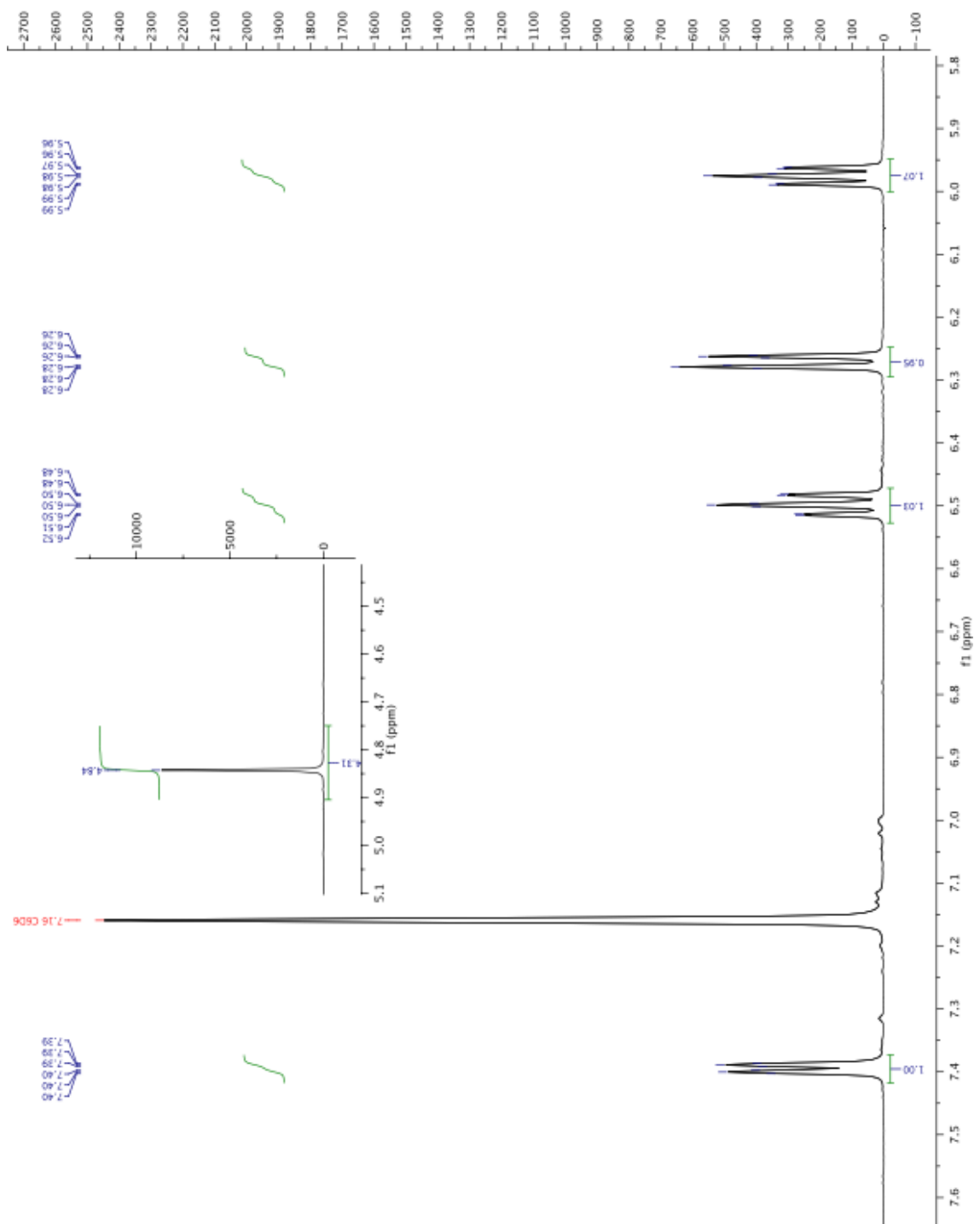


Figure 19.  $^1\text{H-NMR}$  spectrum of  $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(2\text{-pyS})$ . (The solvent is  $\text{C}_6\text{D}_6$ )

## Appendix B

### Excited States of Bisquinoliny Pyridine Rhenium(I) Complexes

Calculated singlet excited-states of *fac*-Re(bqp- $\kappa^2N$ )(CO)<sub>3</sub>Cl in CH<sub>3</sub>CN. The excited state number is followed by the spin multiplicity, symmetry, excitation energy, and oscillator strength *f*. The excitations from occupied to virtual orbitals are listed on the next line, followed by the wavefunction coefficients.

Excited State 1: Singlet-A 3.0297 eV 409.23 nm f=0.0110 <S\*\*2>=0.000  
 123 ->125 -0.11145  
 124 ->125 0.69110

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -1929.10885832

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.1508 eV 393.50 nm f=0.0102 <S\*\*2>=0.000  
 122 ->125 -0.37460  
 123 ->125 0.59427

Excited State 3: Singlet-A 3.2835 eV 377.59 nm f=0.0843 <S\*\*2>=0.000  
 120 ->125 0.10832  
 122 ->125 0.57808  
 123 ->125 0.35141  
 124 ->125 0.12106

Excited State 4: Singlet-A 3.6949 eV 335.55 nm f=0.0410 <S\*\*2>=0.000  
 121 ->125 0.68483

Excited State 5: Singlet-A 3.7517 eV 330.48 nm f=0.0215 <S\*\*2>=0.000  
 124 ->126 0.64458  
 124 ->127 -0.26229

Excited State 6: Singlet-A 3.8517 eV 321.89 nm f=0.0152 <S\*\*2>=0.000  
 120 ->125 0.38155  
 122 ->126 -0.14445  
 123 ->126 0.48268  
 123 ->127 -0.27270

Excited State 7: Singlet-A 3.8911 eV 318.64 nm f=0.1025 <S\*\*2>=0.000  
 120 ->125 0.52626  
 122 ->126 0.27550  
 122 ->127 -0.14319  
 123 ->126 -0.30205

Excited State 8:	Singlet-A	3.9326 eV	315.28 nm	f=0.0130	$\langle S^{*2} \rangle = 0.000$
120 ->125	0.13651				
122 ->126	-0.39709				
122 ->127	0.16675				
123 ->126	-0.15615				
124 ->126	0.17545				
124 ->127	0.44636				
Excited State 9:	Singlet-A	3.9599 eV	313.10 nm	f=0.0278	$\langle S^{*2} \rangle = 0.000$
120 ->125	-0.11705				
122 ->126	0.31728				
122 ->127	-0.24907				
123 ->126	0.20452				
124 ->126	0.18443				
124 ->127	0.46798				
Excited State 10:	Singlet-A	4.0500 eV	306.13 nm	f=0.0067	$\langle S^{*2} \rangle = 0.000$
122 ->127	-0.11690				
123 ->126	0.26402				
123 ->127	0.62069				
Excited State 11:	Singlet-A	4.0710 eV	304.55 nm	f=0.0035	$\langle S^{*2} \rangle = 0.000$
122 ->127	0.25999				
124 ->128	0.32488				
124 ->129	0.35958				
124 ->130	0.34103				
124 ->132	0.10835				
Excited State 12:	Singlet-A	4.1277 eV	300.37 nm	f=0.0316	$\langle S^{*2} \rangle = 0.000$
119 ->125	-0.25860				
122 ->126	0.30723				
122 ->127	0.50384				
123 ->126	0.10550				
124 ->129	-0.13870				
124 ->130	-0.10461				

Calculated singlet excited-states of *fac*-[Re(bqp- $\kappa^2$ N)(CO)<sub>3</sub>(NCCH<sub>3</sub>)]<sup>+</sup> in CH<sub>3</sub>CN. The excited state number is followed by the spin multiplicity, symmetry, excitation energy, and oscillator strength *f*. The excitations from occupied to virtual orbitals are listed on the next line, followed by the wavefunction coefficients.

Excited State 1: Singlet-A 3.3311 eV 372.20 nm f=0.1140 <S\*\*2>=0.000  
126 ->127 0.68572

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -1601.48607223

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.4738 eV 356.91 nm f=0.0085 <S\*\*2>=0.000  
124 ->127 0.55081  
125 ->127 -0.42482

Excited State 3: Singlet-A 3.5985 eV 344.54 nm f=0.0101 <S\*\*2>=0.000  
123 ->127 0.62325  
124 ->127 -0.25329  
125 ->127 -0.19395

Excited State 4: Singlet-A 3.7032 eV 334.80 nm f=0.0792 <S\*\*2>=0.000  
123 ->127 0.30715  
124 ->127 0.34095  
125 ->127 0.51707

Excited State 5: Singlet-A 3.9016 eV 317.77 nm f=0.0469 <S\*\*2>=0.000  
121 ->127 -0.13922  
122 ->127 0.62330  
126 ->128 0.19631  
126 ->129 -0.14124

Excited State 6: Singlet-A 3.9608 eV 313.03 nm f=0.0450 <S\*\*2>=0.000  
122 ->127 -0.23125  
126 ->128 0.56778  
126 ->129 -0.27246

Excited State 7: Singlet-A 4.1209 eV 300.86 nm f=0.0016 <S\*\*2>=0.000  
121 ->127 0.67930  
122 ->127 0.13571

Calculated singlet excited-states of *fac*-[Re(bqp- $\kappa^2$ N)(CO)<sub>3</sub>(NC<sub>5</sub>H<sub>5</sub>)]<sup>+</sup> in CH<sub>3</sub>CN. The excited state number is followed by the spin multiplicity, symmetry, excitation energy, and oscillator strength *f*. The excitations from occupied to virtual orbitals are listed on the next line, followed by the wavefunction coefficients.

Excited State 1: Singlet-A 3.2643 eV 379.82 nm f=0.0870 <S\*\*2>=0.000  
 134 ->137 0.10087  
 135 ->137 0.24701  
 136 ->137 0.64420

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -1717.02116870

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.3572 eV 369.30 nm f=0.0334 <S\*\*2>=0.000  
 135 ->137 0.65663  
 136 ->137 -0.23951

Excited State 3: Singlet-A 3.5474 eV 349.50 nm f=0.0072 <S\*\*2>=0.000  
 133 ->137 0.64375  
 134 ->137 0.27460

Excited State 4: Singlet-A 3.6755 eV 337.32 nm f=0.0620 <S\*\*2>=0.000  
 133 ->137 -0.27561  
 134 ->137 0.63027

Excited State 5: Singlet-A 3.8477 eV 322.23 nm f=0.0163 <S\*\*2>=0.000  
 132 ->137 0.47928  
 136 ->138 -0.44366  
 136 ->139 -0.12990  
 136 ->140 -0.14655

Excited State 6: Singlet-A 3.8799 eV 319.55 nm f=0.1051 <S\*\*2>=0.000  
 132 ->137 0.47933  
 136 ->138 0.44787  
 136 ->140 0.10950

Excited State 7: Singlet-A 4.0038 eV 309.67 nm f=0.0106 <S\*\*2>=0.000  
 136 ->139 0.66285  
 136 ->140 -0.12110

Excited State 8:	Singlet-A	4.0412 eV	306.80 nm	f=0.0253	$\langle S^{*2} \rangle = 0.000$
135 ->138	0.65362				
135 ->140	0.14435				
135 ->143	-0.10188				
Excited State 9:	Singlet-A	4.0869 eV	303.37 nm	f=0.0010	$\langle S^{*2} \rangle = 0.000$
131 ->137	0.69476				
Excited State 10:	Singlet-A	4.1562 eV	298.31 nm	f=0.0104	$\langle S^{*2} \rangle = 0.000$
133 ->138	0.56231				
133 ->140	0.18728				
133 ->145	-0.12165				
134 ->138	0.25572				
135 ->139	-0.12580				
Excited State 11:	Singlet-A	4.1745 eV	297.00 nm	f=0.0264	$\langle S^{*2} \rangle = 0.000$
136 ->138	-0.19499				
136 ->140	0.64237				
Excited State 12:	Singlet-A	4.2030 eV	294.99 nm	f=0.0032	$\langle S^{*2} \rangle = 0.000$
130 ->137	0.66292				
Excited State 13:	Singlet-A	4.2161 eV	294.08 nm	f=0.0400	$\langle S^{*2} \rangle = 0.000$
129 ->137	-0.10682				
130 ->137	0.14852				
133 ->138	0.11459				
133 ->139	-0.11846				
135 ->139	0.60314				
136 ->142	0.11675				
Excited State 14:	Singlet-A	4.2353 eV	292.74 nm	f=0.0299	$\langle S^{*2} \rangle = 0.000$
129 ->137	0.33939				
134 ->138	-0.25712				
134 ->139	-0.18166				
134 ->142	-0.16456				
136 ->141	-0.28244				
136 ->142	-0.31628				
136 ->143	0.10510				



Excited State 15: Singlet-A 4.2407 eV 292.37 nm f=0.0411  $\langle S^2 \rangle = 0.000$

129 ->137	0.23529
133 ->138	-0.18020
134 ->138	0.45110
134 ->139	0.17495
135 ->139	0.20596
136 ->138	-0.13776
136 ->142	-0.20184

Calculated singlet excited-states of *fac*-[Re(bqp- $\kappa^2$ N)(CO)<sub>3</sub>(PPh<sub>3</sub>)]<sup>+</sup> in CH<sub>3</sub>CN. The excited state number is followed by the spin multiplicity, symmetry, excitation energy, and oscillator strength *f*. The excitations from occupied to virtual orbitals are listed on the next line, followed by the wavefunction coefficients.

Excited State 1: Singlet-A 3.4068 eV 363.93 nm f=0.0664 <S\*\*2>=0.000  
183 ->185 0.12420  
184 ->185 0.67844

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -2505.00415752

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.5717 eV 347.13 nm f=0.0033 <S\*\*2>=0.000  
181 ->185 -0.30088  
182 ->185 0.62325  
183 ->185 0.10751

Excited State 3: Singlet-A 3.6141 eV 343.05 nm f=0.1044 <S\*\*2>=0.000  
180 ->185 0.14037  
181 ->185 0.23767  
183 ->185 0.62419  
184 ->185 -0.11663

Excited State 4: Singlet-A 3.6671 eV 338.10 nm f=0.0484 <S\*\*2>=0.000  
180 ->185 0.32081  
181 ->185 0.48059  
182 ->185 0.28787  
183 ->185 -0.25716

Excited State 5: Singlet-A 3.8743 eV 320.02 nm f=0.0125 <S\*\*2>=0.000  
177 ->185 0.12534  
178 ->185 0.10100  
179 ->185 0.11895  
180 ->185 0.54929  
181 ->185 -0.32011  
182 ->185 -0.13577  
184 ->186 -0.11879

Excited State 6:	Singlet-A	3.9069 eV	317.35 nm	f=0.0405	$\langle S^{*2} \rangle = 0.000$
180 ->185	0.11735				
183 ->186	0.18226				
184 ->186	0.62368				
184 ->187	0.15596				
Excited State 7:	Singlet-A	4.0029 eV	309.73 nm	f=0.0288	$\langle S^{*2} \rangle = 0.000$
174 ->185	0.13601				
176 ->185	0.12269				
177 ->185	0.11340				
178 ->185	0.59930				
179 ->185	-0.17621				
183 ->186	0.11516				
Excited State 8:	Singlet-A	4.0720 eV	304.48 nm	f=0.0378	$\langle S^{*2} \rangle = 0.000$
179 ->185	0.46881				
180 ->185	-0.11492				
183 ->186	0.43753				
184 ->186	-0.12908				
Excited State 9:	Singlet-A	4.0827 eV	303.68 nm	f=0.0688	$\langle S^{*2} \rangle = 0.000$
177 ->185	-0.15199				
178 ->185	-0.15047				
179 ->185	-0.41507				
180 ->185	0.14795				
182 ->186	0.14358				
183 ->186	0.41609				
184 ->186	-0.14225				
Excited State 10:	Singlet-A	4.1326 eV	300.01 nm	f=0.0078	$\langle S^{*2} \rangle = 0.000$
175 ->185	0.19777				
176 ->185	0.35817				
177 ->185	0.46395				
178 ->185	-0.15773				
179 ->185	-0.11482				
182 ->186	-0.17763				

Excited State 11: Singlet-A 4.1488 eV 298.84 nm f=0.0055 <S\*\*2>=0.000  
176 ->185 0.53973  
177 ->185 -0.36832  
179 ->185 0.15648

Excited State 12: Singlet-A 4.1582 eV 298.17 nm f=0.0233 <S\*\*2>=0.000  
174 ->185 0.12616  
175 ->185 -0.20900  
176 ->185 0.10535  
177 ->185 0.22464  
178 ->185 -0.18046  
181 ->186 -0.11522  
182 ->186 0.49356  
182 ->189 -0.13883  
183 ->186 -0.10275  
184 ->187 -0.12670

Calculated singlet excited-states of *fac*-[Re(bqp- $\kappa^3$ N)(CO)<sub>3</sub>]<sup>+</sup> in CH<sub>3</sub>CN. The excited state number is followed by the spin multiplicity, symmetry, excitation energy, and oscillator strength *f*. The excitations from occupied to virtual orbitals are listed on the next line, followed by the wavefunction coefficients.

Excited State 1: Singlet-A 3.1381 eV 395.09 nm *f*=0.1678 <S\*\*2>=0.000  
112 ->116 0.15262  
115 ->116 0.68029

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -1468.73564952

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.2269 eV 384.22 nm *f*=0.0206 <S\*\*2>=0.000  
113 ->116 0.23182  
114 ->116 0.64806  
115 ->117 -0.12872

Excited State 3: Singlet-A 3.2987 eV 375.86 nm *f*=0.0066 <S\*\*2>=0.000  
113 ->116 0.66513  
114 ->116 -0.22746

Excited State 4: Singlet-A 3.4398 eV 360.44 nm *f*=0.0233 <S\*\*2>=0.000  
112 ->117 0.14119  
114 ->116 0.13254  
115 ->117 0.67268

Excited State 5: Singlet-A 3.4705 eV 357.25 nm *f*=0.0842 <S\*\*2>=0.000  
112 ->116 0.10777  
114 ->117 0.68596

Excited State 6: Singlet-A 3.5528 eV 348.98 nm *f*=0.0559 <S\*\*2>=0.000  
112 ->116 0.41765  
113 ->117 0.54493  
114 ->117 -0.11217

Excited State 7: Singlet-A 3.5805 eV 346.28 nm *f*=0.1212 <S\*\*2>=0.000  
112 ->116 0.52782  
113 ->117 -0.43820  
115 ->116 -0.13217

Excited State 8:	Singlet-A	3.8647 eV	320.81 nm	f=0.0136	$\langle S^{*2} \rangle = 0.000$
112 ->117	0.66816				
115 ->117	-0.13953				
115 ->118	0.12055				
Excited State 9:	Singlet-A	3.8651 eV	320.78 nm	f=0.0020	$\langle S^{*2} \rangle = 0.000$
112 ->117	-0.12135				
112 ->118	0.12887				
115 ->118	0.66418				
Excited State 10:	Singlet-A	3.9666 eV	312.57 nm	f=0.0005	$\langle S^{*2} \rangle = 0.000$
111 ->116	0.11051				
113 ->118	0.11142				
114 ->118	0.66644				
114 ->122	0.10049				
Excited State 11:	Singlet-A	4.0881 eV	303.28 nm	f=0.0121	$\langle S^{*2} \rangle = 0.000$
111 ->116	0.61447				
113 ->118	-0.26533				
115 ->119	0.13992				
Excited State 12:	Singlet-A	4.1227 eV	300.73 nm	f=0.0357	$\langle S^{*2} \rangle = 0.000$
111 ->116	0.25956				
112 ->119	-0.18445				
113 ->118	0.50155				
114 ->118	-0.10980				
115 ->119	-0.28728				
115 ->123	-0.11524				

Calculated triplet excited-states of *fac*-Re(bqp- $\kappa^2$ N)(CO)<sub>3</sub>Cl in CH<sub>3</sub>CN. The excited state number is followed by the spin multiplicity, symmetry, excitation energy, and oscillator strength *f*. The excitations from occupied to virtual orbitals are listed on the next line, followed by the wavefunction coefficients.

Excited State 1: Triplet-A 2.4940 eV 497.14 nm f=0.0000 <S\*\*2>=2.000  
114 ->125 -0.12444  
119 ->125 -0.12368  
120 ->125 -0.27482  
121 ->125 0.33342  
122 ->125 0.32415  
123 ->125 0.27274  
124 ->125 0.21292

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -1929.12854653

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Triplet-A 2.7816 eV 445.73 nm f=0.0000 <S\*\*2>=2.000  
119 ->132 0.12961  
121 ->126 0.41912  
121 ->127 0.22608  
122 ->126 -0.27657  
122 ->127 -0.12975  
123 ->126 -0.29007  
123 ->127 -0.13547

Excited State 3: Triplet-A 2.9713 eV 417.28 nm f=0.0000 <S\*\*2>=2.000  
122 ->125 -0.14935  
123 ->125 -0.11575  
124 ->125 0.65123

Excited State 4: Triplet-A 3.1000 eV 399.95 nm f=0.0000 <S\*\*2>=2.000  
122 ->125 -0.39592  
123 ->125 0.56814

Excited State 5: Triplet-A 3.3217 eV 373.26 nm f=0.0000 <S\*\*2>=2.000

116 ->125	0.12356
117 ->125	0.19432
119 ->125	0.11002
120 ->125	0.40221
121 ->125	-0.13794
122 ->125	0.38801
123 ->125	0.22330

Excited State 6: Triplet-A 3.5004 eV 354.20 nm f=0.0000 <S\*\*2>=2.000

111 ->125	-0.12233
111 ->127	-0.11734
114 ->125	0.18399
114 ->128	0.10086
116 ->125	-0.13360
120 ->128	-0.14508
121 ->126	-0.11635
121 ->127	0.12654
121 ->128	0.10793
122 ->125	0.11736
122 ->127	0.14723
123 ->126	-0.22842
123 ->127	0.30034
124 ->125	0.12542
124 ->126	0.12468

Excited State 7: Triplet-A 3.5947 eV 344.91 nm f=0.0000 <S\*\*2>=2.000

116 ->125	0.21537
117 ->125	0.46476
121 ->125	0.26364
122 ->125	-0.18621
123 ->125	-0.12103
124 ->126	0.18912
124 ->127	-0.14178

Excited State 8: Triplet-A 3.6456 eV 340.09 nm f=0.0000 <S\*\*2>=2.000

117 ->125	-0.28176
120 ->127	0.10658
124 ->126	0.43612
124 ->127	-0.28584
124 ->131	-0.10915



Excited State 9: Triplet-A 3.7169 eV 333.57 nm f=0.0000 <S\*\*2>=2.000

114 ->125	0.10120
116 ->125	-0.13204
117 ->125	-0.19392
120 ->125	0.27755
121 ->125	0.43416
121 ->127	0.12720
123 ->126	0.10739
124 ->128	-0.12829
124 ->129	-0.10273
124 ->130	-0.17311

Calculated triplet excited-states of *fac*-[Re(bqp- $\kappa^2$ N)(CO)<sub>3</sub>(NCCH<sub>3</sub>)]<sup>+</sup> in CH<sub>3</sub>CN. The excited state number is followed by the spin multiplicity, symmetry, excitation energy, and oscillator strength *f*. The excitations from occupied to virtual orbitals are listed on the next line, followed by the wavefunction coefficients.

Excited State 1: Triplet-A 2.4995 eV 496.03 nm f=0.0000 <S\*\*2>=2.000  
 118 ->127 -0.13800  
 120 ->127 -0.11328  
 122 ->127 -0.21747  
 124 ->127 0.10933  
 125 ->127 0.40858  
 126 ->127 0.43800

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -1601.51663250

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Triplet-A 2.7951 eV 443.58 nm f=0.0000 <S\*\*2>=2.000  
 121 ->134 -0.15717  
 124 ->128 -0.15683  
 124 ->129 -0.12235  
 125 ->128 -0.27134  
 125 ->129 -0.22157  
 126 ->128 0.41374  
 126 ->129 0.29922

Excited State 3: Triplet-A 3.2842 eV 377.52 nm f=0.0000 <S\*\*2>=2.000  
 122 ->127 0.26586  
 124 ->127 0.30150  
 125 ->127 -0.30361  
 125 ->128 0.10432  
 126 ->127 0.34697  
 126 ->130 0.10201

Excited State 4: Triplet-A 3.4072 eV 363.89 nm f=0.0000 <S\*\*2>=2.000  
 119 ->127 -0.36000  
 122 ->127 -0.26791  
 123 ->127 0.19785  
 124 ->127 0.41394  
 125 ->127 -0.11442  
 126 ->127 -0.20202

Excited State 5: Triplet-A 3.4639 eV 357.93 nm f=0.0000 <S\*\*2>=2.000  
119 ->127 -0.24301  
123 ->127 0.44697  
124 ->127 -0.25114  
125 ->127 -0.14416  
126 ->127 0.21735

Excited State 6: Triplet-A 3.5653 eV 347.76 nm f=0.0000 <S\*\*2>=2.000  
118 ->127 -0.18711  
119 ->127 0.10395  
123 ->127 0.37063  
124 ->127 -0.14733  
125 ->127 0.17161  
125 ->128 0.14723  
125 ->129 -0.12719  
126 ->127 -0.23318  
126 ->128 0.20698  
126 ->129 -0.21547

Excited State 7: Triplet-A 3.6595 eV 338.80 nm f=0.0000 <S\*\*2>=2.000  
118 ->127 0.10266  
119 ->127 0.41996  
123 ->127 0.23698  
124 ->127 0.29134  
125 ->128 -0.13836  
125 ->129 0.10968  
126 ->127 -0.12175

Excited State 8: Triplet-A 3.7366 eV 331.81 nm f=0.0000 <S\*\*2>=2.000  
118 ->127 0.10208  
119 ->127 -0.26804  
122 ->127 0.34818  
123 ->127 -0.10846  
124 ->127 0.14174  
124 ->128 0.10264  
125 ->127 0.29117  
125 ->129 0.10664  
126 ->128 0.16332  
126 ->131 0.13422

Calculated triplet excited-states of *fac*-[Re(bqp- $\kappa^2$ N)(CO)<sub>3</sub>(NC<sub>5</sub>H<sub>5</sub>)]<sup>+</sup> in CH<sub>3</sub>CN. The excited state number is followed by the spin multiplicity, symmetry, excitation energy, and oscillator strength *f*. The excitations from occupied to virtual orbitals are listed on the next line, followed by the wavefunction coefficients.

Excited State 1: Triplet-A 2.4883 eV 498.26 nm f=0.0000 <S\*\*2>=2.000  
 127 ->137 -0.12089  
 129 ->142 0.10540  
 130 ->137 -0.11249  
 132 ->137 -0.23821  
 134 ->137 0.35680  
 135 ->137 -0.18350  
 136 ->137 0.44460

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -1717.04968353

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Triplet-A 2.7935 eV 443.83 nm f=0.0000 <S\*\*2>=2.000  
 131 ->146 -0.14228  
 134 ->138 -0.28461  
 134 ->140 0.31433  
 136 ->138 0.34304  
 136 ->140 -0.33761

Excited State 3: Triplet-A 3.1911 eV 388.54 nm f=0.0000 <S\*\*2>=2.000  
 132 ->137 0.19965  
 135 ->137 0.51732  
 136 ->137 0.33381

Excited State 4: Triplet-A 3.3577 eV 369.25 nm f=0.0000 <S\*\*2>=2.000  
 129 ->137 -0.30457  
 132 ->137 0.36250  
 133 ->137 0.11245  
 134 ->137 -0.16879  
 135 ->137 -0.35964  
 136 ->137 0.24972

Excited State 5: Triplet-A 3.4272 eV 361.77 nm f=0.0000 <S\*\*2>=2.000  
129 ->137 -0.25076  
133 ->137 0.52403  
134 ->137 0.23661  
136 ->137 -0.14601

Excited State 6: Triplet-A 3.5138 eV 352.85 nm f=0.0000 <S\*\*2>=2.000  
127 ->137 0.19200  
132 ->141 -0.10151  
133 ->137 0.30560  
134 ->139 0.11185  
135 ->137 0.11196  
135 ->138 -0.18364  
136 ->137 0.23290  
136 ->138 0.19443  
136 ->139 0.24698

Excited State 7: Triplet-A 3.5806 eV 346.27 nm f=0.0000 <S\*\*2>=2.000  
125 ->139 -0.10187  
128 ->144 0.16040  
129 ->137 0.17140  
133 ->137 0.10455  
134 ->137 -0.14195  
134 ->138 0.11151  
135 ->138 0.34863  
135 ->139 -0.16465  
135 ->140 0.22580  
136 ->137 0.12848  
136 ->138 0.20736  
136 ->140 0.12352

Excited State 8: Triplet-A 3.6334 eV 341.23 nm f=0.0000 <S\*\*2>=2.000  
129 ->137 0.45009  
133 ->137 0.22143  
134 ->137 -0.13755  
134 ->138 -0.12393  
135 ->137 -0.17131  
135 ->139 0.18992  
136 ->138 -0.15899  
136 ->140 -0.11165

Excited State 9: Triplet-A 3.6975 eV 335.32 nm f=0.0000  $\langle S^2 \rangle = 2.000$

129 ->137	0.22972
132 ->137	0.33671
134 ->137	0.40339
135 ->139	-0.18965
136 ->138	-0.10812

Calculated triplet excited-states of *fac*-[Re(bqp- $\kappa^2N$ )(CO)<sub>3</sub>(PPh<sub>3</sub>)]<sup>+</sup> in CH<sub>3</sub>CN. The excited state number is followed by the spin multiplicity, symmetry, excitation energy, and oscillator strength *f*. The excitations from occupied to virtual orbitals are listed on the next line, followed by the wavefunction coefficients.

Excited State 1: Triplet-A 2.5473 eV 486.73 nm f=0.0000 <S\*\*2>=2.000  
 170 ->185 0.13852  
 174 ->185 -0.12043  
 176 ->185 -0.10127  
 177 ->185 -0.13226  
 178 ->185 -0.10007  
 183 ->185 0.48567  
 184 ->185 0.35458

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -2505.03574436

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Triplet-A 2.7761 eV 446.61 nm f=0.0000 <S\*\*2>=2.000  
 178 ->186 -0.10857  
 183 ->186 -0.28259  
 183 ->187 0.21320  
 184 ->186 0.44051  
 184 ->187 -0.30745

Excited State 3: Triplet-A 3.2999 eV 375.72 nm f=0.0000 <S\*\*2>=2.000  
 170 ->185 0.10503  
 171 ->185 -0.13480  
 176 ->185 0.12628  
 178 ->185 0.18638  
 181 ->185 -0.15922  
 182 ->185 0.26091  
 183 ->185 -0.10547  
 183 ->186 -0.12408  
 183 ->187 -0.12397  
 183 ->190 -0.12576  
 184 ->185 0.36329

Excited State 4: Triplet-A 3.4042 eV 364.21 nm f=0.0000  $\langle S^{*2} \rangle = 2.000$

171 ->185	0.10324
176 ->185	-0.10783
178 ->185	-0.13134
181 ->185	-0.11634
182 ->185	0.35195
182 ->186	0.16091
182 ->187	0.11192
183 ->185	0.20444
184 ->185	-0.33475
184 ->187	-0.12031

Excited State 5: Triplet-A 3.4795 eV 356.32 nm f=0.0000  $\langle S^{*2} \rangle = 2.000$

171 ->185	0.40715
180 ->185	-0.28617
181 ->185	-0.38269
182 ->185	-0.12229
183 ->185	-0.12692

Excited State 6: Triplet-A 3.5981 eV 344.58 nm f=0.0000  $\langle S^{*2} \rangle = 2.000$

170 ->185	-0.20040
171 ->185	0.10734
181 ->185	-0.10922
182 ->185	0.38575
182 ->186	-0.12012
183 ->186	0.21892
183 ->187	0.18055
183 ->190	0.10229
184 ->185	0.17417
184 ->186	0.15840
184 ->187	0.15251



Excited State 7: Triplet-A 3.6149 eV 342.98 nm f=0.0000 <S\*\*2>=2.000

171 ->185	0.22706
172 ->194	-0.13645
176 ->185	-0.13121
176 ->197	-0.13214
180 ->194	-0.11077
181 ->185	0.26946
181 ->188	0.11616
181 ->189	0.14810
181 ->194	0.15670
183 ->185	-0.19384
184 ->185	0.16872

Calculated triplet excited-states of *fac*-[Re(bqp- $\kappa^3$ N)(CO)<sub>3</sub>]<sup>+</sup> in CH<sub>3</sub>CN. The excited state number is followed by the spin multiplicity, symmetry, excitation energy, and oscillator strength *f*. The excitations from occupied to virtual orbitals are listed on the next line, followed by the wavefunction coefficients.

Excited State 1: Triplet-A 2.4093 eV 514.60 nm f=0.0000 <S\*\*2>=2.000  
111 ->117 0.23437  
112 ->116 -0.16114  
114 ->117 0.23929  
115 ->116 0.56735

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -1468.76243265

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Triplet-A 2.4495 eV 506.16 nm f=0.0000 <S\*\*2>=2.000  
111 ->116 0.26296  
112 ->117 -0.15856  
114 ->116 0.34593  
115 ->117 0.47606

Excited State 3: Triplet-A 3.1290 eV 396.25 nm f=0.0000 <S\*\*2>=2.000  
111 ->116 -0.10650  
113 ->116 0.29310  
114 ->116 0.53732  
115 ->117 -0.23121  
115 ->119 0.14836

Excited State 4: Triplet-A 3.1947 eV 388.09 nm f=0.0000 <S\*\*2>=2.000  
111 ->116 0.12253  
113 ->116 0.52239  
114 ->116 -0.26076  
114 ->118 -0.16384  
115 ->117 0.23328  
115 ->119 0.11587

Excited State 5: Triplet-A 3.2294 eV 383.92 nm f=0.0000 <S\*\*2>=2.000

108 ->116	0.14215
113 ->117	0.10875
114 ->117	0.52890
114 ->119	0.13180
115 ->116	-0.27599
115 ->118	-0.23875

Excited State 6: Triplet-A 3.2939 eV 376.41 nm f=0.0000 <S\*\*2>=2.000

109 ->117	-0.17547
110 ->116	0.15932
112 ->116	0.58686
115 ->116	0.21857
115 ->118	-0.12115

Excited State 7: Triplet-A 3.3560 eV 369.44 nm f=0.0000 <S\*\*2>=2.000

108 ->117	0.12485
109 ->116	-0.25856
110 ->117	0.20038
112 ->117	0.30690
113 ->116	-0.30613
114 ->118	-0.15374
115 ->119	0.30932

Excited State 8: Triplet-A 3.4824 eV 356.03 nm f=0.0000 <S\*\*2>=2.000

109 ->117	0.19645
110 ->116	-0.27290
113 ->117	0.57910
115 ->116	0.11104

Excited State 9: Triplet-A 3.5213 eV 352.10 nm f=0.0000 <S\*\*2>=2.000

108 ->117	0.14717
109 ->116	0.26425
110 ->117	-0.20602
111 ->116	0.31008
112 ->117	-0.19689
112 ->119	-0.13486
113 ->116	-0.15132
114 ->118	-0.20946
115 ->117	-0.23744
115 ->119	0.14217

Excited State 10: Triplet-A 3.6091 eV 343.53 nm f=0.0000 <S\*\*2>=2.000

108 ->116	-0.14351
109 ->117	-0.13195
110 ->116	0.15851
111 ->117	-0.23378
114 ->117	0.31757
115 ->118	0.49181

## Appendix C

### Mulliken Population Analyses of Re(I) Complexes

The Fragment Analysis Based on Mulliken Populations for *fac*-Re(bqp- $\kappa^2N$ )(CO)<sub>3</sub>Cl (**1**) in the Singlet Ground State.<sup>a</sup>

Molecular Orbital	E, eV	Re										CO <sup>b</sup>		bqp- $\kappa^2N^c$		Cl <sup>d</sup>	
		s	P <sub>x</sub>	P <sub>y</sub>	P <sub>z</sub>	d <sub>z</sub> <sup>2</sup>	d <sub>xz</sub>	d <sub>yz</sub>	d <sub>x<sup>2</sup>-y<sup>2</sup></sub>	d <sub>xy</sub>	$\Sigma_{s,p,d}$	$\Sigma_{s,p,d}$	$\Sigma_{s,p,d}$	$\Sigma_{s,p,d}$			
119 (O)	-6.89	0.02	0.03	0.00	0.11	0.09	-0.01	0.46	0.00	0.16	0.53	98.15	0.44				
120 (O)	-6.77	0.02	0.01	0.05	0.03	1.37	0.00	3.15	0.02	0.24	2.13	83.70	9.29				
121 (O)	-6.35	0.06	0.18	0.00	-0.01	0.06	0.02	0.52	0.35	1.40	2.57	94.50	0.33				
122 (O)	-5.88	0.18	0.06	-0.01	0.03	4.19	0.12	15.29	4.83	37.78	26.12	11.24	0.16				
123 (O)	-5.04	0.04	0.61	2.26	0.08	18.24	0.02	9.97	0.27	9.72	20.38	2.84	35.56				
124 (O)	-4.90	0.00	1.23	0.51	0.02	6.54	13.20	11.04	11.05	0.00	20.96	3.82	31.62				
125 (V)	-2.40	0.03	0.32	0.05	0.04	0.09	0.01	0.14	0.40	0.00	1.11	97.52	0.29				
126 (V)	-1.78	0.03	0.05	0.13	0.07	0.00	0.16	0.00	0.00	0.06	1.09	98.40	-0.01				
127 (V)	-1.42	0.03	0.40	0.05	0.01	0.03	0.56	0.01	0.00	0.25	1.72	96.94	0.01				

<sup>a</sup>The orbital occupancy status is given in parenthesis (O = occupied, V = virtual). <sup>b</sup>Sum of the percent population for the three carbon and three oxygen atoms present in the three carbonyl (CO) ligands. <sup>c</sup>Sum of the percent populations for the twenty-three carbon, three nitrogen, and fifteen hydrogen atoms present in the 2,6-bis(quinoline)pyridine (bqp- $\kappa^2N$ ) ligand. <sup>d</sup>Sum of the percent populations for the one chlorine atom present in the chloride ligand.

The Fragment Analysis Based on Mulliken Populations for  $fac-[Re(bqp-\kappa^2N)(CO)_3(NCCCH_3)]^+$  (**2**) in the Singlet Ground State.<sup>a</sup>

Molecular Orbital	E, eV	Re										CO <sup>b</sup>		bqp- $\kappa^2N$ <sup>c</sup>		CH <sub>3</sub> CN <sup>d</sup>	
		s	P <sub>x</sub>	P <sub>y</sub>	P <sub>z</sub>	d <sub>z<sup>2</sup></sub>	d <sub>xz</sub>	d <sub>yz</sub>	d <sub>x<sup>2</sup>-y<sup>2</sup></sub>	d <sub>xy</sub>	$\Sigma_{s,p,d}$	$\Sigma_{s,p,d}$	$\Sigma_{s,p,d}$	$\Sigma_{s,p,d}$			
123 (O)	-9.01	0.04	0.08	0.18	0.03	15.05	7.17	4.88	11.10	3.34	13.94	38.36	5.83				
124 (O)	-8.85	0.01	-0.10	0.04	-0.08	2.71	0.03	32.45	1.19	16.74	17.62	19.81	9.57				
125 (O)	-8.75	0.02	0.05	0.80	0.00	5.60	0.24	0.61	0.09	17.59	13.39	59.54	2.07				
126 (O)	-8.49	-0.01	0.03	0.14	0.19	7.74	0.19	2.82	0.09	9.77	6.64	71.33	1.08				
127 (V)	-5.53	-0.05	0.87	0.80	0.02	0.14	0.12	0.11	0.08	0.09	9.22	88.42	0.17				
128 (V)	-4.52	0.02	1.48	0.10	0.08	0.01	0.05	0.04	0.10	0.05	14.78	82.58	0.71				

<sup>a</sup>The orbital occupancy status is given in parenthesis (O = occupied, V = virtual). <sup>b</sup>Sum of the percent population for the three carbon and three oxygen atoms present in the three carbonyl (CO) ligands. <sup>c</sup>Sum of the percent populations for the twenty-three carbon, three nitrogen, and fifteen hydrogen atoms present in the 2,6-bis(quinoline)pyridine (bqp- $\kappa^2N$ ) ligand. <sup>d</sup>Sum of the percent populations for the two carbon, three hydrogen, and one nitrogen atoms present in the acetonitrile ligand.

The Fragment Analysis Based on Mulliken Populations for *fac*-[Re(bqp- $\kappa^2N$ )(CO)<sub>3</sub>(NC<sub>5</sub>H<sub>5</sub>)]<sup>+</sup> (3) in the Singlet Ground State.<sup>a</sup>

Molecular Orbital	E, eV	Re										CO <sup>b</sup>		bqp- $\kappa^2N^c$		NC <sub>5</sub> H <sub>5</sub> <sup>d</sup>	
		s	P <sub>x</sub>	P <sub>y</sub>	P <sub>z</sub>	d <sub>z</sub> <sup>2</sup>	d <sub>xz</sub>	d <sub>yz</sub>	d <sub>x<sup>2</sup>-y<sup>2</sup></sub>	d <sub>xy</sub>	$\Sigma_{s,p,d}$	$\Sigma_{s,p,d}$	$\Sigma_{s,p,d}$	$\Sigma_{s,p,d}$			
133(O)	-9.11	0.08	0.84	0.19	0.06	17.51	6.44	17.69	1.04	20.90	26.04	8.74	0.47				
134(O)	-9.01	0.07	-0.03	0.65	-0.05	1.97	1.49	21.92	0.80	5.76	14.98	52.08	0.36				
135(O)	-8.92	-0.01	-0.04	0.24	0.07	16.90	2.94	2.01	18.76	20.01	24.83	9.10	5.17				
136(O)	-8.66	0.07	0.05	0.02	0.28	8.92	0.08	10.66	0.11	1.95	7.95	69.58	0.32				
137(V)	-5.18	-0.05	0.18	0.56	0.15	0.01	0.20	0.24	0.08	0.03	1.94	96.21	0.47				
138(V)	-4.46	0.00	0.94	0.56	0.95	0.28	0.15	0.01	0.09	0.14	4.39	8.99	83.50				

<sup>a</sup>The orbital occupancy status is given in parenthesis (O = occupied, V = virtual). <sup>b</sup>Sum of the percent population for the three carbon and three oxygen atoms present in the three carbonyl (CO) ligands. <sup>c</sup>Sum of the percent populations for the twenty-three carbon, three nitrogen, and fifteen hydrogen atoms present in the 2,6-bis(quinoline)pyridine (bqp- $\kappa^2N$ ) ligand. <sup>d</sup>Sum of the percent populations for the five carbon, five hydrogen, and one nitrogen atoms present in the pyridine ligand.



The Fragment Analysis Based on Mulliken Populations for  $\text{fac-[Re(bqp-}\kappa^2\text{N)(CO)}_3\text{(PPh}_3\text{)]}^+$  (4) in the Singlet Ground State.<sup>a</sup>

Molecular Orbital	$E, \text{eV}$	Re										CO <sup>b</sup>		bqp- $\kappa^2\text{N}^c$		PPh <sub>3</sub> <sup>d</sup>	
		s	P <sub>x</sub>	P <sub>y</sub>	P <sub>z</sub>	d <sub>z</sub> <sup>2</sup>	d <sub>xz</sub>	d <sub>yz</sub>	d <sub>xy</sub>	d <sub>x<sup>2</sup>-y<sup>2</sup></sub>	d <sub>xy</sub>	$\Sigma_{s,p,d}$	$\Sigma_{s,p,d}$	$\Sigma_{s,p,d}$	$\Sigma_{s,p,d}$		
181 (O)	-8.92	0.00	0.49	0.18	-0.01	2.97	0.20	2.95	0.01	2.06	2.60	86.80	1.77				
182 (O)	-8.50	0.09	-0.08	0.56	0.14	0.02	0.05	0.80	4.53	10.90	9.37	69.46	4.17				
183 (O)	-8.27	0.46	0.27	0.45	0.82	5.99	3.17	0.46	20.83	4.35	14.49	24.96	23.76				
184 (O)	-8.19	0.09	0.03	0.01	0.16	6.44	3.49	9.14	0.11	12.50	10.98	48.32	8.73				
185 (V)	-5.15	-0.01	0.45	0.80	0.16	0.07	0.44	0.06	0.43	0.07	10.19	82.46	4.88				
186 (V)	-4.33	0.02	2.04	0.21	0.07	0.11	0.03	0.02	-0.01	0.03	19.47	46.91	30.00				

<sup>a</sup>The orbital occupancy status is given in parenthesis (O = occupied, V = virtual). <sup>b</sup>Sum of the percent population for the three carbon and three oxygen atoms present in the three carbonyl (CO) ligands. <sup>c</sup>Sum of the percent populations for the twenty-three carbon, three nitrogen, and fifteen hydrogen atoms present in the 2,6-bis(quinoline)pyridine (bqp- $\kappa^2\text{N}$ ) ligand. <sup>d</sup>Sum of the percent populations for the eighteen carbon, fifteen hydrogen, and one phosphorous atoms present in the triphenyl phosphine ligand.

The Fragment Analysis Based on Mulliken Populations for *fac*-[Re(bqp- $\kappa^3N$ )(CO)<sub>3</sub>]<sup>+</sup> in the Singlet Ground State.<sup>a</sup>

Molecular Orbital	E, eV	Re										CO <sup>b</sup>		bqp- $\kappa^3N$ <sup>c</sup>	
		s	P <sub>x</sub>	P <sub>y</sub>	P <sub>z</sub>	d <sub>z</sub> <sup>2</sup>	d <sub>xz</sub>	d <sub>yz</sub>	d <sub>x<sup>2</sup>-y<sup>2</sup></sub>	d <sub>xy</sub>	$\Sigma_{s,p,d}$	$\Sigma_{s,p,d}$			
112(O)	-9.64	0.07	0.05	0.10	0.08	3.88	4.56	9.13	7.02	4.75	12.96	57.38			
113(O)	-9.43	0.16	0.78	1.02	0.21	0.08	0.40	7.59	5.44	37.54	24.09	22.69			
114(O)	-9.21	0.01	-0.06	-0.01	0.18	15.51	3.25	5.44	9.66	0.00	13.16	52.86			
115(O)	-9.10	0.03	-0.13	0.16	0.68	20.25	0.41	21.57	1.90	2.87	18.41	33.85			
116(V)	-5.34	0.01	0.59	0.46	0.14	0.00	0.39	0.27	0.01	0.00	2.35	95.77			
117(V)	-4.94	0.02	0.02	0.17	0.30	0.08	0.70	0.00	0.12	0.09	1.49	97.01			

<sup>a</sup>The orbital occupancy status is given in parenthesis (O = occupied, V = virtual). <sup>b</sup>Sum of the percent population for the three carbon and three oxygen atoms present in the three carbonyl (CO) ligands. <sup>c</sup>Sum of the percent populations for the twenty-three carbon, three nitrogen, and fifteen hydrogen atoms present in the 2,6-bis(quinoline)pyridine (bqp- $\kappa^3N$ ) ligand.

## Appendix D

### Optimized Geometry of Re(I) Complexes

*fac*-Re(bqp- $\kappa^2$ N)(CO)<sub>3</sub>Cl

Atom	Coordinates		
	X	Y	Z
Re	1.89041	0.44687	-2.7169
C	3.48216	0.23626	-1.6933
C	1.53166	-1.3623	-2.196
C	2.82941	-0.1582	-4.3121
O	1.43932	-2.4559	-1.8062
O	3.43752	-0.5082	-5.2371
O	4.46137	0.07462	-1.0793
N	2.5104	2.59207	-3.2632
C	2.15973	3.16743	-4.4631
C	3.55065	3.10321	-2.6032
C	0.94607	2.80886	-5.1232
C	3.00642	4.15818	-5.0665
C	4.36349	4.14493	-3.0803
H	3.78371	2.65353	-1.6497
C	0.72623	3.31331	-6.4042
C	-0.1926	2.0226	-4.5593
C	2.72178	4.65133	-6.3644
C	4.12024	4.63898	-4.3375
H	5.18678	4.49711	-2.4695
C	1.61369	4.2033	-7.0404
H	-0.1702	3.01358	-6.9357
C	-1.4705	2.56064	-4.7838
N	-0.0298	0.79403	-3.9961
H	3.39404	5.38184	-6.8045
H	4.75865	5.39708	-4.7816
H	1.39381	4.55102	-8.0444
C	-2.5994	1.78407	-4.5686
H	-1.5604	3.57988	-5.1379
C	-1.1244	-0.0199	-3.9392
C	-2.4122	0.45619	-4.2111
H	-3.5937	2.18821	-4.7292
C	-1.012	-1.4847	-3.6857
H	-3.2487	-0.2292	-4.1457
C	-0.3096	-2.3255	-4.6148
C	-1.7557	-2.0736	-2.6762

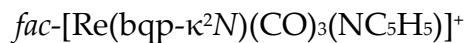
C	-0.3369	-3.7447	-4.4184
N	0.32909	-1.7572	-5.6781
C	-1.7767	-3.4742	-2.4886
H	-2.3272	-1.4437	-2.0024
C	-1.0712	-4.2965	-3.3366
C	0.36493	-4.5527	-5.3504
C	0.95908	-2.5498	-6.5254
H	-2.3554	-3.8929	-1.6709
H	-1.0793	-5.375	-3.2021
C	1.01912	-3.9594	-6.4039
H	0.36755	-5.6319	-5.2211
H	1.45455	-2.0627	-7.364
H	1.56291	-4.5445	-7.1384
Cl	0.80883	1.28655	-0.9063

*fac*-[Re(bqp- $\kappa^2$ N)(CO)<sub>3</sub>(NCCH<sub>3</sub>)]<sup>+</sup>

Atom	Coordinates		
	X	Y	Z
Re	1.19827	-0.1381	0.07812
N	1.43959	1.88861	-0.0307
C	1.38495	2.6051	1.11009
C	1.6208	2.60897	-1.2131
C	1.2731	1.99715	2.50631
C	1.38215	4.00989	1.11783
C	2.03737	2.06718	-2.5828
C	1.46004	4.00861	-1.2436
C	0.52341	0.86338	2.74587
C	1.91381	2.65282	3.54818
C	1.36813	4.7174	-0.066
H	1.36731	4.53602	2.0496
C	3.38023	1.72853	-2.8298
C	1.08856	1.97791	-3.6014
H	1.45421	4.53216	-2.1786
C	0.11885	0.60669	4.06638
N	0.14584	0.05404	1.76707
C	1.69971	2.24853	4.86229
H	2.57529	3.46502	3.33441

H	1.29248	5.7879	-0.0645
C	3.76221	1.34419	-4.1229
N	4.30438	1.85381	-1.8568
C	1.45423	1.48422	-4.8556
H	0.07714	2.27175	-3.4122
C	0.75077	1.25989	5.12814
C	-0.9202	-0.2864	4.30573
C	-0.9578	-0.7254	1.93313
H	2.25082	2.70099	5.65808
C	2.79486	1.17788	-5.1232
C	5.11795	1.16167	-4.4154
C	5.62389	1.77823	-2.1358
H	0.70952	1.34242	-5.6097
H	0.50968	1.00436	6.1361
C	-1.5235	-0.901	3.21477
H	-1.2502	-0.4861	5.30474
H	-1.4058	-1.2197	1.0946
H	3.07974	0.82622	-6.0925
C	6.06116	1.41187	-3.4171
H	5.42916	0.84878	-5.3905
H	6.34464	2.00215	-1.3752
H	-2.3446	-1.5079	3.35126
H	7.10862	1.32701	-3.6282
C	2.9402	-0.3076	1.14291
O	3.99997	-0.4643	1.80588
C	2.29303	-0.5403	-1.6076
O	3.0014	-0.8427	-2.6013
C	0.8464	-2.1469	0.24789
O	0.62969	-3.384	0.35243
N	-0.3395	-0.4212	-1.0437
C	-1.1646	-0.9897	-1.5052
C	-2.218	-1.9403	-2.0177
H	-2.8599	-1.4625	-2.7189
H	-1.7184	-2.762	-2.4922
H	-2.7877	-2.2928	-1.1876

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Atom	Coordinates		
	X	Y	Z
Re	1.19716	-0.29472	-0.05859
N	1.5154	1.96554	-0.07779
C	1.38063	2.64355	1.10129
C	1.68951	2.69408	-1.21768
C	1.30808	1.97258	2.43392
C	1.28993	4.04326	1.13067
C	2.02811	2.06425	-2.53219
C	1.61701	4.08984	-1.22426
C	0.4063	0.90856	2.73864
C	1.99368	2.56275	3.49007
C	1.39029	4.77809	-0.04176
H	1.1149	4.54193	2.07503
C	3.4099	1.85393	-2.84846
C	1.07134	1.88349	-3.514
H	1.74593	4.6142	-2.16371
C	0.07332	0.63675	4.10234
N	-0.14068	0.15957	1.72551
C	1.77074	2.19632	4.83482
H	2.70776	3.35186	3.27874
H	1.3043	5.85963	-0.02935
C	3.76226	1.42568	-4.16748
N	4.34566	2.07562	-1.87926
C	1.4251	1.44288	-4.81175
H	0.02974	2.09447	-3.29455
C	0.7869	1.28439	5.14275
C	-0.97428	-0.27999	4.36424
C	-1.1453	-0.66984	2.01234
H	2.34474	2.67864	5.61909
C	2.74399	1.21877	-5.13463
C	5.1394	1.23112	-4.44799
C	5.61538	1.88146	-2.18776
H	0.64566	1.29695	-5.55319
H	0.54704	1.04541	6.17411
C	-1.62559	-0.88793	3.31502
H	-1.25614	-0.48515	5.39291

H	-1.56724	-1.22185	1.17974
H	3.02396	0.89063	-6.13215
C	6.06949	1.45783	-3.4609
H	5.44051	0.90602	-6.13215
H	6.33887	2.06712	-1.39517
H	-2.45136	-1.57194	3.47258
H	7.13115	1.32089	-3.63831
C	2.7567	-0.54477	1.04949
O	3.70495	-0.71633	-1.69687
C	2.25974	-0.79507	-1.57838
O	2.87225	-1.20606	-2.47669
C	0.77786	-2.16058	0.11985
O	0.53069	-3.2894	0.24242
N	-0.6627	0.07389	-1.28501
C	-1.50715	1.08755	-0.99556
C	-0.9661	-0.71806	-2.33915
C	-2.65715	1.34484	-1.73501
H	-1.24613	1.70409	-0.14509
C	-2.09707	-0.52704	-3.12302
H	-0.27339	-1.52255	-2.55353
C	-2.96275	0.52431	-2.81975
H	-3.29488	2.17591	-1.45527
H	-2.28664	-1.19574	-3.95529
H	-3.85288	0.69922	-3.41553

*fac*-[Re(bqp- $\kappa^2$ N)(CO)<sub>3</sub>(PPh<sub>3</sub>)]<sup>+</sup>

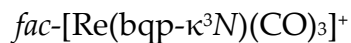
Atom	Coordinates		
	X	Y	Z
Re	0.66746	-0.62419	0.27804
N	1.28265	1.28434	0.56862
C	1.0816	1.87848	1.76601
C	1.8675	2.06244	-0.42336
C	0.5407	1.18	2.9837
C	1.3245	3.24865	1.96405
C	2.5108	1.60141	-1.73604
C	1.9515	3.4674	-0.29885
C	-0.4315	0.17767	2.89163



C	1.0125	1.62537	4.22513
C	1.7017	4.06124	0.91214
H	1.1788	3.68752	2.93596
C	3.7873	1.0374	-1.7285
C	1.8180	1.81296	-2.93661
H	2.2388	4.07765	-1.12765
C	-1.1561	-0.07995	4.05789
N	-0.7052	-0.46532	1.73181
C	0.4410	1.16139	5.40181
H	1.8132	2.31832	4.26161
H	1.7976	5.12546	1.04386
C	4.3851	0.71975	-2.94553
N	4.4474	0.88513	-0.57265
C	2.3702	1.37212	-4.13626
H	0.8463	2.29217	-2.92911
C	-0.6874	0.34941	5.31719
C	-2.3437	-0.7611	3.96911
C	-1.9518	-1.02001	1.58534
H	0.8600	1.42661	6.34858
C	3.6653	0.84094	-4.14543
C	5.7198	0.3192	-2.96628
C	5.7750	0.61659	-0.57041
H	1.8080	1.44023	-5.04046
H	-1.19746	0.05848	6.21591
C	-2.79828	-1.15979	2.70116
H	-2.91557	-0.97661	4.85128
H	-2.28938	-1.34282	0.62571
H	4.11468	0.53885	-5.07014
C	6.43361	0.29714	-1.76634
H	6.19662	0.05287	-3.88785
H	6.33962	0.649	0.33838
H	-3.77078	-1.57226	2.60317
H	7.47892	0.04149	-1.76583
C	1.99492	-1.15115	1.76455
O	2.80183	-1.47147	2.66816
C	1.98462	-1.17043	-1.18175
O	2.82518	-1.56311	-2.0193
C	0.00584	-2.60469	0.16944
O	-0.47042	-3.78008	0.0593
P	-0.56205	0.10076	-1.57208

C	-1.96832	-0.95954	-1.1492
C	-3.07243	-0.44027	-0.46169
C	-1.94453	-2.30427	-1.52901
C	-4.15512	-1.27972	-0.16919
H	-3.09813	0.59096	-0.16658
C	-3.01849	-3.14491	-1.20944
H	-1.10086	-2.6941	-2.06192
C	-4.12699	-2.63183	-0.53708
H	-5.00783	-0.8904	0.33591
H	-2.99144	-4.18142	-1.47876
H	-4.95716	-3.27093	-0.30135
C	0.01404	-0.33252	-3.25461
C	0.8728	-1.41697	-3.45924
C	-0.40406	0.43815	-4.35772
C	1.30424	-1.74431	-4.7548
H	1.19358	-2.00168	-2.62499
C	0.0509	0.12392	-5.64549
H	-1.06695	1.26991	-4.21771
C	0.90004	-0.96973	-5.84525
H	1.93935	-2.591	-4.91222
H	-0.25402	0.71819	-6.47806
H	1.2356	-1.21191	-6.83201
C	-1.09391	1.83543	-1.54837
C	-0.96363	2.6439	-2.68124
C	-1.61458	2.36308	-0.36817
C	-1.37737	3.97705	-2.63488
H	-0.55522	2.23985	-3.57703
C	-1.998	3.70086	-0.30222
H	-1.69802	1.74015	0.49452
C	-1.89088	4.50712	-1.44087
H	-1.30341	4.58659	-3.50955
H	-2.37539	4.10178	0.61596
H	-2.19523	5.52662	-1.39972

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Atom	Coordinates		
	X	Y	Z
Re	1.20281	-0.2903	-0.0737
N	1.51683	1.97056	-0.0869
C	1.37556	2.64794	1.09168
C	1.6941	2.69893	-1.2261
C	1.30139	1.97592	2.42394
C	1.28196	4.04743	1.12015
C	2.03856	2.06729	-2.5378
C	1.61977	4.09461	-1.2331
C	0.4066	0.90485	2.72489
C	1.97917	2.56979	3.48314
C	1.3861	4.78226	-0.0518
H	1.10272	4.5462	2.06367
C	1.26891	0.93881	-2.9708
C	3.18858	2.40967	-3.2251
H	1.75357	4.61926	-2.1716
C	0.07368	0.62544	4.08699
N	-0.134	0.15529	1.70894
C	1.75647	2.19733	4.82644
H	2.68816	3.36443	3.27546
H	1.30021	5.86393	-0.039
C	1.69286	0.21315	-4.1287
N	0.15757	0.5911	-2.2579
C	3.59264	1.69848	-4.3805
H	3.80234	3.23115	-2.8696
C	0.78192	1.27606	5.13035
C	-0.9672	-0.3003	4.34393
C	-1.1341	-0.6811	1.99049
H	2.32488	2.68157	5.61354
C	2.86117	0.62045	-4.8246
C	0.90975	-0.9008	-4.5277
C	-0.5395	-0.4534	-2.6677
H	4.49329	2.0044	-4.9038
H	0.5417	1.03065	6.16048
C	-1.6134	-0.9083	3.2916
H	-1.2472	-0.5121	5.37168

H	-1.5513	-1.2313	1.15457
H	3.17114	0.06325	-5.7048
C	-0.2077	-1.237	-3.8001
H	1.2045	-1.4728	-5.4035
H	-1.4197	-0.7079	-2.079
H	-2.4341	-1.5993	3.44445
H	-0.8309	-2.0819	-4.0743
C	2.75999	-0.532	1.03865
O	3.69928	-0.6857	1.7031
C	2.26361	-0.7905	-1.5957
O	2.87521	-1.2036	-2.4935
C	0.78701	0.10417	-2.1564
O	0.53671	-3.284	0.2309

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