Rapid Synthesis of Ligand-Based Radicals from Chromium(II) Compounds

Addison N. Desnoyer

A Thesis Submitted in Partial Fulfilment of the Requirements for
CHEMISTRY 449

University of British Columbia Okanagan
April 2011
© Addison N. Desnoyer, 2011
Abstract

The existence of metal complexes that contain ligand-based radicals has been known for years, yet has mainly been regarded as a spectroscopic oddity. More recently, the effects of these redox non-innocent ligands on the reactivities of first-row transition metals during catalytic processes has been examined. In an effort to study the reactivities of some of these complexes, a series of octahedral Cr(III) complexes with both redox innocent and non-innocent ligands was synthesized. The square planar Cr(II) compound Cr(DPM)$_2$ was found to be an excellent single electron reductant for a variety of neutral diimines to give the corresponding octahedral Cr(DPM)$_2$(LX•) complexes. In addition, the use of a variety of Cr(II) compounds as single electron reductant prior to protonolysis of the resulting Cr(bpy) complex with a variety of ligands of the form H(R,R′-acac) was found to give the corresponding Cr(R,R′-acac)$_2$(bpy•) complex, allowing for greater tuning of the ancillary ligands. The radical complexes were found to be intensely coloured and air sensitive, and were primarily characterized by UV/vis spectrophotometry. In addition, the complex Cr(DPM)$_2$(bpy•) was found to rapidly and quantitatively react with trityl bromide via an outer-sphere single electron transfer mechanism, generating the trityl radical and the cationic Cr(DPM)$_2$(bpy) complex.
Table of Contents

1. Introduction.................................................................................................................................. 1
2. Results and Discussion .................................................................................................................. 8
3. Conclusion ...................................................................................................................................... 23
4. Experimental .................................................................................................................................. 24
5. References ...................................................................................................................................... 35
6. Appendix ........................................................................................................................................ 38
**List of Figures**

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MO diagram of diimine π system</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>Oxidation states of a diimine ligand</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>Wieghardt's synthesis of mono-and-disubstituted Cr(LX•) complexes</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>Holm's synthesis of Cr(DPM)_2</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>Crystal structure of ZW499</td>
<td>6</td>
</tr>
<tr>
<td>6</td>
<td>Δ and Λ enantiomers of octahedral complexes</td>
<td>6</td>
</tr>
<tr>
<td>7</td>
<td>Synthesis of Cr(DPM)_2</td>
<td>9</td>
</tr>
<tr>
<td>8</td>
<td>Structure of Cr(II) bis-chelate polymer</td>
<td>10</td>
</tr>
<tr>
<td>9</td>
<td>Synthesis of Cr(DPM)_2(bpy•) via SE transfer</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>UV/vis spectrum of Cr(DPM)_2(bpy•) in Et_2O</td>
<td>11</td>
</tr>
<tr>
<td>11</td>
<td>Synthesis of py-imn</td>
<td>13</td>
</tr>
<tr>
<td>12</td>
<td>Synthesis of py-ox</td>
<td>13</td>
</tr>
<tr>
<td>13</td>
<td>Synthesis of Cr(DPM)_2(LX•) complexes via SE transfer</td>
<td>14</td>
</tr>
<tr>
<td>14</td>
<td>Synthesis of Cr(R,R'-acac)_2(bpy•) via protonolysis</td>
<td>16</td>
</tr>
<tr>
<td>15</td>
<td>Synthesis of Cr(R,R'-acac)_2(bpy•) complexes via amide protonolysis</td>
<td>18</td>
</tr>
<tr>
<td>16</td>
<td>Activation of trityl bromide by Cr(DPM)_2(bpy•) via OS-SET</td>
<td>20</td>
</tr>
<tr>
<td>17</td>
<td>Decomposition of the trityl radical in the presence of dioxygen</td>
<td>21</td>
</tr>
<tr>
<td>18</td>
<td>Movassaghi's dimerization of br-hpl</td>
<td>22</td>
</tr>
<tr>
<td>19</td>
<td>Synthesis of [Cr(DPM)_2(bpy)]I</td>
<td>23</td>
</tr>
</tbody>
</table>
**List of Abbreviations**

The following is a list of abbreviations and symbols employed in this Thesis, most of which are in common use in the chemical literature.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ad</td>
<td>adamantyl, tricyclo[3.3.1.1]decanyl, C\textsubscript{10}H\textsubscript{15}</td>
</tr>
<tr>
<td>Ar</td>
<td>aryl</td>
</tr>
<tr>
<td>t\textsubscript{Bu}</td>
<td>tert-butyl, C\textsubscript{4}H\textsubscript{9}</td>
</tr>
<tr>
<td>°C</td>
<td>degrees Celsius</td>
</tr>
<tr>
<td>δ</td>
<td>chemical shift</td>
</tr>
<tr>
<td>Cp</td>
<td>η\textsuperscript{5}-cyclopentadienyl, C\textsubscript{5}H\textsubscript{5}</td>
</tr>
<tr>
<td>D</td>
<td>deuterium, \textsuperscript{2}H</td>
</tr>
<tr>
<td>d</td>
<td>doublet, or days</td>
</tr>
<tr>
<td>Dpp</td>
<td>2,6-diisopropylphenyl, C\textsubscript{12}H\textsubscript{17}</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl, C\textsubscript{2}H\textsubscript{5}</td>
</tr>
<tr>
<td>Et\textsubscript{2}O</td>
<td>diethyl ether (C\textsubscript{4}H\textsubscript{10}O)</td>
</tr>
<tr>
<td>EtOAc</td>
<td>ethyl acetate (C\textsubscript{4}H\textsubscript{8}O\textsubscript{2})</td>
</tr>
<tr>
<td>equiv</td>
<td>equivalents</td>
</tr>
<tr>
<td>g</td>
<td>grams</td>
</tr>
<tr>
<td>h</td>
<td>hours</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz (s\textsuperscript{-1})</td>
</tr>
<tr>
<td>J</td>
<td>coupling constant (Hz)</td>
</tr>
<tr>
<td>L</td>
<td>neutral, 2e donor ligand, or litre (10\textsuperscript{3} m\textsuperscript{3})</td>
</tr>
<tr>
<td>M</td>
<td>molar (mol·L\textsuperscript{-1}), or metal</td>
</tr>
<tr>
<td>m</td>
<td>multiplet</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>Me</td>
<td>methyl, CH₃</td>
</tr>
<tr>
<td>mg</td>
<td>milligram, 10⁻³ g</td>
</tr>
<tr>
<td>min</td>
<td>minutes</td>
</tr>
<tr>
<td>µL</td>
<td>microlitre (10⁻⁶ L)</td>
</tr>
<tr>
<td>mL</td>
<td>millilitre (10⁻³ L)</td>
</tr>
<tr>
<td>µmol</td>
<td>micromole (10⁻⁶ mole)</td>
</tr>
<tr>
<td>mmol</td>
<td>millimole (10⁻³ mole)</td>
</tr>
<tr>
<td>mol</td>
<td>mole (6.022·10⁻²³ particles)</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>OTf</td>
<td>triflate, CF₃SO₃⁻</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl, C₆H₅</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>py</td>
<td>pyridyl, C₅H₄N</td>
</tr>
<tr>
<td>q</td>
<td>quartet</td>
</tr>
<tr>
<td>R</td>
<td>alkyl</td>
</tr>
<tr>
<td>RO</td>
<td>reverse osmosis</td>
</tr>
<tr>
<td>RT</td>
<td>room temperature</td>
</tr>
<tr>
<td>s</td>
<td>singlet</td>
</tr>
<tr>
<td>t</td>
<td>triplet</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran (C₅H₄O)</td>
</tr>
<tr>
<td>X</td>
<td>halide; or anionic, 1e donor ligand</td>
</tr>
<tr>
<td>Xyl</td>
<td>2,6-dimethylphenyl, C₈H₉</td>
</tr>
</tbody>
</table>
Acknowledgements

A special thanks goes out to Dr. Kevin Smith, for his never-ending patience, continuous stream of new ideas and infectious enthusiasm. I thank both Cory MacLeod and Wen Zhou for their helpful advice and guidance during this project. I should also thank Cory for his daily inquiries as to the status of this Thesis, which certainly aided the writing process. Looming due dates can be excellent motivational tools.

I would also like to thank everyone in the Smith and McNeil Research Groups for making the lab a fun place to explore the wonders of nature, without blowing too many things up along the way.

Finally, I would like to acknowledge my Mum and Dad, for always supporting me in whatever direction I chose to go.

Oh, and a big thank you to anyone who has ever bought me coffee. I would not have made it this far without it.
Quotations

“…he stood dumbfounded, amazed by the stubborn fidelity of matter.”

-Lois McMaster Bujold, *The Curse of Chalion*

“Can’t stop the spirits when they need you,

This life is more than just a read through”

- The Red Hot Chili Peppers, *Can’t Stop*
1. Introduction

The production of a wide variety of compounds on an industrial scale hinges on the reactivity of metal catalysts. The most effective of these catalysts are based around the “noble metals” such as rhodium, palladium and platinum. These metals tend to react via well-defined two electron processes, often with changes to the oxidation state of the metal centre. The most common example of these involves the oxidative addition/reductive elimination steps that are quite often required during the catalytic cycles of many organometallic reactions.\(^1\) Unfortunately, the cost of these noble metals is prohibitively high, which has spurred research into their possible substitution using more readily abundant metals.

Metals from the first row of the transition block, such as Fe, Cr and Co, are excellent candidates to replace noble metals. These “base metals”, however, tend to favour single electron (SE) processes over two electron processes.\(^2\) In fact, many metalloenzymes utilize this SE reactivity for biocatalysis. Galactose oxidase and vitamin B\(_{12}\) are perhaps the most notable and well-studied examples of metalloenzymes that utilize SE reduction/oxidation, or redox, during their respective catalytic mechanisms.\(^3\)

A common theme among the active sites of these enzymes is the presence of an extended \(\pi\) network. The delocalization of the \(\pi\) symmetry orbitals among the numerous atoms in the conjugated system allows for the lowering of the overall energy of these molecular orbitals (MOs). A consequence of this orbital symmetry is that the energy required to either reduce or oxidize these ligands is much lower than the corresponding energy required to alter the electronic structure of many of the classic ligands in inorganic chemistry. These redox active ligands are termed “redox non-innocent”, and have been heavily investigated by spectroscopists seeking insight into the unusual structure and bonding of their compounds.\(^2\)
Unlike the redox changes typically associated with metal centres, where the removal/addition of an electron occurs in the metal-based d-orbitals, redox changes of metal complexes that contain non-innocent ligands involve the formation of a radical species, that is, a compound where a single unpaired electron is localized along the atoms of the ligand backbone. Qualitatively, the energy required to add a single electron to the \( \pi \) system of these non-innocent ligands, dubbed the reduction potential, can be traced to the stability of the radical formed. Diimines and quinones are two classes of ligands that are especially efficacious at stabilizing radical species by delocalizing the radical along their conjugated network of \( \pi \) bonds.\(^2\)

Figure 1 - MO diagram of diimine \( \pi \) system
The general molecular orbital (MO) description of the $\pi$ system of a radical LX• diimine ligand is shown in Figure 1. The model calls for the placement of the unpaired electron in an orbital that is $\pi$ antibonding with respect to the C=N double bond of the ligand, but one that is also $\pi$ bonding with respect to the two C atoms. Thus, a useful tool for the determination of radical character is comparison of the bond lengths of the reduced ligand to that of the neutral ligand. Convenient representations of the various possible oxidation states of a diimine ligand are shown in Figure 2.⁴

![Figure 2- Oxidation states of a diimine ligand](image)

Octahedral Cr(III) complexes provide a particularly useful framework for studying ligand-based radicals, as these complexes have strong metal-ligand bonds, slow dissociation rates and effective antiferromagnetic coupling between the single unpaired electron of the ligand and the three non-bonding chromium-based electrons.⁵ Antiferromagnetic coupling is a through space interaction where the spin of one species will affect the spin of another, resulting in an overall decrease in the magnetic moment through the coupling of the two species. In addition, redox changes at the non-innocent ligand will result in minimal structural changes of the overall complex due to the relative inertness of the overall structure, which will facilitate electron transfer processes.⁶

A common method for the synthesis of M(LX•) complexes involves the reduction of a neutral diimine with metallic sodium, followed by metathesis of the $in situ$ generated monoanion
on the appropriate metal salt. This method has been used for the preparation of bis(α-imino-
pyridine) complexes of Cr, Fe, Zn and Mn, all of which have been determined by a myriad
of spectroscopic techniques to consist of a divalent metal centre and two monoanion radical
ligands. Unfortunately, this method is a poor general synthetic approach, as both mono-and-
disubstitution of the metal centre during metathesis can occur based on the stoichiometry. In
addition, the sodium metal can also act as a reductant on the Cr(III) centre. For example,
reduction of ArNCRCR’NAr where Ar = Xyl, R = H and R’ = Me with additional sodium gave
the disubstituted Cr(II) complex following metathesis, while the diimine where Ar = Dpp and R
= R’ = Me gave the monosubstituted Cr(III) complex under similar reaction conditions.8

\[
\text{Cr(acac)}_3 + \begin{array}{c}
\text{Ar} \\
\text{R} \\
\text{R'}
\end{array} \xrightarrow{\text{Na}} \text{Cr}^{III}(\text{acac})_2(\text{LX}^\bullet) \quad \text{Ar = Dpp} \\
\text{R = R'} = \text{Me}
\]

\[
\text{Cr(acac)}_3 + 2 \begin{array}{c}
\text{Ar} \\
\text{R} \\
\text{R'}
\end{array} \xrightarrow{3 \text{ Na}} \text{Cr}^{II}(\text{LX}^\bullet)_2 \quad \text{Ar = Xyl} \\
\text{R = Me} \\
\text{R' = H}
\]

Figure 3- Wieghardt's synthesis of mono-and-disubstituted Cr(LX•) complexes

Theopold et al. report a gentler route for the synthesis of diimine LX• complexes, using
Cr(II) as the reductant instead of sodium. Unlike the previous method, even smaller Ar groups
do not induce disubstitution of Cr centre. In addition, the overall stability of octahedral Cr(III)
complexes will prevent further reactivities from occurring once the redox has taken place. This
synthetic methodology allows for a greater degree of steric tuning of the LX• ligand, as well as a
more general route to the preparation of a wider variety of possible monosubstituted LX• complexes. Thus, the ability of the Cr(II) centre to reduce redox non-innocent ligands offers the possibility of a promising synthetic route to the controlled synthesis of well-defined Cr(III) LX• complexes.4

A useful class of ancillary ligands for these desired radical compounds is the acetylacetonates, which are both redox innocent and historically well-studied. They also have the advantages of strong metal-ligand bonds, with poor ligand lability. Holm and co-workers have reported that the majority of these bis-chelate complexes of Cr(II) are actually polymeric in both the solid phase and in non-coordinating solvents, and that only the derivative substituted with bulky 1Bu groups is square planar and monomeric both in the solid state and in solution.9

![Chemical structure and reaction scheme](image)

Figure 4- Holm's synthesis of Cr(DPM)$_2$

Thus, Holm’s compound was identified as an ideal SE reductant for neutral bidentate ligands. Preliminary experiments by Wen Zhou, using the square planar Cr(II) compound and a diimine of the form [XylN(CMe)$_2$]$_2$ resulted in the isolation of a promising octahedral Cr(III) compound, ZW499, whose crystal structure is given in Figure 5.10
The crystals are highly disordered, a phenomenon attributed to co-crystallization of the various Δ and Λ enantiomers. Although the complex itself contains no chiral atoms, the relative orientation of the bidentate ligands induces the “handedness” of the complex.\textsuperscript{11}

Figure 5- Crystal structure of ZW499

Figure 6 demonstrates the different enantiomers possible with tris(bidentate) octahedral complexes. The stereochemistry of a particular complex can be found by rotating the octahedron so that three donor atoms, one from each ligand, form the points of a triangle. The direction of the twist of the ligand, that is, the direction of the helix formed going from the front donor atom to the back donor atom along the ligand backbone, gives the enantiomeric designation. A

Δ enantiomer     Λ enantiomer
complex that twists to the right is designated Δ (from the Latin *dextro*), while a complex that twists to the left is designated Λ (from the Latin *laevo*).11

Thus, Holm’s complex offers several clear advantages as a synthetic precursor, notably the expected solubility in non-polar solvents due to the presence of the large alkyl groups. In addition, the fact that the tBu groups are fairly removed from the Cr atom hints that 1H NMR spectroscopy could be a useful characterization technique despite the paramagnetism of the Cr centre. Unfortunately, the use of these specific ligands has also been found to encourage co-crystallization of both the Δ and Λ enantiomers, leading to disordered crystals containing multiple polymorphs that are difficult to study using single crystal X-ray diffraction studies,12,13 the primary characterization technique for paramagnetic organochromium chemistry.

An interesting consequence of the addition of a chiral bidentate chelate to the octahedron involves the potential to control the stereochemistry of the resulting complex. This could allow for altered reactivity of the compound, and may improve the quality of the crystals obtained to allow for less problematic structural analysis via X-ray diffraction studies. In addition, the low cost associated with chiral amino alcohols points to their potential usefulness as starting materials for the synthesis of chiral bidentate ligands.14

The C-C and C-N bond lengths of the diimine ligand of ZW499 are remarkably similar to those reported by both Theopold and Wieghardt for their LX• complexes,4,8 which supports the successful SE reduction of the diimine. In particular, the C-N bond is longer than that found in the neutral, uncoordinated ligand, while the C-C bond is shorter. In addition, ZW499 is intensely coloured in solution, which is also a hallmark of LX• complexes as a consequence of the transitions that the radical can undergo. These transitions result in distinctive UV/vis absorbance
bands, especially in the near infrared region. The exact transitions that a LX• radical can undergo can be calculated using time-dependent density functional theory (DFT).

Thus, while traditional characterization techniques like NMR and X-ray crystallography are rendered less than effective by the paramagnetism of the Cr(III) and the disorder inherent in the crystals from the ancillary ligands, the presence of the unpaired electron on the ligand allows for a distinctive spectroscopic handle for the characterization of octahedral Cr(III) LX• complexes through UV/vis spectrophotometry.

Recent catalytic systems for organic synthesis that include bipyridine and phenanthroline, as well as some of their substituted derivatives, have been shown involve radical intermediates. In addition, the systems have demonstrated remarkably similar results for a wide range of first-row transition metals, and in some cases the presence of a transition metal is not even necessary if the reaction is performed at high temperature. This suggests that the key to the reactivity is not the transition metal, but rather the LX• group.

Thus, the use of well-defined Cr(R,R’-acac)2(LX•) offers the possibility of mimicking the reactivity observed for other LX• systems, but with the added potential benefits of performing the reaction at lower temperatures, controlling the stereochemistry of the organic product through use of chiral ligands as well as improving the selectivity for a specific substrate by changing the reducing power of the LX• complex through modification of the LX• and ancillary ligands.

2. Results and Discussion

The goal of this research project was to examine the synthesis, characterization and reactivity of octahedral Cr(III) complexes that contain both redox innocent and non-innocent ligands. Initial experiments with the square planar complex Cr(DPM)2, where DPM is the anion
of dipivaloylmethane, have shown it to be a promising candidate for the SE reduction of diimine-type ligands, generating the octahedral LX\(^-\) complex upon chelation.

The synthesis of Cr(DPM)\(_2\) followed the literature procedure with slight modifications.\(^9\) To a stirring solution of 2 equiv of dipivaloylmethane (HDPM) in THF was added 2 equiv of \(^n\)BuLi in hexanes. After stirring for 2 h at room temperature, 1 equiv of CrCl\(_2\) was added and the resulting red-brown solution was stirred overnight. Following removal of the solvent \textit{in vacuo} and extraction with hexanes, Cr(DPM)\(_2\) was isolated as dark brown crystals following recrystallization from hexanes.\(^9\)

![Synthesis of Cr(DPM)\(_2\)](image)

Figure 7 - Synthesis of Cr(DPM)\(_2\)

The Cr(DPM)\(_2\) compound is a useful precursor for multiple reasons. First, the bulky \(^{1}\)Bu groups should increase the solubility of any resulting complexes in non-polar, non-coordinating solvents. Secondly, the DPM derivative is the only acetylacetonate (acac) derivative of Cr(II) that is monomeric in both the solid state and in solution, as the other, less bulky bis-chelate compounds were found to oligomerize.\(^9\) It was initially believed that this was due to a secondary interaction of the open coordination site of one Cr monomer with the O atom of another monomer. However, a later study by Cotton et al. concluded that the tendency of the less bulky bis-chelates to polymerize was due to interactions of the electron-rich methines of the ligands with the Cr centre of another monomer, giving a pseudo-octahedral geometry and a stacked polymer.\(^{18}\) Thus, the presence of the sterically demanding \(^{1}\)Bu groups in Cr(DPM)\(_2\) are required to shield the methine carbons from interacting with other Cr atoms.
A prime candidate for reduction by Cr(II) is 2,2’-bipyridine (bpy), which shares the diimine framework outlined in Figure 1, but also has a more extensive π system, which should allow for a more energetically favoured reduction to form the desired monoanionic radical species. π Radicals of bpy are also fairly common in the literature, having made appearances bound to transition metals, main group elements, lanthanides and actinides.¹⁹⁻²³

Addition of bpy to a solution of Cr(DPM)₂ in Et₂O or toluene results in an immediate colour change from brown to an intensely dark green. The UV/vis spectrum of the complex in Et₂O or
toluene shows a fairly complex set of absorbance bands, most notably the strong band in the near-IR region, which is characteristic of ligand-based radicals complexes. The green solution is also quite air sensitive, as exposure to air causes an immediate fading of the green colour to colourless. In addition, all the absorbance bands in the UV/vis spectrum disappear as well.

![UV/vis spectrum of Cr(DPM)$_2$(bpy•) in Et$_2$O](image)

Figure 10- UV/vis spectrum of Cr(DPM)$_2$(bpy•) in Et$_2$O

Paramagnetic $^1$H NMR analysis of the dark green solution, generated by the addition of bpy and Cr(DPM)$_2$ to C$_6$D$_6$, gave a spectrum that showed the typical broadness and low signal intensity of paramagnetic compounds. It was hoped that the methyl protons of the $^1$Bu group would be far enough removed from the metal centre that a more definitive signal would be observed from them. Unfortunately, this was not the case. The spectrum did show a broad peak centred around 2.5 ppm, as well as a small peak around 17 ppm, but nothing diagnostic could be ascertained as to the structure of the complex.
The colour and behaviour of the green solution support the formation of the desired radical complex in situ. However, isolating the complex proved difficult. After removing the Et₂O solvent in vacuo, the extraction of the green residue with hexanes was attempted. Dissolution of the residue in hexanes unexpectedly incited a colour change from green to brown, and after standing at -35 °C a pale brown solid was isolated. Redissolving this brown product in Et₂O did not cause the colour to change back to green, indicating that the brown product is a decomposition product of the radical complex. Indeed, the UV/vis spectrum of the brown product shows a very different set of absorbance peaks, confirming that the original green complex had undergone further reaction.

Attempted recrystallization of the complex from Et₂O also proved fruitless. Concentrating a fresh solution of Cr(DPM)₂(bpy•) and storing it at -35 °C resulted in no precipitate formation. In addition, the solution changed colour from green to brown after 17 d, indicating that the complex is relatively unstable in solution even without changing solvents.

Despite the difficulties isolating the bpy radical complex, the method of direct addition of a bidentate L₂ ligand to Cr(DPM)₂ seemed to result in a very rapid and very clean reaction. This type of reaction is quite practical for the synthetic chemist, as there are no unwanted byproducts that must be removed by work-up. To explore the scope of diimines that can react with Cr(DPM)₂ to give octahedral radical complexes, a variety of related diimines and quinones were reacted with Cr(DPM)₂ and analyzed spectroscopically via UV/vis.

The bidentate ligand 2-(2′-pyridyl)imidazoline (py-imn) has previously been used as a ligand for hydrogen atom transfer (HAT) reactions,24 and also has the diimine framework found in bpy. The imidazoline, however, has a less expansive π system, and so should result in a less stable radical complex than the corresponding bpy• complex.
The ligand was prepared following slight modifications to the literature procedure. A substoichiometric amount (1/4 of an equiv) of elemental S was added to an equiv of 2-pyridylcarbonitrile (pyCN) and refluxed for 6 min in ethylenediamine. After cooling to RT, the resulting green solution was diluted with cold RO water and extracted with CH$_2$Cl$_2$. The combined organic extracts were dried, and the solvent was removed in vacuo to give a yellow solid, which was purified by recrystallization from boiling ligroine.

A second bidentate ligand, 4,4-dimethyl-2-(2’pyridyl)oxazoline (py-ox), was also identified as a ligand that should give a radical species less stable than the bpy• complex. Besides sharing the same π framework as py-imn, the py-ox contains geminal methyl groups which should provide additional steric strain on the metal centre. In addition, the presence of the O atom in place of the NH group should further destabilize the radical.

The synthesis of py-ox followed the general procedure used for py-imn, but with a few modifications. A substoichiometric amount (1/4 of an equiv) of elemental S and an equiv of pyCN were dissolved in 2-amino-2-methylpropanol and refluxed for 1 h. After work-up, the crude product was isolated as a dark brown oil, which was shown to be mostly the desired
product by $^1$H NMR. The crude oil was purified by elution on a silica column using 2 : 1 EtOAc/hexanes, giving the py-ox as a thick yellow oil.

The quinones examined yielded solutions that were quite pale compared to the others. In addition, the UV/vis spectra of these complexes showed no near IR absorbance bands, and were insensitive to air exposure. Thus, it seems unlikely that the desired radical species were formed; or if they were, they are not persistent enough in solution to be detected before decomposing.
The $L_2$ ligands that contain at least one N donor atom, in contrast, all formed darkly coloured solutions when added to Cr(DPM)$_2$. The UV/vis spectra of these coloured solutions all show absorbance bands above 800 nm, and all are air sensitive, indicating that the desired radical complexes have been formed.

The results of these experiments indicate that Cr(DPM)$_2$ can successfully reduce a variety of diimine-type ligands to give the corresponding octahedral ligand-based radical complexes. These reactions are quite clean and very rapid, occurring almost instantly even at dilute concentrations. Unfortunately, these SE transfer reactions are only suitable with the Cr(DPM)$_2$ compound, because the other bis-chelates of Cr(II) are polymeric.$^9$

An alternate synthetic route to the desired Cr(III) complexes involves the reduction of a bidentate $L_2$ ligand by a different Cr(II) compound to give the desired LX• complex, followed by protonolysis of the ancillary ligands of the Cr(III) complex with 2 equiv of a neutral, protonated acac-type ligand.
This method allows for the alteration of the R and R’ groups of the acac ligands, allowing for another handle to tune both the steric and electronic properties of the final Cr(III) complex. This method also affords relatively innocuous byproducts, avoiding many of the ionic byproducts common to metathesis reactions that often require an additional purification step before isolation. A downside of this approach is the relative slowness of the reaction when compared to the electron-transfer reactions examined previously.

The first Cr(II) protonolysis precursor examined was Cp₂Cr. Addition of bpy to a solution of Cp₂Cr in Et₂O resulted in the expected increase in the intensity of the colour of the brown solution. Treating an aliquot of this solution with HDPM resulted in no immediate colour change, but after stirring for ca. 5 minutes, the colour changed from dark brown to the expected dark green. UV/vis analysis of this solution shows a mixture of the peaks characteristic of
Cr(DPM)$_2$(bpy•), as well as residual peaks from unreacted Cp$_2$Cr(bpy•). This highlights the slowness of the protonolysis method relative to the SE transfer method.

After standing overnight, the solution of Cp$_2$Cr(bpy•) had developed a fine precipitate, which would not dissolve despite vigorous mixing. It was determined that despite the success of the protonolysis reaction, another Cr(II) precursor should be examined. Cr[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ was chosen as a second protonolysis precursor because it is both easily prepared and the presence of the additional alkyl groups should increase the solubility of any resulting complexes in Et$_2$O.
Addition of bpy to a dilute solution of Cr\([\text{N(SiMe}_3\text{)}_2]\)\(_2\)(THF)\(_2\) in Et\(_2\)O caused an immediate colour change from essentially colourless to a very dark purple. This substantial colour change has been noted previously\(^{26}\). The species generated, Cr\([\text{N(SiMe}_3\text{)}_2]\)\(_2\)(bpy), has been previously synthesized and characterized by Wen Zhou. Addition of aliquots of this solution to an excess of protonated acac-type ligands resulted in a distinct colour change after stirring for ca. 1 h. Of note is the fact that all the acac ligands with either one or two electron-donating substituents are green, while those with two electron-withdrawing groups are brown.
All of the complexes generated are quite air-sensitive, and all except the CF$_3$/Ph ligand show near IR absorbance bands around 865 nm.

Despite the paramagnetism of the Cr(III) complexes, the progress of these protonolysis reactions can be monitored via $^1$H NMR by the formation of the diamagnetic byproducts. For example, a sample of Cr[N(SiMe$_3$)$_2$]$_2$(bpy•) dissolved in C$_6$D$_6$ gives a rather unattractive spectrum which shows broad paramagnetic peaks at approximately 48, 42 and 17 ppm, typical for high spin Cr bis(trimethylsilyl)amido complexes. As is to be expected, the solvent peak due to residual C$_6$D$_5$H is by far the most prominent feature of the spectrum. However, after the addition of HDPM, the solution changes from purple to green, and no longer shows the previous paramagnetic peaks, instead displaying a broad hump at approximately 2.5 ppm previously ascribed to Cr(DPM)$_2$(bpy•). Indeed, the most prominent peak in the spectrum is no longer the residual solvent peak, but a large singlet at close to 0 ppm attributed to the methyl groups of the hexamethyldisilazane byproduct. A less prominent singlet attributed to the $^t$Bu groups of unreacted HDPM can also be observed. An interesting experiment for future work with these reactions would involve time-dependent NMR studies to determine the rate constants associated with these protonolysis reactions, as the colour change observed is much slower than the NMR timescale.

Another interesting note from this series of experiments was the fact that although the Cr(Me,Me-acac)$_2$(bpy•) complex displays almost identical UV/vis absorbance bands to those of Cr(DPM)$_2$(bpy•), the colour of the Me,Me-acac complex faded after ca. 3 h, while the DPM complex is stable in solution for days. The identical absorbance bands indicate that the difference between the stabilities of the complexes is likely due to a steric, rather than an electronic effect. A possible mechanism for the decomposition of the Me,Me-acac complex could be a bimolecular
one. In addition, the fact that the Me,Me-acac complex decomposes to a colourless solution while the DPM complex decomposes to a brown one could indicate the presence of multiple decomposition pathways for these complexes.

An appealing aspect of both the SE transfer reactivity of Cr(DPM)$_2$ as well as the protonolysis methods examined is that they do not require the changing of solvents or the removal of ionic salt byproducts. This highlights their usefulness for high throughput screening, as the complexes can be rapidly generated in situ and do not require time-consuming work-up steps before they can undergo additional reactivity.

The radical of Cr(DPM)$_2$(bpy•) resides in a $\pi^*$ antibonding orbital which is comprised almost solely of bpy orbital character. This is in sharp contrast to the various other CpCr(LX•) complexes studied in the Smith Group, where the presence of the Cp ring causes a bleed of Cp orbital character into the MO occupied by the radical. As such, Cr(DPM)$_2$(bpy•) was predicted to undergo different modes of reactivity than other previously examined complexes, most notably outer-sphere single electron transfer (OS-SET) of alkyl halides.$^{28}$

![Figure 16- Activation of trityl bromide by Cr(DPM)$_2$(bpy•) via OS-SET](image.png)

Addition of Cr(DPM)$_2$(bpy•) to a hexanes solution of trityl bromide results in an instant fading of the characteristic dark green colour of the complex and the formation of a bright pink
precipitate. After filtering the slurry through celite to remove the pink solid, UV/vis analysis of the clear, colourless hexanes solution showed the absorbance band characteristic of the trityl radical. Indeed, air exposure of the solution caused the band to fade, again consistent with the decomposition of the trityl radical in oxygen to give a tritylperoxide compound. The UV/vis spectra of the solution before and after air exposure is shown in Appendix 6.1

\[ \text{Ph}_{3}C \rightarrow \text{Ph}_{3}CO \]

Figure 17- Decomposition of the trityl radical in the presence of dioxygen

Kanno and co-workers have reported that the Cr(III) salt \([\text{Cr(Me,Me-acac)}_{2}(\text{bpy})]\)Cl is a pink solid, acquired from heating \(\text{Cr(Me,Me-acac)}_{3}\) and bpy in concentrated HCl for 2 d. The presence of the pink solid, which is quite insoluble in hexanes, supports the formation of the ionic complex \([\text{Cr(DPM)}_{2}(\text{bpy})]\)Br, which in turn supports the OS-SET mechanism of reactivity predicted for \(\text{Cr(DPM)}_{2}(\text{bpy})\).

In order to test the ability of \(\text{Cr(DPM)}_{2}(\text{bpy})\) to activate a more robust C-X bond via OS-SET, the radical complex was reacted with bromohexahydropyrrolloindole (br-hpl), which was prepared by Caitlyn Liberto during the course of her Honours Thesis. Movassaghi and co-workers have reported that the br-hpl reacts with stoichiometric \(\text{Co(PPh}_{3}\))Cl to give the organic dimer, possibly through bromide atom abstraction to form the hpl organic radical, which will then undergo a coupling reaction to give the dimer. It was expected that \(\text{Cr(DPM)}_{2}(\text{bpy})\) would mimic this proposed mechanism, generating the hpl dimer following radical formation via bromide abstraction.
The radical complex Cr(DPM)$_2$(bpy•) was generated \textit{in situ} by the addition of Cr(DPM)$_2$ to bpy in C$_6$D$_6$. To this dark green solution was added an equiv of br-hpl, resulting in an immediate colour change from green to red, and the formation of a slightly soluble pink residue. Addition of a few drops of the reaction mixture to ca. 5 mL of hexanes resulted in the formation of a light pink precipitate, which was collected by filtration through celite. However, the supernatant of this solution was still unexpectedly pink. This is in contrast to the complete precipitation of the pink complex observed from the reaction with trityl bromide. In addition, the C$_6$D$_6$ solution was still a dark red colour following filtration, a dramatically different result from the complete colour fading observed from the reaction with trityl bromide. This could be indicative of a slower overall reaction due to the stronger C-Br bond of br-hpl, or it could signal that the complex has undergone further undesired reactivity. Unfortunately, paramagnetic $^1$H NMR analysis of the reaction mixture was inconclusive as to the fate of the organic fragment.
Cr(DPM)$_2$(bpy$$^•$$) was also tested for its ability to act as an electron source by mechanisms other than activation of C-X bonds via reaction with elemental I$_2$. To a dark green solution of Cr(DPM)$_2$ and bpy in hexanes was added 0.5 equiv of I$_2$, resulting in no immediate colour change. After stirring for ca. 30 min, the solution had developed a fine pink precipitate. After stirring overnight, the precipitate was isolated via vacuum filtration and washed with hexanes. The pink solid, which is hexanes insoluble, is again consistent with the formation of a [Cr(R,R’-acac)$_2$(bpy)] halide salt. The filtrate was still a green colour, indicating that unreacted Cr(DPM)$_2$(bpy$$^•$$) remained despite the long reaction time. It is possible that after the initial reduction of I$_2$, the iodide formed reacted with residual I$_2$ to give the triiodide anion, which may have interfered with any further reduction of I$_2$.

3. Conclusion

In an effort to investigate the reactivity of Cr complexes with ligand-based radicals, a synthetic route involving the use of a square planar Cr(II) compound as a single electron reductant on a variety of diimines and quinones was examined. The complexes formed were characterized by UV/vis spectroscopy, and it was determined that Cr(DPM)$_2$ was indeed an
effective reductant for the clean and rapid generation of octahedral Cr(III) L• complexes with diimines but not with quinones.

An alternate method for the generation of octahedral L• complexes via protonolysis was also examined, and was found to successfully give the corresponding Cr(R,R’-acac)₂(bpy•) complexes. This method allows for greater tuning of the ancillary ligands, but does require longer reaction times. In addition, the steric.s of the ancillary ligands was found to have a marked effect on the stability of some of the complexes.

Cr(DPM)₂(bpy•) was found to rapidly and quantitatively activate trityl bromide via OS-SET to give the trityl radical and the corresponding cationic Cr(DPM)₂(bpy) complex. However, attempts to apply this reactivity to br-hpl resulted in inconclusive results, as the organic fragment remained uncharacterized despite the formation of the cationic Cr(DPM)₂(bpy) complex. In addition, Cr(DPM)₂(bpy•) was found to undergo slow and incomplete oxidation by I₂, possibly due to interference from the triiodide anion.

4. Experimental

General Methods

All of the reactions, with the exceptions of the syntheses of 2-(2’-pyridyl)imidazoline and 4,4-dimethyl-2-(2’-pyridyl)oxazoline, were carried out in anhydrous, oxygen-free conditions using an inert-atmosphere glovebox complete with active oxygen and moisture removing catalyst columns. The THF, Et₂O, hexanes and toluene solvents were made anhydrous using Grubbs/Dow columns. Anhydrous “sure-seal” grade reagents, such as n-butyllithium in hexanes, were purchased from Aldrich and used as received. If not otherwise stated, the reagent was purchased from Aldrich and used as received.
UV/vis spectra were collected using a Varian Cary 50 Bio UV/vis spectrophotometer with air-tight UV/vis cells. NMR data were collected on a Varian 400 MHz Mercury Plus Spectrometer using J Young air sensitive NMR tubes when required.

Chromocene, Cr(N[SiMe₃]₂)₂(bpy•) and [XylNCMe]₂ were prepared and provided by Wen Zhou.¹⁰

AD95 \[ \text{CrCl}_2 + 2 \text{HDPM} + 2 \text{nBuLi} \]

The Cr(DPM)₂ was prepared following slight modifications to the literature procedure. A solution of n-butyllithium (8.5 mL, 1.6 M in hexanes, 14 mmol) was added dropwise to a stirring solution of dipivaloylmethane (2.4941 g, 13.5 mmol) in THF. After 2 h, CrCl₂ (0.8351 g, 6.79 mmol) was added to give a light green suspension, which became a dark brown-red solution after 5 min. After stirring overnight, the solvent was removed in vacuo to give a dark brown residue, which was extracted with hexanes and filtered through celite. The dark brown solution was concentrated to incipient crystallization, and after standing at -35 °C gave dark brown crystals which were collected in two fractions (1.3217 g, 46.8 % yield).

AD96 \[ \text{Cr(DPM)}_2 + \text{bpy} \]

Cr(DPM)₂ (0.0181 g, 0.0433 mmol) was dissolved in 1 pipette of toluene to give a brown-orange solution. To this was added a second solution of 2,2’-bipyridine (0.0059 g, 0.0380 mmol) in 1 pipette of toluene, resulting in an immediate colour change from brown to dark green. UV/vis (toluene; \( \lambda_{\text{max}} \, \text{nm} \)) 875, 660, 599, 547, 454.

AD118 \[ \text{pyCN} + \text{S} + \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \]
2-pyridylcarbonitrile (0.8135 g, 7.81 mmol) and elemental S (0.0661 g, 2.06 mmol) were dissolved in ethylenediamine (2.20 mL, 32.8 mmol), giving rise to a green solution. The stirring solution was then placed in a 120 °C oil bath. The solution became a much darker green, refluxed vigorously for 2 min, then settled noticeably. After being heated for 6 minutes, the solution was allowed to cool to RT. The solution was diluted with RO water (ca. 10 mL) and extracted repeatedly with CH$_2$Cl$_2$. The combined organic extracts were dried with anhydrous Na$_2$SO$_4$, filtered and the solvent was removed in vacuo to yield a dark green oil. After sitting overnight, the oil solidified to give a yellow solid. After recrystallization from ligroine, a very pale yellow solid was isolated as flakes (0.8380 g, 72.9 % yield).

AD110  Cr(DPM)$_2$ + 2-(2’-pyridyl)imidazoline

Cr(DPM)$_2$ (0.0521 g, 0.124 mmol) was dissolved in 1 pipette Et$_2$O to give a brown solution. To this was added a second solution of 2-(2’-pyridyl)imidazoline (0.0182 g, 0.124 mmol) in 2 pipettes of Et$_2$O, resulting in an immediate colour change to an intensely dark green colour. After stirring for 2.5 h, a small aliquot was removed for UV/vis, and the solvent was removed in vacuo to give a dark green residue. Extraction of the residue with 3 pipettes of hexanes resulted in a dark brown solution, which was filtered and left to stand at -35 °C overnight, which resulted in the formation of a fine brown powder. After decanting the supernatant, the product was isolated as a fine, light brown powder (10.4 mg, 4.7 % yield). UV/vis (Et$_2$O; $\lambda_{\text{max}}$, nm) 803, 596, 545, 437, 332.

AD116  Cr(DPM)$_2$ + AgOTf + 2-(2’-pyridyl)imidazoline
Cr(DPM)$_2$ (0.0994 g, 0.238 mmol) was dissolved in Et$_2$O to give a brown solution. AgOTf (0.0637 g, 0.248 mmol) was added, turning the solution green. The solution was stirred for 15 minutes. When a brown residue began to appear, the solution was filtered through celite, giving a dark green solution. 2-(2’-pyridyl)imidazoline (0.0356 g, 0.241 mmol) was added, and the solution became turbid and brown. After stirring overnight, the supernatant was decanted, and the precipitate was washed with Et$_2$O and isolated as a pale pink powder (4.8 mg, 3.2 % yield).

AD124  pyCN + S + H$_2$NC(Me)$_2$CH$_2$OH

2-pyridylcarbonitrile (0.8307 g, 7.98 mmol) and elemental S (0.0660 g, 2 mmol) were suspended in 2-amino-2-methylpropan-1-ol (3.2 mL, 33.4 mmol) and refluxed for 1 h, during which the yellow suspension became a dark green solution. After cooling to RT, the solution was diluted with RO water (ca. 10 mL) and the aqueous phase was extracted repeatedly with CH$_2$Cl$_2$. The combined organic extracts were dried with anhydrous Na$_2$SO$_4$, filtered and the solvent was removed in vacuo to yield a dark brown oil. The residue was purified via column chromatography, eluting with a 2:1 mixture of EtOAc/hexanes on silica to yield a thick yellow oil (0.2742 g, 19.5 % yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$H 1.43 (6H, s), 4.22 (2H, s), 7.37-7.40 (1H, m), 7.77 (1H, dt, J = 7.6, 2.0 Hz), 8.08 (1H, d, J = 8 Hz), 8.70 (1H, m). The $^1$H NMR spectrum is shown in Appendix 6.2.

AD125  Cr(DPM)$_2$ + 4,4-dimethyl-2-(2’-pyridyl)oxazoline

Cr(DPM)$_2$ (0.0592 g, 0.141 mmol) was dissolved in 1 pipette Et$_2$O to give a brown solution. To this was added a second solution of 4,4-dimethyl-2-(2’-pyridyl)oxazoline (0.0248 g,
0.141 mmol) dissolved in 1 pipette of Et$_2$O, which resulted in an immediate colour change to very dark brown-red. UV/vis (Et$_2$O; $\lambda_{\text{max}}$, nm) 811, 589, 543, 471, 353.

**AD127** \( \text{Cr(DPM)}_2 + \text{acenaphthenequinone} \)

\( \text{Cr(DPM)}_2 \) (0.0513 g, 0.123 mmol) was dissolved in 1 pipette Et$_2$O to give a brown solution. To this was added a second solution of acenaphthenequinone (0.0220 g, 0.121 mmol) dissolved in 1 pipette of Et$_2$O, which resulted in an immediate colour change to very dark brown-green. UV/vis (Et$_2$O; $\lambda_{\text{max}}$, nm) 771, 692, 629, 453.

**AD128** \( \text{Cr(DPM)}_2 + \text{1,10-phenanthroline monohydrate} \)

\( \text{Cr(DPM)}_2 \) (0.0497 g, 0.119 mmol) was dissolved in 1 pipette Et$_2$O to give a brown solution. To this was added a second solution of 1,10-phenanthroline monohydrate (0.0240 g, 0.121 mmol) dissolved in 1 pipette of Et$_2$O, which resulted in an immediate colour change to very dark green. UV/vis (Et$_2$O; $\lambda_{\text{max}}$, nm) 850, 598, 471.

**AD129** \( \text{Cr(DPM)}_2 + \text{benzil} \)

\( \text{Cr(DPM)}_2 \) (0.0481 g, 0.115 mmol) was dissolved in 1 pipette Et$_2$O to give a brown solution. To this was added a second solution of benzil (0.0259 g, 0.123 mmol) dissolved in 1 pipette of Et$_2$O, which resulted in an immediate colour change to dark orange-red. UV/vis (Et$_2$O; $\lambda_{\text{max}}$, nm) 691, 639, 531, 458.

**AD130** \( \text{Cp}_2\text{Cr} + \text{bpy} + 2 \text{HDPM} \)
Cp₂Cr (0.0119 g, 0.0653 mmol) and 2,2'-bipyridine (0.0103 g, 0.0659 mmol) were dissolved in Et₂O and made up to 10.0 mL. The solution was a dark brown-red colour. Separately, a solution of HDPM (0.0333 g, 0.179 mmol) in Et₂O was also prepared and made up to 10.0 mL. A small aliquot of the clear, colourless HDPM solution (1.0 mL) was then added to 1.0 mL of the stock Cp₂Cr(bpy•) solution and stirred. After ca. 5 minutes, the solution had become a dark green colour. This solution was then diluted to a total volume of 10.0 mL with Et₂O. This solution was still too intensely coloured for UV/vis analysis, so a small aliquot (1.0 mL) was removed and diluted to a total volume of 10.0 mL using Et₂O. UV/vis (Et₂O; λ_max, nm (ε, M⁻¹cm⁻¹)) 870 (1710), 657 (1950), 595 (1530), 546 (1500), 446 (2750).

A small aliquot (1.0 mL) of the stock Cp₂Cr(bpy•) solution was diluted to a total volume of 10.0 mL, and the resulting pale brown-red solution did not require further dilution for UV/vis analysis. UV/vis (Et₂O; λ_max, nm (ε, M⁻¹cm⁻¹)) 868 (207), 449 (580).

AD131 \[ \text{Cp}_2\text{Cr(bpy•)} + 2 \text{dibenzoylmethane} \]

Dibenzoylmethane (0.0369 g, 0.165 mmol) was dissolved in Et₂O and made up to a total volume of 10.0 mL. A small aliquot (1.0 mL) of this clear, colourless solution was then added to a small aliquot (1.0 mL) of the stock Cp₂Cr(bpy•) from AD130 and stirred. The stock solution had developed a dark precipitate after standing overnight, so the mixture was shaken really well for ca. 4 minutes, then added quickly to the dibenzoylmethane as a slurry. The solid chunks dissolved within ca. 3 min of addition, but no colour change was observed. After stirring for ca. 1 h, the brown colour had darkened, and after ca. 3 h, the solution was a very dark brown-green. The solution was diluted to a total volume of 10.0 mL with Et₂O. This solution was too intensely
coloured for UV/vis analysis, so a small aliquot (1.0 mL) was removed and diluted to a total volume of 10.0 mL. UV/vis (Et$_2$O; $\lambda_{\text{max}}$, nm) 639.

**AD133**  
Cr(DPM)$_2$ + L$_2$

Cr(DPM)$_2$ (0.1998 g, 0.478 mmol) was dissolved in Et$_2$O to give a brown solution, which was made up to a total volume of 25.0 mL.

2,2'-bipyridine: 1.0 mL (20 µmol) of the stock Cr(DPM)$_2$ solution was added to 2,2'-bipyridine (0.0037 g, 23.7 µmol), resulting in an immediate colour change from brown to dark green. This solution was diluted by the addition of 10.0 mL of Et$_2$O. 1.0 mL of this solution was then removed, and diluted by the addition of another 10.0 mL aliquot of Et$_2$O. UV/vis (Et$_2$O; $\lambda_{\text{max}}$, nm ($\epsilon$, M$^{-1}$cm$^{-1}$)) 865 (2500), 657 (3310), 596 (2430), 545 (2340), 446 (4860).

2-(2'-pyridyl)imidazoline: 1.0 mL (20 µmol) of the stock Cr(DPM)$_2$ solution was added to 2-(2'-pyridyl)imidazoline (0.0031 g, 21.1 µmol), resulting in an immediate colour change from brown to dark green. This solution was diluted by the addition of 10.0 mL of Et$_2$O. 1.0 mL of this solution was then removed, and diluted by the addition of another 10.0 mL aliquot of Et$_2$O. UV/vis (Et$_2$O; $\lambda_{\text{max}}$, nm ($\epsilon$, M$^{-1}$cm$^{-1}$)) 807 (1890), 596 (1550), 549 (1560).

4,4-dimethyl-2-(2'-pyridyl)oxazoline: 1.0 mL (20 µmol) of the stock Cr(DPM)$_2$ solution was added to 4,4-dimethyl-2-(2'-pyridyl)oxazoline (0.0046 g, 26.1 µmol), resulting in an immediate colour change from brown to dark brown-red.
This solution was diluted by the addition of 10.0 mL of Et$_2$O. 1.0 mL of this solution was then removed, and diluted by the addition of another 10.0 mL aliquot of Et$_2$O. UV/vis (Et$_2$O; $\lambda_{\text{max}}$, nm ($\varepsilon$, M$^{-1}$cm$^{-1}$)) 812 (2530), 589 (1780), 543 (1940), 471 (3210).

**AD134**  
Cr(DPM)$_2$ + L$_2$ Continued

**1,10-phenanthroline:** 1.0 mL (20 µmol) of the stock Cr(DPM)$_2$ solution was added to 1,10-phenanthroline monohydrate (0.0047 g, 23.7 µmol), resulting in an immediate colour change from brown to dark brown-red. This solution was diluted by the addition of 10.0 mL of Et$_2$O. 1.0 mL of this solution was then removed, and diluted by the addition of another 10.0 mL aliquot of Et$_2$O. UV/vis (Et$_2$O; $\lambda_{\text{max}}$, nm ($\varepsilon$, M$^{-1}$cm$^{-1}$)) 857 (3140), 598 (2690), 471 (6660).

**acenaphthenequinone:** 1.0 mL (20 µmol) of the stock Cr(DPM)$_2$ solution was added to acenaphthenequinone (0.0040 g, 21.9 µmol), resulting in an immediate colour change from brown to orange-red. This solution was diluted by the addition of 10.0 mL of Et$_2$O. 1.0 mL of this solution was then removed, and diluted by the addition of another 10.0 mL aliquot of Et$_2$O. UV/vis (Et$_2$O; $\lambda_{\text{max}}$, nm($\varepsilon$, M$^{-1}$cm$^{-1}$)) 773 (962), 692 (1120), 630 (955), 452 (4760).

**9,10-phenanthrenequinone:** 1.0 mL (20 µmol) of the stock Cr(DPM)$_2$ solution was added to 9,10-phenanthrenequinone (0.0049 g, 23.5 µmol), resulting in an immediate colour change from brown to pale orange. This solution was diluted by
the addition of 10.0 mL of Et₂O. 1.0 mL of this solution was then removed, and
diluted by the addition of another 10.0 mL aliquot of Et₂O. UV/vis (Et₂O; λ_{max};
\text{nm}(\epsilon, \text{M}^{-1}\text{cm}^{-1})) 494 (1550).

\text{[XylNCMe]_2}: 1.0 mL (20 \mu mol) of the stock Cr(DPM)_2 solution was added to
\text{[XylNCMe]_2} (0.0061 g, 20.9 \mu mol), resulting in an immediate colour change
from brown to dark red. This solution was diluted by the addition of 10.0 mL of
Et₂O. 1.0 mL of this solution was then removed, and diluted by the addition of
another 10.0 mL aliquot of Et₂O. UV/vis (Et₂O; \lambda_{max}, \text{nm}) 850, 663, 580, 457.

\text{2-benzoylpyridine}: 1.0 mL (20 \mu mol) of the stock Cr(DPM)_2 solution was added
to 2-benzoylpyridine (0.0041 g, 22.4 \mu mol), resulting in an immediate colour
change from brown to dark brown-red. This solution was diluted by the addition
of 10.0 mL of Et₂O. 1.0 mL of this solution was then removed, and diluted by the
addition of another 10.0 mL aliquot of Et₂O. UV/vis (Et₂O; \lambda_{max}, \text{nm}(\epsilon, \text{M}^{-1}\text{cm}^{-1}))
849 (1510), 741 (1950), 612 (3420), 482 (8840).

\text{AD135} \hspace{1cm} \text{Cr(DPM)\textsubscript{2} + bpy + Ph\textsubscript{3}CBr}

1.0 mL (9.6 \mu mol) of AD133 Cr(DPM)_2 stock solution was added to 2,2′-bipyridine
(0.0031 g, 19.8 \mu mol) dissolved in 10.0 mL of Et₂O to give an intensely dark green solution. 1.0
mL of this solution was then added to trityl bromide (0.0095 g, 29.4 \mu mol), resulting in an
immediate fading of the dark green colour and the formation of a pale precipitate. After stirring
for 1 h, the slurry was filtered through celite, leaving a bright pink solid behind on the filter pad. (Et₂O; \( \lambda_{\text{max}} \), nm) 513.

\[ \text{AD137} \quad \text{Cr}[\text{N(SiMe}_3)_2]_2(\text{bpy}) + 2 \text{HDPM} \]

A sample of Cr[N(SiMe₃)₂]₂(bpy•) (0.0111 g, 21.3 µmol) dissolved in C₆D₆ was provided by Wen Zhou. The \(^1\)H NMR spectrum of ZW718 is shown in Appendix 6.3. HDPM (9 µL, 43.7 µmol) was added to the NMR tube, and the solution was allowed to sit for ca. 5 min. The solution changed from a dark purple to a dark green colour. The \(^1\)H NMR spectrum of the final reaction mixture is shown in Appendix 6.4.

\[ \text{AD138} \quad \text{Cr}[\text{N(SiMe}_3)_2]_2(\text{bpy}) + \text{RCOCH}_2\text{COR’} \]

A stock solution of ZW718 (0.0139 g, 26.7 µmol) was made up to 25.0 mL using Et₂O to give a purple solution. 2.0 mL (2.14 µmol) of the purple stock ZW718 solution was diluted with 10.0 mL of Et₂O. (Et₂O; \( \lambda_{\text{max}} \), nm) 504.

- **benzoylacetone**: 2.0 mL (2.1 µmol) of stock ZW718 solution was added to benzoylacetone (0.0018 g, 11.1 µmol) and diluted with 10.0 mL of Et₂O. After stirring for 1 h, the colour changed from purple to green. (Et₂O; \( \lambda_{\text{max}} \), nm (\( \varepsilon \), M⁻¹cm⁻¹)) 865 (1950), 638 (2890), 500 (3440), 443 (4220).

- **dibenzoylmethane**: 2.0 mL (2.1 µmol) of stock ZW718 solution was added to dibenzoylmethane (0.0008 g, 3.57 mmol) and diluted with 10.0 mL of Et₂O. After stirring for 1 h, the colour changed from purple to brown. (Et₂O; \( \lambda_{\text{max}} \), nm (\( \varepsilon \), M⁻¹cm⁻¹)) 863 (1260), 640 (2870), 512 (3440).
4,4,4-trifluoro-1-phenylbutane-1,3-dione: 2.0 mL (2.1 µmol) of stock ZW718 solution was added to 4,4,4-trifluoro-1-phenylbutane-1,3-dione (0.0015 g, 6.94 µmol) and diluted with 10.0 mL of Et₂O. After stirring for 1 h, the colour changed from purple to brown-orange. (Et₂O; λ<sub>max</sub>, nm (ε, M⁻¹cm⁻¹)) 716 (1020), 496 (2340).

dipivaloylmethane: 2.0 mL (2.1 µmol) of stock ZW718 solution was added to dipivaloylmethane (8 µL, 40 µmol) and diluted with 10.0 mL of Et₂O. After stirring for 1 h, the colour changed from purple to green. (Et₂O; λ<sub>max</sub>, nm (ε, M⁻¹cm⁻¹)) 865 (1940), 657 (2790), 596 (2130), 545 (2120), 446 (4130).

acetylacetone: 2.0 mL (2.1 µmol) of stock ZW718 solution was added to acetylacetone (1 µL, 8 µmol) and diluted with 10.0 mL of Et₂O. After stirring for 1 h, the colour changed from purple to green. (Et₂O; λ<sub>max</sub>, nm (ε, M⁻¹cm⁻¹)) 865 (1520), 656 (2230), 591 (1630), 540 (1650), 446 (3200).

\[ \text{AD139} \quad \text{Cr(DPM)}_2 + \text{bpy} + \text{I}_2 \]

\text{Cr(DPM)}_2 (0.1050 g, 0.251 mmol) was dissolved in hexanes to give a brown solution. A hexanes solution of 2,2'-bipyridine (0.0398 g, 0.255 mmol) was added, turning the solution a dark green colour. After stirring for 20 min, I₂ (0.0348 g, 0.137 mmol) was added, resulting in no immediate colour change. After stirring for ca. 30 min, the solution had developed a fine pink
precipitate. The solution was stirred overnight, and the solid was isolated by vacuum filtration and washed with hexanes (0.1178 g, 66.9 % yield).

5. References


10) Zhou, W. University of British Columbia Okanagan, unpublished results.


20) Theopold, K.H.; Leelasubcharoen, S.; Lam, K.; Concolino, T.E.; Rheingold, A.L.


6. Appendix

6.1- UV/vis spectra of AD135 before and after air exposure.
6.2 - $^1$H NMR of AD124
6.3- Paramagnetic $^1\text{H}$ NMR of ZW718$^{10}$
6.4- Paramagnetic $^1$H NMR of AD137