Reactivity of CpCr(III) N-Heterocyclic Carbene Diiodide

By

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A Thesis Submitted in Partial Fulfillment of Requirements for
CHEMISTRY 449

The University of British Columbia - Okanagan

April 2010

Abstract

Chromium complexes are well known for their applications in alkene and alkyne trimerization. In this thesis, a previously synthesized $CpCr(NHC)I_2$ complex (where NHC stands for *N*-heterocyclic carbene), were investigated for alkyne trimerization. The objective was to optimize the reduction and initial alkyne-coupling steps of the mechanism to isolate a well-defined chromacyclopentadiene complex which could later be used for synthetically applicable alkyne trimerization. Initial attempts to utilize the complex to couple two alkyne substrates appeared promising; however, obstacles in spectral analysis prevented any conclusive characterization of the desired complex. The possibility of bimolecular decomposition with similar complexes reported by Jolly[6a] led to the synthesis of a novel $CpCr(^{i}Pr\text{-}NHC)Cl$ with bulkier isopropyl substituents on the NHC ancillary ligand. Applications of $CpCr(^{i}Pr\text{-}NHC)Cl$ in alkyne trimerization appear to be very promising as the isopropyl substituent likely prevents decomposition and improves the crystalline structure of the compound which is helpful for characterization. A number of other $CpCr(L)X_2$ compounds were also tested for reactivity in alkyne trimerization which illustrated the significance of ancillary ligand electron-donating abilities in this type of reactivity.

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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.

Ad	adamantyl, tricyclo[3.3.1.1]decanyl, $C_{10}H_{15}$-
*t*Bu	*tert*-butyl, Me_3C-
ºC	degree Celsius
Col	2,4,6-trimethylpyridine
Cp	cyclopentadienyl, η^5-C_5H_5
Cp*	pentamethylcyclopentadienyl, η^5-$(CH_3)_5C_5H_5$
Cy	cyclohexyl, C_6H_{11}-
DBU	1,8-diazabicyclo[5.4.0]unec-7-ene
equiv	equivalents
Et	ethyl, CH_3CH_2
g	grams
L	neutral, 2-electron-donor ligand; or litre, 10^{-3} m^{-3}
M	molar, $molL^{-1}$
Me	methyl, CH_3-
Mes	mesityl, 1,3,5-trimethylphenyl $(CH_3)_3C_6H_2$
mg	milligram, 10^{-3} g
min	minutes
mL	millilitre, 10^{-3} L
mmol	millimole, 10^{-3} mole
mM	millimolar, 10^{-3} $molL^{-1}$
mol	mole, $6.022 \cdot 10^{-23}$ particles
NHC	*N*-heterocyclic carbene
Np	neopentyl, 2,2-dimethylpropyl, $(CH_3)_3CCH_2$-
OTs	tosylate, $CH_3C_6H_4SO_3^-$
Ph	phenyl, C_6H_5-
^{i}Pr	*iso*-propyl, $(CH_3)_2CH$-
py	pyridine, C_5H_5N
R	alkyl
THF	tetrahydrofuran, C_4H_4O
X	halide or other anionic 1-electron-donor ligand

I sincerely thank Dr. Kevin Smith for his constant encouragement, guidance and support throughout this project, as well as Cory, Lydia and Wen for their patience and invaluable help in the lab.

Introduction

Chromium organometallic complexes are well known for their contributions in carbon-carbon bond formation. Perhaps the most recognized application of these chromium complexes in organic bond formation is the polymerization of ethylene.[1] Various chromium catalysts are also utilized in the selective trimerization of ethylene.[2] The commonly accepted mechanism for trimerization seen in Figure 1 involves the coordination of two alkene substrates followed by oxidative coupling to form a five-membered chromium metallacycle complex. The coordination and insertion of a third alkene is then followed by β-hydrogen elimination to form 1-hexene with remarkably high selectivity. This selectivity of this mechanism is highly dependent on the relative rates of ethylene insertion and β-hydrogen elimination at each step. The insertion of a third alkene substrate must be quicker than the β-hydrogen elimination of the chromacyclopentane and the β-hydrogen elimination of the chromacycloheptane must be quicker than the insertion of a fourth alkene substrate.

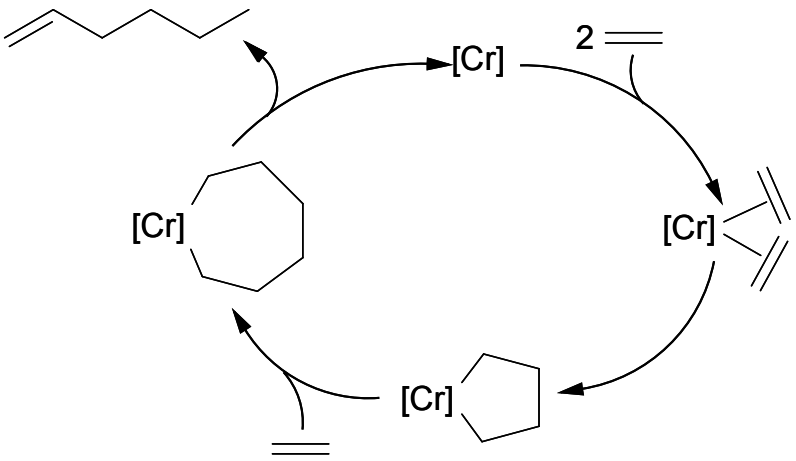

Figure 1. Proposed mechanism for the selective trimerization of ethylene to form 1-hexene.

The chromacycloheptane (compared with the chromacyclopentane) will more rapidly undergo β-hydrogen elimination as the flexibility of the seven-membered ring allows for greater interactions between the chromium and the β-hydrogen.[3] Following the loss of 1-hexene two new ethylene substrates can coordinate to the metal center to complete the catalytic cycle.

The structure of the catalytically active species is less evident. This is mainly because there is only a minute quantity of the active species present in situ which decreases the possibility of analysis and characterization. Other obstacles in characterization are the presence of a large excess of AlR_3 co-catalyst in many systems and the paramagnetic nature of the mid-valent chromium species presumed to be involved [Cr(I), Cr(II), Cr(III) and/or Cr(IV)] which drastically reduces the use of NMR.[1] The oxidation states of the chromium throughout the mechanism are also unclear as it is difficult to discern whether Cr(III)/Cr(I) or Cr(IV)/ Cr(II) schemes are involved.

The research of Agapie et al. exhibits several well-defined chromium catalysts with the ability to selectively produce α-olefins by a similar mechanism in the absence of co-catalyst.[4] The same catalyst is also found to perform alkyne trimerization which selectively combines three unsaturated substrates resulting in relatively stable η^6- arene Cr(I) complexes by a very similar mechanism (Figure 2).

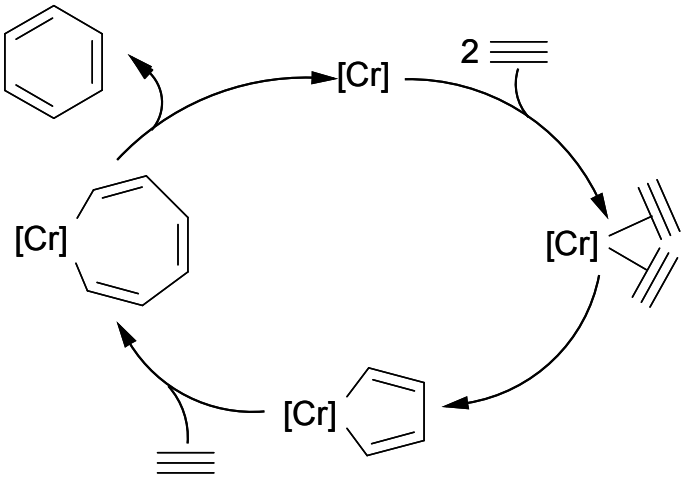

Figure 2. Proposed mechanism for the selective trimerization of acetylene to form benzene.

Applications of this reactivity in synthetic organic chemistry has been extended in the work of Takahashi et al.[5] Their work includes transmetallation from zirconium to chromium, and consequently, the oxidative coupling to form the metallacycle is performed at a zirconium metal center and then transmetallated to $CrCl_3$ where further insertion and elimination occurs. The resulting chromium complex allows a third, different, unsaturated substrate to be added after the formation of the chromacyclopentadiene complex to form an arene complex with non-uniform substitution (Figure 3). More specifically, the complex is successful in adding various nitrile substituents to produce substituted pyridine derivatives. This incorporation of the nitrile substrates has thus far been found to be chromium specific. This reactivity makes use of the Cr(III) oxidation state as $CrCl_2$, a Cr(II) complex, was not able to undergo the same reaction whereas Cr(III) sources, such as $Cp^*Cr(THF)Cl_2$, are able. This suggests that the mechanism involves Cr(III)/Cr(I) oxidation states rather than Cr(IV)/Cr(II). In addition, their results showed that in the absence of the chromium transmetallation no product was formed and the zirconapentadiene complex remained

unreacted. Unfortunately, the transmetallation and insertion steps are performed in situ and are not well-defined.

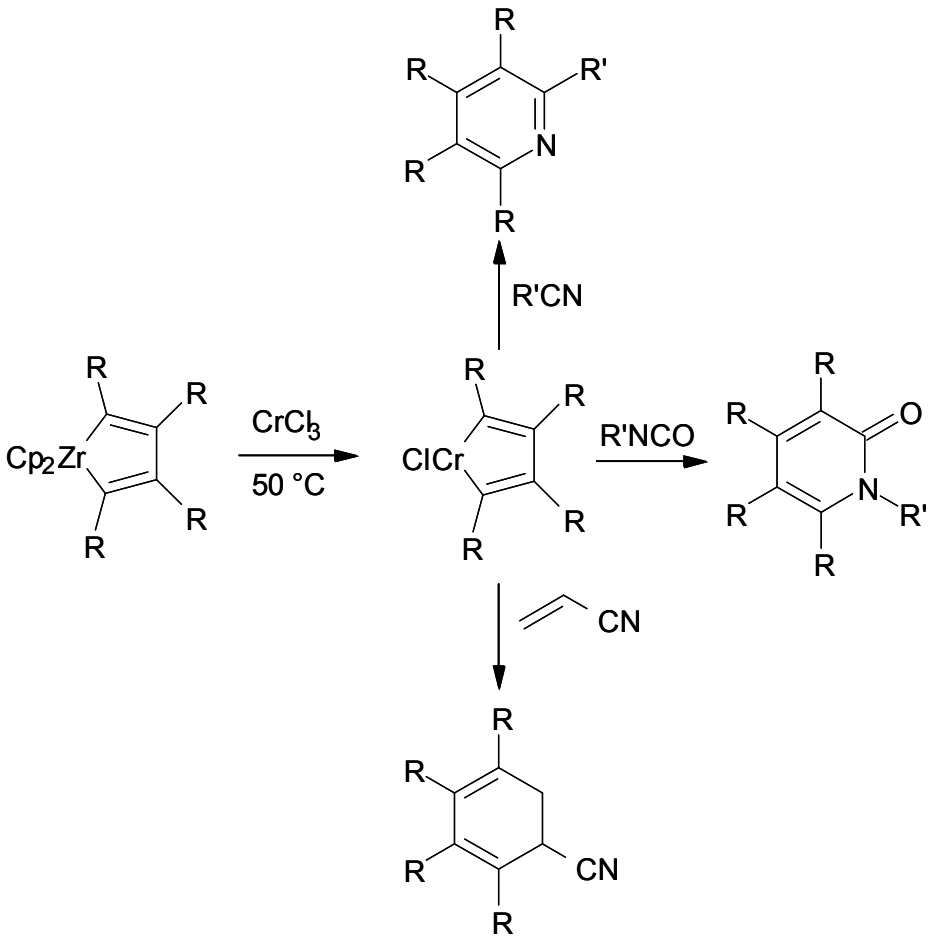

Figure 3. Applications of the trimerization of unsaturated substrates in synthetic organic chemistry.

Alkyne trimerization using Cp*Cr(THF)Cl_2 has also been explored by Jolly.[6] The Cp*Cr(THF)Cl_2 is reduced with highly active Mg* (generated by thermal decomposition of MgH_2) in the presence of MeCCMe.

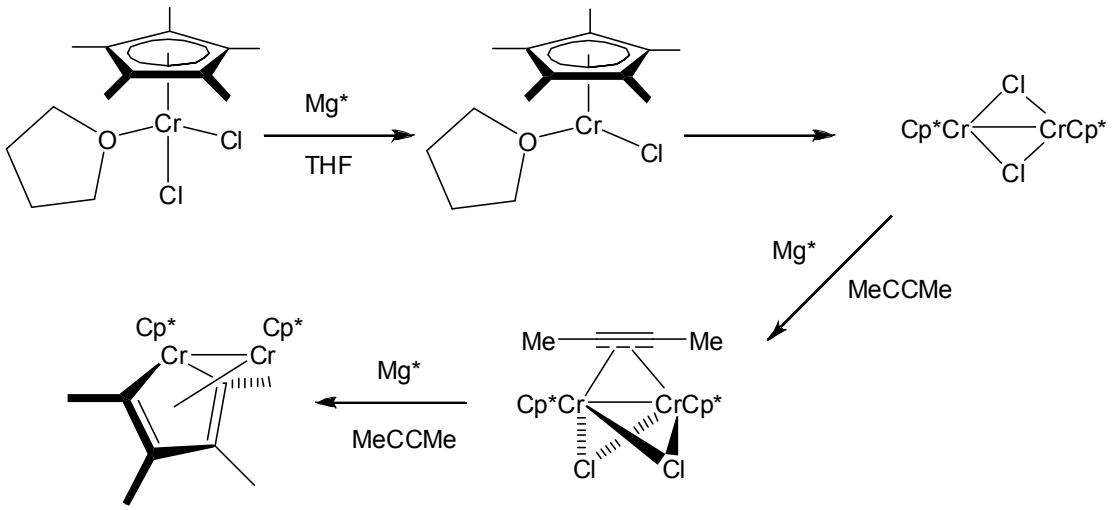

Figure 4. Formation of a bimetallic species in the trimerization of alkynes with $Cp^*Cr(THF)Cl_2$.[6]

Analysis by X-ray diffraction shows that the reaction proceeds by an initial reduction from Cr(III) to Cr(II) followed by dimerization and the formation of a strong metal-metal bond. This robust Cr-Cr bond is preserved in the subsequent reduction and coupling steps contrary to the monomeric complexes employed in the research mentioned above. This bond is surprisingly difficult to break[7] and prevents any further monomeric chemistry with the complex. An additional drawback is that the complex is restricted from being extended to CpCr chemistry (instead of Cp*Cr) as the bridging [$CpCr(\mu$-Cl)] complex is unstable with respect to Cp_2Cr and $CrCl_2$.

The objective of this project is to react a chromium complex with the general structure $CpCr(L)X_2$ with reductant in the presence of an alkyne, RCCR, to prepare a well defined $CpCr(L)(C_4R_4)$ complex as seen in Figure 5.

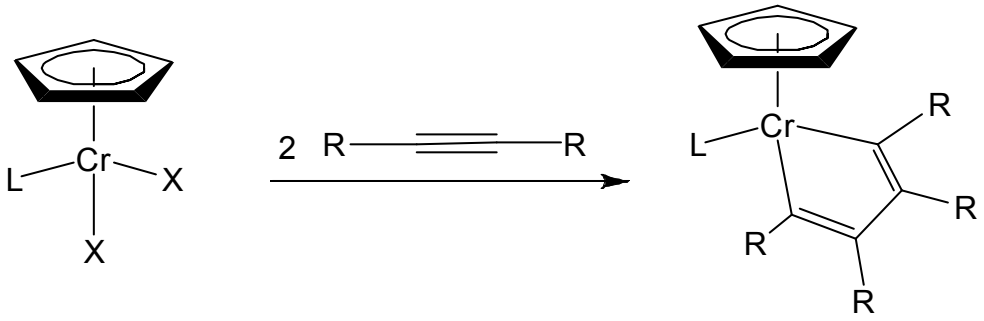

Figure 5. Formation of chromium metallacycle by reduction in the presence of alkyne substrate.

For this type of application it is important that the neutral ancillary ligand, L, forms a strong bond with the chromium. This will help to prevent bimolecular reactions during the initial reduction as well as block the coordination site of a third RCCR substrate.[8] Once the conditions for $CpCr(L)(C_4R_4)$ synthesis are optimized, the reactivity will be extended to complexes with progressively weaker Cr-L interactions. Ideally an optimal Cr-L bond strength will be reached in order to allow for the coordination and insertion of a third substrate without disturbing the initial formation of the $CpCr(L)(C_4R_4)$ intermediate. The resulting $CpCr(L)(C_4R_4)$ complex can then be reacted with other RC≡X and R_2C=X substrates for applications in organic synthesis.[5] Further research may also explore the possibility of catalytic reactivity with the chromium complex as well as possible routes including radical chemistry to merge previous research explored by the Smith research group.

The specific chromium complex explored in this project has an *N*-heterocyclic carbene neutral ligand (NHC) as well as two anionic iodide ligands as synthesized in Jeff Therrien's Honors Thesis.[9] This reaction is related to the synthesis of $CpCr(pyridine)Br_2$ from Cp_2Cr and pyridinium tribromide.[10]

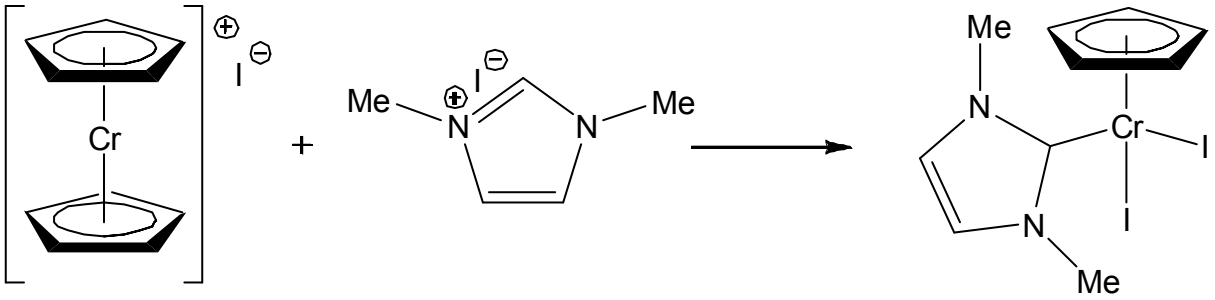

Figure 6. Synthesis of $CpCr(NHC)I_2$

This complex is especially suited for the synthesis of the desired CrC_4R_4 metallacycle for two main reasons. First, the Cr-NHC bond is especially strong due to strong sigma-donor interactions,[11] which, as mentioned previously is required for the prevention of bimolecular decomposition as well as the coordination and insertion of a third substrate. Second, the relatively weak Cr-I bonds are advantageous for the reduction to CpCr(II) and CpCr(I) in the initial steps of the mechanism as well as for potential salt metathesis reactions.

A third, practical advantage of this complex is that small changes to the ligands or oxidation state of the chromium generally result in pronounced changes to the colour of the complex. As a result, UV-visible spectroscopy (UV-vis) was used significantly throughout the project to screen reactions, and often the progress of a reaction could be monitored simply by visual observation.

Results and Discussion

The central focus in this project involves reducing the chromium complex $CpCr(NHC)I_2$ in the presence of two equivalents of akyne substrate to produce the coupled chromacyclopentadiene complex. The initial attempt to form the chromium metallacycle by reducing $CpCr(NHC)I_2$ in the presence of diphenylacetylene is shown in Figure 7. Colour

changes were recorded from green to pale peach to red signaling the presence of starting material CpCr(NHC)I_2, followed by the reduced intermediate CpCr(NHC)I and finally the chromacyclopentadiene complex respectively.

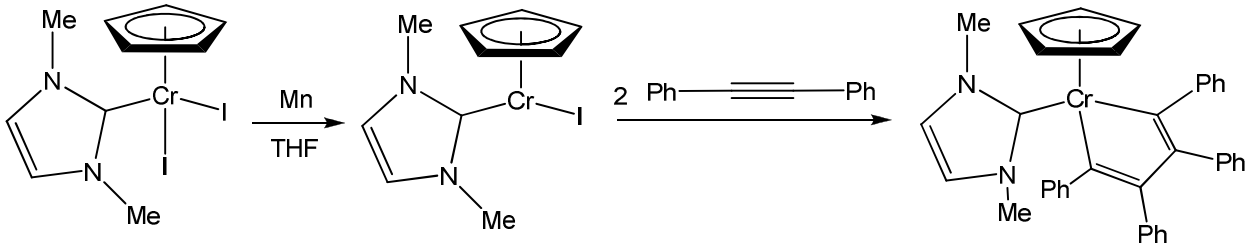

Figure 7. Synthesis of chromium metallacycle from the reduction of CpCr(NHC)I_2 in the presence of alkyne.

The presence of two distinguishable colour changes provides some information concerning the mechanism of the reaction. First, it supports the postulation that the formation of the metallacycle is preceded by the reduction of Cr(III) to Cr(II) as there are two colour changes for the two mechanistic steps rather than one. Second, since the colour due to the Cr(II) intermediate is much less intense than either the reactant or the product, the Cr(II) intermediate will only be visible if all of the green starting material is used up before the red product is produced. The visual observation of the Cr(II) intermediate demonstrates that the reduction of CpCr(NHC)I_2 to CpCr(NHC)I is relatively fast, while the formation of the chromium metallacycle is much slower and consequently the rate determining step.

The subsequent analysis necessary to confirm the presence of the metallacycle requires a relatively elaborate method since common NMR and X-ray diffraction techniques are prohibited by the paramagnetic nature and poor crystalline structure of the complex. Instead of examining the metallacycle directly, the complex was treated with an H-X source

in an attempt to induce protonolysis of the bidentate organic ligand, and UV-visible spectroscopy was used to test for the expected chromium byproduct (Figure 8).

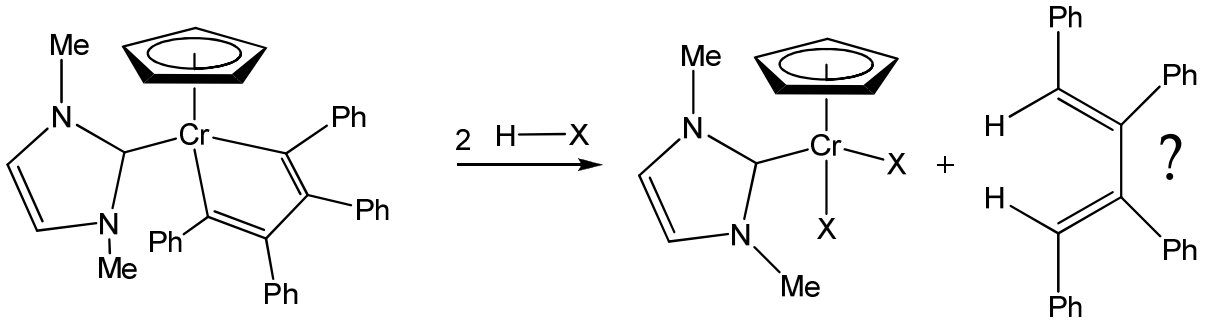

Figure 8. Attempted protonolysis of CpCr(NHC)(C_4Ph_4) resulting in CpCr(NHC)X_2 byproduct.

The syntheses of possible CpCr(NHC)X_2 byproducts were attempted by a range of salt metathesis reactions (Figure 9) to determined which anionic X ligands would form stable chromium compounds and as a result which H-X sources would be suitable for protonolysis to generate stable Cr byproducts. The compounds were each analyzed with UV-visible spectroscopy to test if they produce distinguishable UV-Vis spectra for latter comparison with the protonolysis byproducts. The stable CpCr(NHC)X_2 complexes may also be tested in the future for reactivity in alkyne trimerization as it is possible that the compounds are able generate chromium metallacycles in the presence of Mn and RCCR as seen with CpCr(NHC)I_2.

A series of AgX salt metathesis reactions were attempted in order to synthesize several CpCr(NHC)X_2 complexes as seen in Figure 9. The advantages of using silver metal in this type of synthesis are twofold. Since the AgI byproduct is extremely insoluble in THF it can be easily separated from the product. Also, the formation of the highly stable AgI salt helps to drive the reaction to completion. The results showed that salt metathesis reactions

with AgOTs to form CpCr(NHC)$(OTs)_2$, produced isolatable aqua coloured crystals. The reaction with AgO_2CPh resulted in a colour change from green to blue; however, no crystals were isolated. Finally, the reaction with AgF produced a large quantity of insoluble brownish grey precipitate and no product was isolated.

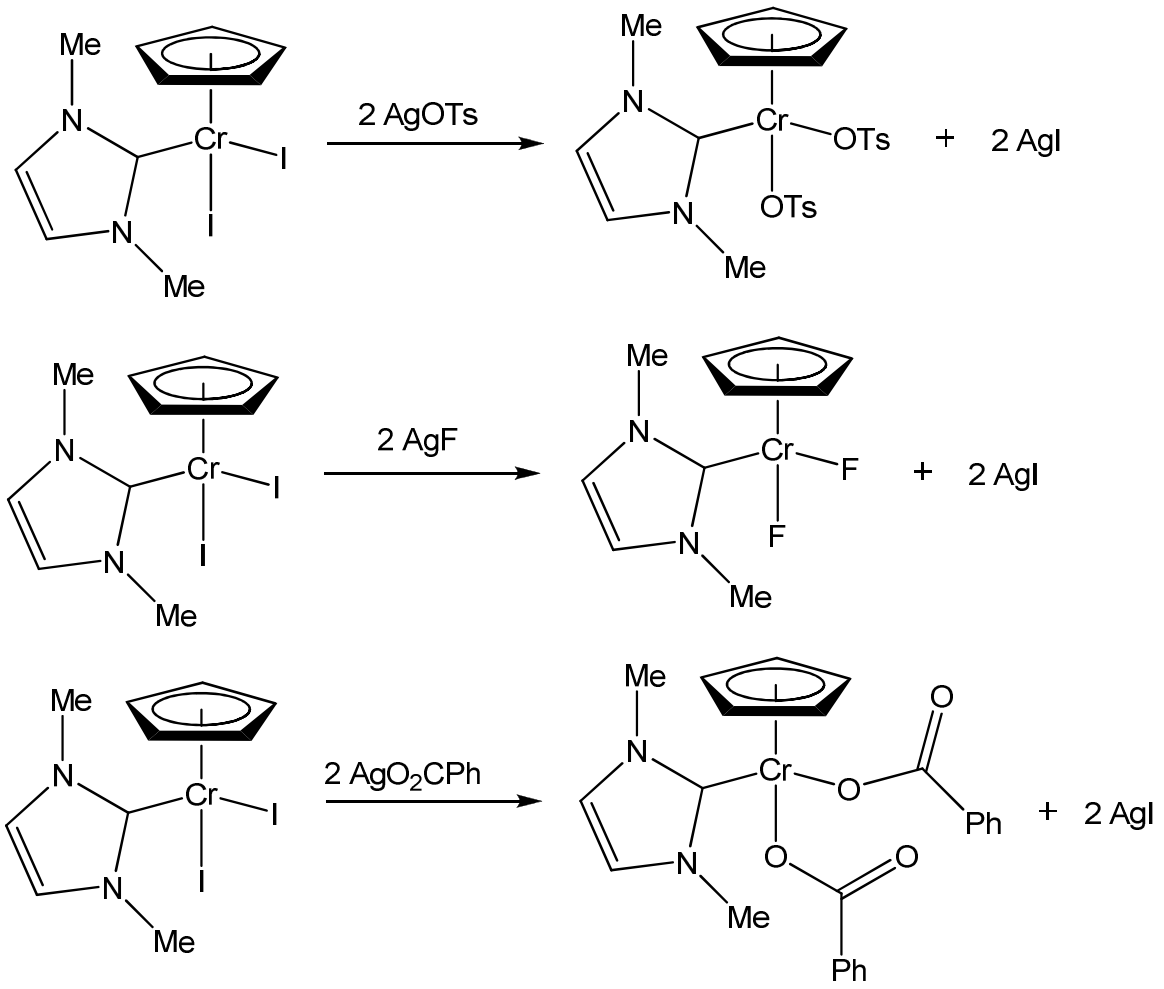

Figure 9. The attempted synthesis of various CpCr(NHC)X_2 complexes by salt metathesis with Ag.

Two salt metathesis reactions with $PbCl_2$ and $ZnCl_2$ to form CpCr(NHC)Cl_2 were also attempted (Figure 10). Both reactions resulted in a noticeable colour change from the green CpCr(NHC)I_2 starting material to the indigo CpCr(NHC)Cl_2 product. The reaction with $PbCl_2$ produced isolatable indigo crystals whereas no crystals were isolated from the

$ZnCl_2$ reaction. These blue colours are also seen with other $CpCr(L)Cl_2$ complexes in the literature.[12] The lead metathesis was preferred over the zinc metathesis in these syntheses as the PbI_2 byproduct is highly insoluble in THF and easily separated from the product in solution.

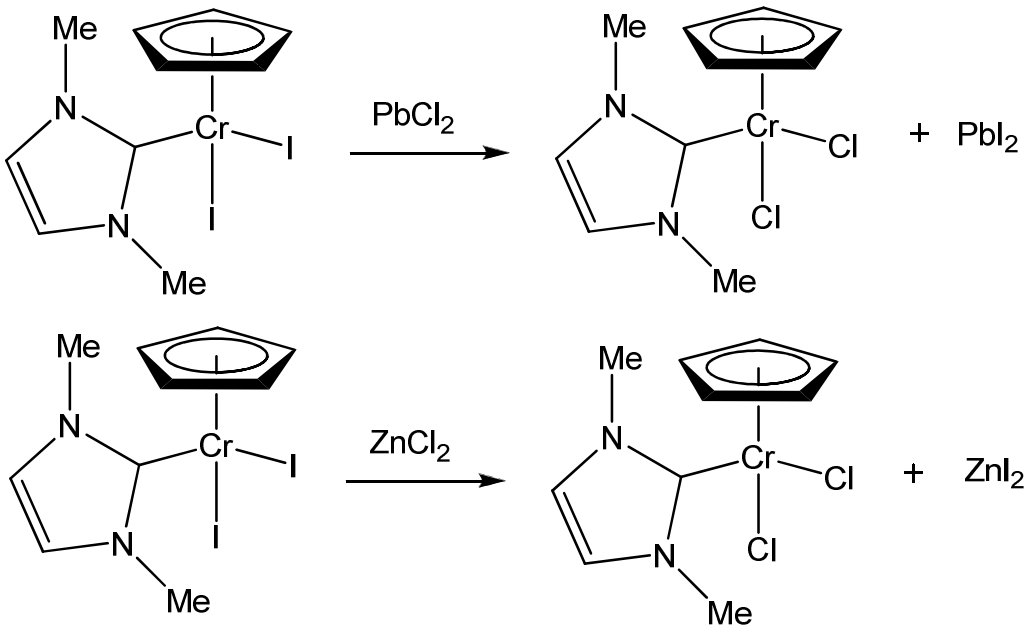

Figure 10. The synthesis of $CpCr(NHC)Cl_2$ from $CpCr(NHC)I_2$ by the salt metathesis with $PbCl_2$ and $ZnCl_2$.

The results suggest that protonolysis H-X reagents where X=OTs, Cl or $PhCO_2$, will from stable $CpCr(NHC)X_2$ compounds and are most appropriate for this application.

In addition to the Ag, Pb, and Zn salt metathesis reactions, several Grignard syntheses were attempted. The reaction of $CpCr(NHC)I_2$ with MeMgCl, effectively produced dark red crystals of $CpCr(NHC)(CH_3)_2$ (Figure 11).

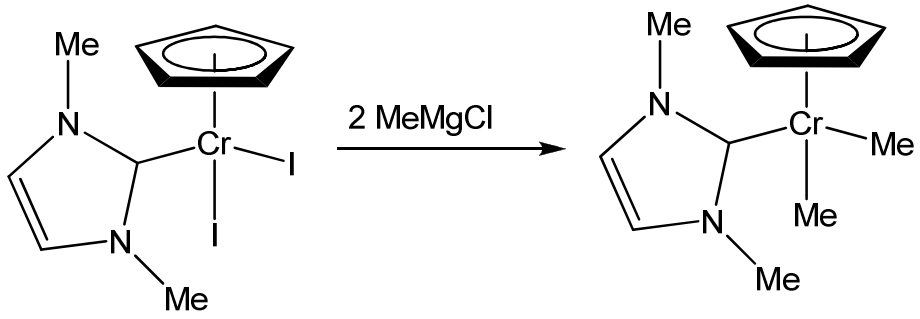

Figure 11. Synthesis of $CpCr(NHC)(CH_3)_2$ from $CpCr(NHC)I_2$ by Grignard reagent MeMgCl.

Other Grignard reactions were also attempted with $ClMgCH_2SiMe_3$, $ClMgCH_2CMe_2Ph$, and MesMgI. The reaction with $ClMgCH_2SiMe_3$ was found to produce large purple crystals; however, they appeared to melt after the removal of the supernatant solution and were not isolated. The remaining reactions with $ClMgCH_2CMe_2Ph$ and MesMgI were much less stable.

The protonolysis reactions were attempted with a variety of H-X sources of varied pK_as and which were partially selected for their ability to generate stable Cr byproducts as tested in the previous salt metathesis reactions. The protonolysis of $CpCr(NHC)(CH_3)_2$ was attempted prior to the protonolysis of the metallacycle as it is closely related to a well-defined complex in the literature[13] whereas the metallacycle is less defined. The methyl complex is expected to loosely mimic the reactivity of the metallacycle. The complex was reacted with three H-X sources including Col·HOTs, $HOCMe_2Ph$, and $PhCO_2H$ as seen in Figure 12. The reactions with Col·HOTs and $PhCO_2H$ showed colour changes from the red colour of the $CpCr(NHC)(CH_3)_2$ starting material to a purplish intermediate possibly suggesting a mixture of the red starting material and blue-coloured product, however, the solutions then proceeded to an unexpected green colour. The protonolysis reaction with $HOCMe_2Ph$ resulted in no colour change. This is likely due to the fact that the $HOCMe_2Ph$

alcohol is the weakest of the three acids. This result contrasts the successful protonolysis of $Cp^*Cr(py)(CH_3)_2$ with HO^tBu reported by Theopold.[14]

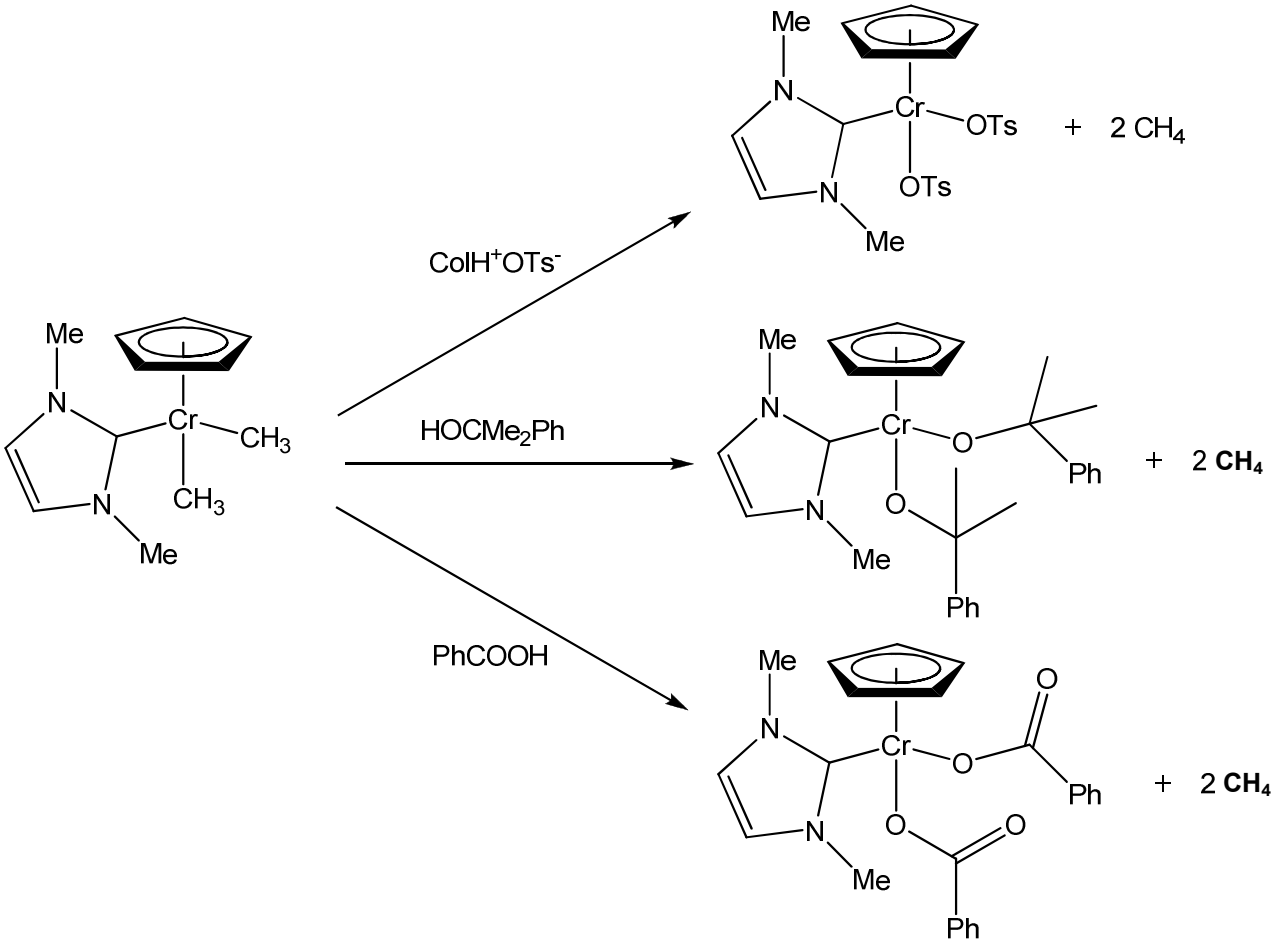

Figure 12. Protonolysis attempts of $CpCr(NHC)(CH_3)_2$ with various H-X sources.

Despite unfavourable results in the protonolysis of the $CpCr(NHC)(CH_3)_2$, an array of protonolysis reactions were still attempted with the chromacyclopentadiene complex as it is possible that the sp^2 hybridized orbitals of the pi system are more prone to protonation than the sp^3 hybridized orbitals in the methyl compound. The protonolysis was attempted with a variety of H-X sources including DBU·HOTs, $HOCMe_2Ph$, $PhCO_2H$, $C_6H_4(OH)_2$, and $HNEt_3Cl$ as shown in Figure 13.

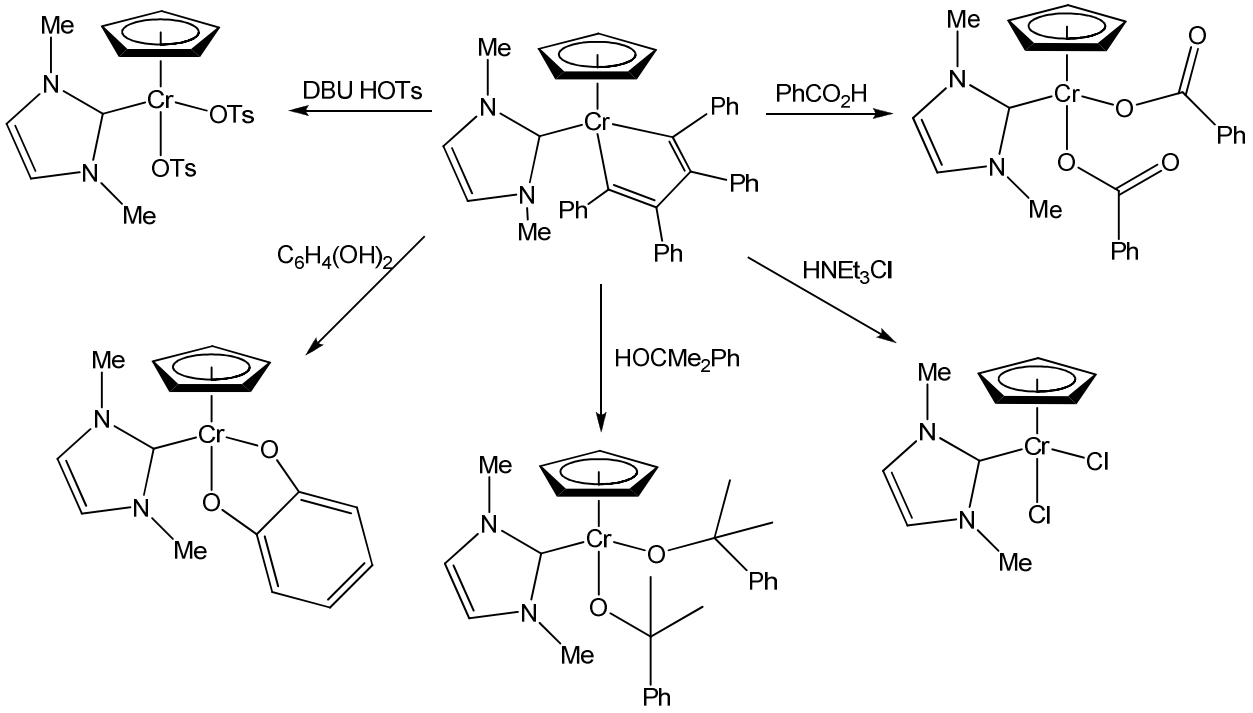

Figure 13. Protonolysis attempts of CpCr(NHC)(C_4Ph_4) with various H-X sources

The results of the protonolysis reactions with the metallacycle also failed to produce the expected blue colours of the CpCr(NHC)X_2 byproducts.

Next, the alkyne coupling chemistry was extended to additional CpCr(L)X_2 compounds to test if the reactivity seen in Figure 7 (including the reduction of the chromium followed by the formation of a metallacycle) is unique to the CpCr(NHC)I_2 complex. Reacting CpCr(NHC)Cl_2 with Mn reductant in the presence of diphenylacetylene did not produce a colour change for 5 days and the red colour of the metallacycle was never observed. This suggests that the compound was either unsusceptible to the Mn reductant, or it was unable to coordinate and couple the alkyne substrates. Comparatively, the reaction of CpCr(THF)Cl_2 with Mn and diphenylacetylene did undergo the expected colour change from blue to red which implies that it was able to coordinate and couple two alkynes similar to the CpCr(NHC)I_2 complex. In addition, when the same reaction was performed in the

absence of the alkyne substrate the resulting red product was analyzed by UV-vis and found to contain Cp_2Cr which suggests that the unstable reduced complex undergoes ligand redistribution to form Cp_2Cr and $CrCl_2$. This provides evidence that the alkyne substrates are involved in the reaction.

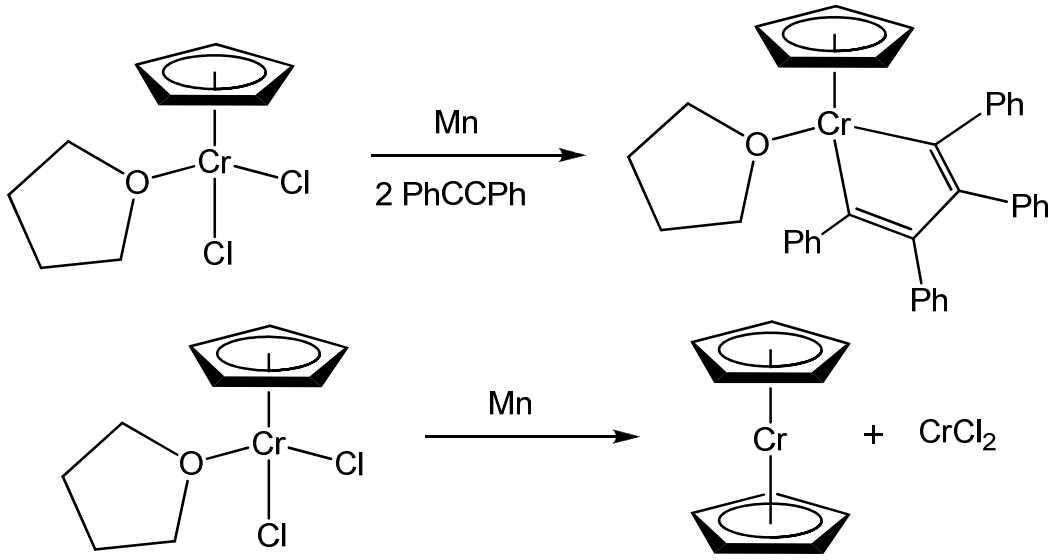

Figure 14. The reduction of $CpCr(THF)Cl_2$ in the presence and absence of alkyne substrate.

The combined results of attempts to reduce the various $CpCr(L)X_2$ in the presence of alkyne demonstrate that the ability to reduce the Cr(III) complex depends on the electron donating properties of the ancillary ligands. Comparing the reactivity of $CpCr(THF)Cl_2$ and $CpCr(NHC)Cl_2$, the NHC compound is not reduced while the THF compound is reduced. This is because the stronger sigma donor characteristics of the NHC ligand increase the electron density at the Cr(III) which decreases the likelihood of reduction to Cr(II).[11] Conversely the THF ligand is a much weaker electron donor and therefore is more readily reduced. This trend is also seen in Jolly's research. Unlike $CpCr(THF)Cl_2$, the reduction of $Cp^*Cr(THF)Cl_2$ requires a much stronger reducing agent, active magnesium (Mg*), which is produced by thermal decomposition of MgH_2 (Figure 4). This suggests that the stronger

electron donating Cp* ligand increases the Cr(III)-Cl bond dissociation energy. Comparing the reactivity of $CpCr(NHC)Cl_2$ and $CpCr(NHC)I_2$, the iodide complex can be reduced (Figure 7) while the chloride complex can not, as the Cr-I bonds are weaker than the Cr-Cl bonds. The relationship between the electron donating abilities of the ancillary ligands and the reduction potential of the complex will be a significant consideration in future attempts to optimize the Cr-L interactions.

This research by Jolly also demonstrates that in the absence of a bulky ancillary ligand, dimerization may occur to form a strong Cr-Cr bond as shown in Figure 4. The formation of a similar bimetallic species may explain why the protonolysis attempts to remove the organic ligands of $CpCr(NHC)(CH_3)_2$ and $CpCr(NHC)(C_4Ph_4)$ did not produce the blue colours of the expected Cr byproducts. In order to avoid this type of bimolecular decomposition the sterics at the NHC ligand were increased by replacing the methyl groups with iso-propyl substituents. The addition of iso-propyl substituents was also used to increase the crystallinity of the complex.[15] The CpCr(^{i}Pr-NHC)Cl complex was successfully synthesized by reacting the organic ligand with Cp_2Cr (Figure 15). This reaction can be compared to a similar reaction by Tilset et al. where Cp_2Cr is reacted with Mes-NHC^+Cl^- to produce CpCr(Mes-NHC)Cl which is also purple-coloured.[16] Conversely, reacting Cp_2Cr with Me-NHC^+I^- as reported by Therrien, results in a mixture of insoluble Cr(II) halide and unreacted Cp_2Cr.[9] It is unclear whether the additional sterics of the ^{i}Pr-NHC ligand or the nature of the halide is important in forming the stable Cr(II) CpCr(L)X complex.

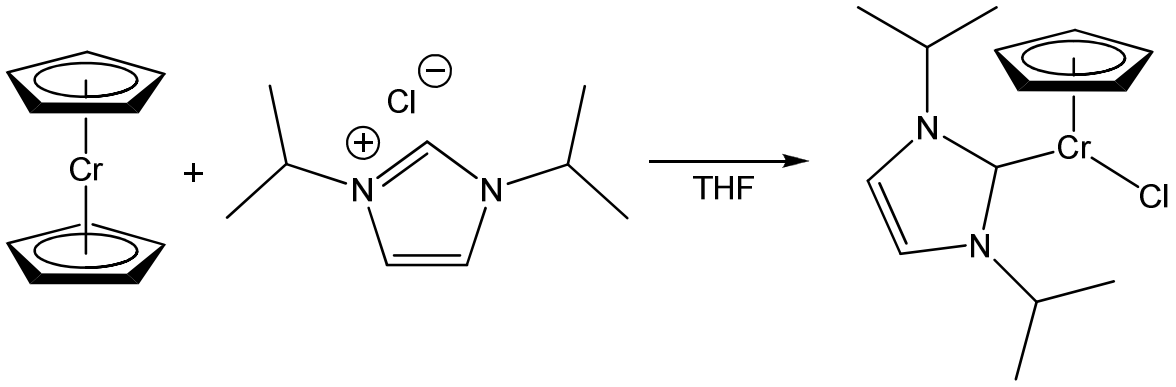

Figure 15. Synthesis of CpCr(^{i}Pr-NHC)Cl.

The CpCr(^{i}Pr-NHC)Cl complex was isolated as beautiful purple crystals and is very promising for future reactivity studies for three main reasons. First, the improved crystalline structure will allow for direct analysis by X-ray diffraction to provide more conclusive information concerning the formation of the metallacycle. Second, as mentioned previously, it is expected that the increased steric bulk will prevent bimolecular decomposition affording a more stable complex for alkyne coupling. And third, due to the increased bulk around the metal center, the complex is stable in the Cr(II) oxidation state. This provides a starting material that eliminates the initial C(III) to Cr(II) reduction step altogether and is equipped to perform alkyne trimerization without activation. This may be especially useful in potential catalytic applications.

The CpCr(^{i}Pr-NHC)Cl complex was further investigated by preliminary screening of the reactivity of a stock solution with organic halides. Reacting the purple CpCr(^{i}Pr-NHC)Cl complex with $CDCl_3$ resulted in an indigo-coloured solution which is consistent with the blue-indigo colour of CpCr(NHC)Cl_2, as well as closely related reactions performed by Tilset et al.[16] The reaction of CpCr(DBU)Cl with $CDCl_3$ reported in Therrien's thesis also produced the same indigo colour change.[9]

Reacting CpCr(^{i}Pr-NHC)Cl with a variety of alkyl iodides caused the pink-purple solution to turn to a darker grey-purple. The alkyl iodides reacted with CpCr(^{i}Pr-NHC)Cl resulting in this colour change are listed in order of the rate of colour change from fastest to slowest: cyclohexyl iodide (CyI), adamantyl iodide (AdI), neopentyliodide (NpI) and iodobenzene (PhI). After an additional 20 hours, the adamantyl iodide and neopentyliodide reactions exhibited an additional colour change to green. The proposed mechanism of the reaction involves the steps shown in Figure 16.

$$Cr + R{-}X \rightarrow Cr{-}X + R\cdot$$
$$Cr + R\cdot \rightarrow Cr{-}R$$

$$Cr{-}R \leftrightarrow Cr + R\cdot$$

Figure 16. Proposed reaction mechanism for the activiation of organic halides with Cr.[17]

The mechanism is strongly supported by the colour change observations mentioned above. The rate of the initial colour change to grey-purple is shown to decrease with increasing C–X bond dissociation energies[18] which is consistent with the mechanism; as stronger R–X bonds will less likely be broken to form the Cr–X bond. The mechanism also suggests that sterically bulky alkyl, R, groups will reversibly bind to the chromium allowing the possibility of the Cr–R bond to break and be subsequently replaced with a Cr–X bond. Assuming that the grey-purple colour is likely caused by a combination of the purple Cr–CH_3 complex and green Cr–I complex and the green colour results singly from the Cr–I bond, the appearance of the green colour with the most bulky R–I groups, AdI and NpI, supports the premise of reversible binding of bulky R groups at the chromium. The results suggest that in the reactions with AdI and NpI, a mixture of the Cr–I and Cr–R products

were present initially, the reversible Cr–Ad and Cr–Np bonds were eventually exchanged for irreversible Cr–I bonds resulting in a green solution.

Reacting CpCr(^{i}Pr-NHC)Cl with methyl iodide, MeI, also provided confirmation of the proposed mechanism. The reaction was much slower than the CyI, AdI and NpI reactions due to the stronger C-I bond dissociation energy in MeI. In addition no colour change to green was observed with the MeI as the small methyl ligand is less prone to reversible binding at the chromium. In addition the highly unstable CH_3· radical is very unlikely to form, which also prevents this reversible binding.[17]

The CpCr(NHC)I_2 complex was also tested for its reactivity with the methyl iodide in the presence of manganese powder reducing agent. The green solution underwent a colour change to red-purple overnight indicating the presence of CpCr(NHC)(Me)I. Interestingly, the solution does not form the red dimethyl complex despite the fact Cr-CH_3 bonds are much stronger than those of Cr-I. This unpredicted result can be clarified in light of the previous reduction reactions with CpCr(L)X_2 complexes which demonstrated that the reduction potential of the complex is dependent on the electron donating abilities of the ancillary ligands. As a result, the exchange of the iodide ligand with the higher electron donating methyl substituent prevents further reduction of the complex which is necessary to bind an additional methyl ligand. This may be a useful route to further CpCr(NHC)(R)I compounds which might be alkylated to form CpCr(NHC)(R)(R') complexes.

Conclusion

The attempted alkyne coupling reaction with $CpCr(NHC)I_2$ produced colour changes which strongly support the formation of a chromacyclopentadiene complex through a reduced Cr(II) intermediate. Attempts to confirm the presence of the metallacycle by analyzing the chromium byproducts of protonolysis were not conclusive. Comparing this reactivity with closely related $Cp^*Cr(THF)Cl_2$ systems by Jolly,[6] it seems likely that the unexpected results seen in the protonolysis reactions are the consequence of bimolecular decomposition. Further screening of the complex's reactivity also revealed possible applications in alkyl-halide activation.

A series of stable $CpCr(L)X_2$ complexes were synthesized, including $CpCr(NHC)Cl_2$, $CpCr(NHC)OTs_2$, $CpCr(NHC)(CH_3)_2$ and $CpCr(THF)Cl_2$. Of these, only $CpCr(THF)Cl_2$, along with the previously synthesized $CpCr(NHC)I_2$ complex, were reduced in the presence of Mn and PhCCPh which demonstrates the relationship between the electron donating abilities of ancillary ligands and the chromium-halide hemolytic bond dissociation energy of the complex. The trend suggests that more electron donating ligands lead to decreased reducibility at the metal center.

Lastly, $CpCr(^{i}Pr\text{-}NHC)Cl$ was synthesized with increased sterics at the neutral NHC ligand to prevent possible bimolecular decomposition and improve the crystalline structure of the complex for more direct analysis by X-ray diffraction. The isolated purple crystals provide a promising foundation for further applications in alkyne trimerization as it is stable in the Cr(II) oxidation state which would allow the initial reduction from Cr(III) to be eliminated from the mechanism.

Experimental

General Methods

All of the reactions, apart from the synthesis of 1,3-diisopropylimidazolium chloride, were performed in anhydrous, oxygen-free conditions using an inert-atmosphere glovebox complete with active oxygen and moisture removing catalyst columns. The THF, Et_2O, hexanes and toluene solvents were made anhydrous using Grubbs/Dow columns. Anhydrous "sure-seal" grade reagents, such as $ClMgCH_2SiMe_3$ in Et_2O, $ClMgCH_2CMe_2Ph$ in Et_2O, and MeMgI in Et_2O 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 cells.

General Syntheses

Cp_2Cr was synthesized by Wen Zhou from $CrCl_2$ (anhydrous powder, Strem) and 2 equivalents of NaCp (1.0 M in THF, Aldrich). $CpCr(THF)Cl_2$ was prepared by Wen Zhou by the reaction of HCl/Et_2O with Cp_2Cr in THF.[19] 1,3-Dimethylimidazolium iodide was prepared from methyl imidazole and MeI using the previously described procedure.[9]

EY34 Synthesis of $CpCr(NHC)I_2$

The synthesis of $CpCr(NHC)I_2$ was modified from the previously described procedure.[9] 1,3-Dimethylimidazolium iodide ([NHC][I]) (43.11 mg, 0.1924 mmol) was added to a stirring

greenish brown suspension of chromocenium iodide ([Cp_2Cr][I]) (53.2 mg, 0.172 mmol) in THF (10 mL). The reaction was left to stir overnight. After 4 days, the solvent was removed from the solution in vacuo. The solid was the redissolved in hexanes (5 mL) to produce a cloudy blue-green solution. After the precipitate settled, the clear and colourless supernatant solution was removed from the solid. The remaining solid was dissolved in THF (10 mL) and filtered through Celite in a pipette resulting in an intense green solution which was placed in the freezer (-35 ˚C) overnight. The next day a small sample of dark black crystals were isolated. The remaining supernatant was concentrated by evaporation and returned to the freezer. Two days later, another small fraction of crystals were isolated, and the supernatant was concentrated by evaporation and returned to the freezer.

EY22 Synthesis of CpCr(NHC)(C_4Ph_4)

PhCCPh (83.70 mg, 0.4917 mmol) and manganese powder (169.8 mg, 3.091 mmol) were added to a stirring green solution of CpCr(NHC)I_2 (99.1 mg, 0.244 mmol) in THF (8 mL). No immediate colour change was observed, so the reaction was left to stir overnight. The next day, the solution was fairly intense red. The solvent was removed in vacuo and the dark brown-red solid was redissolved in ether (5 x 2 mL) and filtered through Celite in a pipette in small portions. The resulting intense red solution was placed in the freezer at -35 ˚C. One week later, some small crystals were isolated. Hexanes (1 mL) were added to the supernatant solution, and a fine precipitate was removed by filtration through Celite in a pipette. The solution was returned to the freezer. Two months later a solid layer of dark red product was isolated (14.4 mg, 10.8 % yield).

EY24 Synthesis of CpCr(NHC)($OTs)_2$

AgOTs (140.4 mg, 0.5029 mmol) was added to a stirring green solution of $CpCr(NHC)I_2$ (101.6 mg, 0.2496 mmol) in THF (10 mL). AgOTs appeared insoluble initially. After 5 minutes solution appeared teal and after 22 hours solution was blue. The solution was filtered through Celite in a pipette and then concentrated by evaporation and placed in freezer (-35 ˚C) and left to stand. After 5 days only some fine precipitate visible, so the solution was re-filtered through Celite in a pipette and concentrated down by evaporation and added diethylether (2 mL) resulting in a temporary biphasic mixture. After the solution appeared homogeneous, it was returned to the freezer (-35 ˚C) to stand producing bright blue crystals (50.3 mg, 40.7 %). UV/Vis (THF; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)): 625 (438), 475 (170).

EY23 Synthesis of $CpCr(NHC)(O_2CPh)_2$

AgO_2CPh (55.46 mg, 0.2422 mmol) was added to a stirring green solution of $CpCr(NHC)I_2$ (48.8 mg, 0.120 mmol) in THF (10 mL). An immediate colour change to teal and then blue was noticed after 5 min. The solution was filtered through Celite in a pipette to remove greyish brown precipitate. The solvent was removed in vacuo, and hexanes (5 mL) were added to dissolve product. The product appeared to be insoluble in hexanes, so ether (5 mL), and then toluene (5 mL) were attempted, however both were unsuccessful. The solvents were removed in vacuo a second time and successfully dissolved the solid with pure ether (2 mL) and placed in the freezer (-35 ˚C). No crystals appeared after 5 days, so the solution was concentrated by evaporation and hexanes were added (2 mL). Solid precipitate crashed out immediately. After the solution settled, no blue crystals were visible only brown/murky solution.

EY26 Synthesis of $CpCr(NHC)F_2$

AgF (29.4 mg, 0.231 mmol) was added to a stirring green solution of $CpCr(NHC)I_2$ (47.0 mg, 0.115 mmol) in THF (10 mL) resulting in no immediate colour change. After reacting for three days, lots of solid was present, and the solution was a greyish brown suspension.

EY25 Synthesis of $CpCr(NHC)Cl_2$

$ZnCl_2$ (150 μL, 0.66 mmol; 0.5 M in THF) was added via plastic syringe to a stirring green solution of $CpCr(NHC)I_2$ (54.1 mg, 0.133 mmol) in THF (10 mL). Solution turned teal after 3 min and blue after 20 min. The solution was left to react overnight. No product was isolated, as the solution was used in a subsequent reaction. UV/Vis (THF; λ_{max}, nm): 666.

EY28 Synthesis of $CpCr(NHC)Cl_2$

$PbCl_2$ (38.82mg, 0.1395 mmol) was added to a stirring green solution of $CpCr(NHC)I_2$ (53.9 mg, 0.132 mmol) in THF (10 mL). $PbCl_2$ appeared to be insoluble, so the reaction was left to stir overnight. The resulting indigo solution was filtered through Celite in a pipette. The solution was concentrated by evaporation and re-filtered through Celite in a pipette. The resulting solution was placed in the freezer (-35 ˚C). Some fine, blue crystals were isolated (11.4 mg, 0.0508 mmol, 38.4%). UV/Vis (THF; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)): 575 (246), 286 (1389).

EY29 Synthesis of $CpCr(NHC)(CH_3)_2$

MeMgI (275 μL, 0.825 mmol; 3.0 M in THF) was added to a stirring green solution of $CpCr(NHC)I_2$ (153.1 mg, 0.3761 mmol) in THF (10 mL) resulting in an immediate colour change to a reddish solution. After 1 day, the solution was red. 1,4-dioxane (900 μL) was

added resulting in large quantity of white precipitate. After settling, the solution was filtered through Celite on a glass frit and the solvent was removed in vacuo. The product was dissolved in hexanes (4 mL) to form an intense red solution and filtered through Celite in a pipette. Ether was added (4 mL) to help dissolve the solid. The solution was filtered a second time through Celite in a pipette and place in the freezer (-35 ˚C). A small quantity of long, fine crystals was isolated. UV/Vis (THF; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)): 403 (739), 484 (506), 740 (303).

EY18 Synthesis of CpCr(NHC)(CH_2SiMe_3)$_2$

CH_2CSiMe_3MgCl (0.50 mL, 1.0 M in Et_2O, 0.50 mmol) was added to a stirring green solution of CpCr(NHC)I_2 (97.1 mg, 0.219 mmol) in Et_2O (10 mL) causing an immediate change to purple. After 1 hour the solution was a more intense purple colour and 1,4-dioxane was added to the reaction causing a white precipitate to form immediately. After allowing the precipitate to settle, the supernatant was filtered through Celite in a pipette and placed in the freezer at -35 ˚C overnight. No precipitate was visible the next day, and so the solvent was removed in vacuo. The solid was redissolved in hexanes (1mL), filtered through Celite in a pipette and returned to the freezer (-35 ˚C). The solution produced large purple crystals; however, they were not isolated as they appeared to melt after the removal of the solvent.

EY19 Synthesis of CpCr(NHC)(CH_2CMe_2Ph)$_2$

$CH_2CMe_2PhMgCl$ (0.50 mL, 0.5 M in Et_2O, 0.25 mmol) was added to a stirring pale green, inhomogeneous solution of undissolved CpCr(NHC)I_2 (46.5 mg, 0.105 mmol) in Et_2O (10

mL). The colour of the solution changed to brown immediately and golden brown after 1 hour. The solution was left to react overnight. The following day a fine precipitate was visible in the solution. 1,4 dioxane (0.45 mL) was added resulting in the formation of an additional precipitate. The solution was filtered through Celite over a glass frit, and then the solvent was removed in vacuo. The oily brownish yellow product was redissolved in a minimal amount hexanes and then placed in the freezer (-35 ˚C). The following day dark purple solid was visible in the vial along with a crystalline pale yellow solid which appeared stable in the presence of O_2 and H_2O. The dark purple solid was not isolated due to the pale yellow contamination.

EY21 Synthesis of CpCr(NHC)(Mes)I

MesMgI (0.15 mL, 1.0 M in Et_2O, 0.15 mmol) was diluted in Et_2O (3 mL) and then added to a stirring pale green, inhomogeneous solution of undissolved CpCr(NHC)I_2 (62.8 mg, 0.154 mmol) in Et_2O (8 mL). The solution immediately began to turn pink and gradually darkened into a red colour. Some insoluble starting material was still present, so THF (2 mL) was added to the solution. The THF was not effective, so the dark starting material was removed from the reaction. The solution was left to react overnight. 1,4-dioxane (0.15 mL) was added to the resulting reddish purple solution generating white precipitate. The solution was filtered over a glass frit and filtrate was rinsed with hexanes (10 mL). The resulting purple solution was still slightly cloudy, and it was filtered through Celite again in a pipette. The solution was concentrated by evaporation and then placed in the freezer (-35 ˚C). Only fine precipitate was visible and so no product was isolated.

EY30-32 Protonolysis attempts of CpCr(NHC)$(CH_3)_2$

A red stock solution of CpCr(NHC)(CH_3)$_2$ in THF (3 mL) with an unknown concentration was made and divided into three vials with stir bars. To each of these solutions was added one of 2,4,6-trimethylpyridinium p-toluenesulfonate (Col·HOTs, 5 mg), 2-phenyl-2-propanol ($CH_3C(Ph)(OH)CH_3$, 8 mg), or benzoic acid ($C_6H_5CO_2H$, 3 mg). The resulting colour changes in each reaction are listed below:

Col·HOTs: After several minutes, the colour changed to dark brown. After one day, the solution appeared to be greyish purple in colour, and after an additional 5 days, the solution was greyish green.

$CH_3C(Ph)(OH)CH_3$: No colour change was observed after 6 days.

$C_6H_5CO_2H$: After several minutes, the colour changed to red/brown colour. After one day, the solution appeared to be greyish purple in colour, and after an additional 5 days, the solution was greyish green.

EY41 Protonolysis attempts of CpCr(NHC)(C_4Ph_4)

A red solution of CpCr(NHC)(C_4Ph_4) was formed in situ by reacting PhCCPh (21.7 mg, 1.48 mmol) and Mn powder (37.3 mg, 0.679 mmol) with a 7.0 mL solution of CpCr(NHC)I_2 (8.60 mM, 0.0612 mmol) in THF. Five 1.0 mL aliquots of this solution were transfered into to five separate vials containing one of benzoic acid ($C_6H_5CO_2H$, 17.9 mg, 0.147 mmol), 2-phenyl-2-propanol ($CH_3C(Ph)(OH)CH_3$ 20.3 mg, 0.149 mmol), (DBU·HOTs, 48.7, 0.150 mmol), triethylamonium hydrochloride ($HNEt_3Cl$, 19.4 mg, 0.141

mol) or 1,2-dihydroxy benzene (Pyrocatechol, 16.12 mg, 0.146 mg). Each of the solutions started as a honey brown colour, and little change was noted after 3 days.

EY37 Reactions with $CpCr(THF)Cl_2$ + Mn + PhCCPh

An stock solution of $CpCr(THF)Cl_2$ was made (105.5 mg in 50.0 mL THF, 8.11 mM) in a volumetric flask. The solution was then reacted as follows with three different sets of reagents.

10 Mn + 2 PhCCPh: The blue stock solution (7.00 mL, 0.0568 mmol) was transferred to a vial containing manganese powder (36.4 mg, 0.663 mmol) and PhCCPh (21.7 mg, 0.127 mmol) and then stirred. After 1 hour, the solution began to appear more green and then orange after an addition hour. The next day, the solution was red, and the intensity continued to increase throughout the day. After the colour remained constant, the solution (4 mL) was filtered through Celite in a pipette, diluted, and analyzed with UV-Vis spectroscopy. UV/Vis (THF; λ_{max}, nm): 624.

10 Mn + 10 PhCCPh: The blue stock solution (7.00 mL, 0.0568 mmol) was transferred to a vial containing manganese powder (35.3 mg, 0.643 mmol) and PhCCPh (21.7 mg, 0.533 mmol) and then stirred. After 2 hours, the solution began to appear more brown-green. After 4 hours the solution was brown. The next day, the solution was red, and much more intense than the solution containing only 2 equivalents of PhCCPh.

10 Mn: The blue stock solution (7.00 mL, 0.0568 mmol) was transferred to a vial containing manganese powder (40.7 mg, 0.741 mmol). The solution appeared to be yellowish green after 30 minutes and pale orange after 3 hours. The appearance of the solution then remained relatively unchanged. The solution (4 mL) was filtered through Celite in a pipette and analyzed with UV-Vis spectroscopy. UV/Vis (THF; λ_{max}, nm): 455.

EY38(H) CpCr(NHC)OTs$_2$ + Mn + PhCCPh

An aliquot of aqua coloured CpCr(NHC)OTs$_2$ stock solution (5.0 mL, 4.24 mM in THF, 0.0212 mmol) was added to a vial containing manganese powder (13.5 mg, 0.246 mmol) and PhCCPh (36.0 mg, 0.211 mmol). No colour change was observed after several days.

EY38(I) CpCr(NHC)Cl$_2$ + Mn + PhCCPh

An aliquot of indigo coloured CpCr(NHC)Cl$_2$ stock solution (3.9 mL, 5.1 mM in THF, 0.020 mmol) was added to a vial containing manganese powder (13.8 mg, 0.251 mmol) and PhCCPh (33.4 mg, 0.196 mmol). No colour change was observed after 1 day. After 5 days, however, solution appeared to be colourless.

EY44 Synthesis of CpCr(^{i}Pr-NHC)Cl

[^{i}Pr-NHC][Cl] (21.58 mg, 0.1143 mmol) (prepared as described in the literature,[20] and washed with acetone prior to use[16]) was added to a stirring orange-red solution of Cp$_2$Cr (20.9 mg, 0.115) in THF (10 mL). The reaction was left to stir overnight. The solvents of the resulting red-purple solution were removed in vacuo. The product was then redissolved in

ether (5x1 mL aliquots) and filtered through Celite in a pipette after each small addition of ether. The resulting solution was placed in the freezer and left to stand at -35 ˚C. After three days, bright purple crystals were isolated from the solution (10.7 mg, 0.0351 mmol, 30.6%). UV/Vis (THF; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)): 668 (95.4), 516 (147).

EY46 Reactions with CpCr(^{i}Pr-NHC)Cl + R-I

A 1 mL aliquot of pink-purple stock solution of CpCr(^{i}Pr-NHC)Cl (1mL, 0.702 μM, 0.702 mM in THF) was added one of $CDCl_3$ (9.9 mg, 0.082 mmol), cyclohexyliodide (CyI) (30.8 mg, 0.147 mmol), 1-iodo-adamantane (AdI) (33.6 mg, 0.128 mmol), neopentyl iodide (NpI) (65.6 mg, 0.331 mmol), Iodobenzene (PhI) (51.0 mg, 0.250 mmol) and iodomethane (MeI) (70 μL, 2.0 M solution in (^{t}BuMe)$_2$O, 0.140 mmol). The resulting observations are listed below:

$CDCl_3$: The solution turned blue-indigo after several minutes and more intense blue after 2 hours. UV/Vis (THF; λ_{max}, nm): 577.

CyI: The solution immediately turned a purple-grey colour. UV/Vis (THF; λ_{max}, nm): 587, 484.

AdI: The colour became darker after 10 minutes and appeared purple-grey after 25 minutes. The solution was green/blue after 22 hours. UV/Vis (THF; λ_{max}, nm): 690, 591.

NpI: The solution became darker after 15 minutes and purple grey after 25 minutes. The solution was blue-green after 22 hours. UV/Vis (THF; λ_{max}, nm): 590, 685.

PhI: Colour appeared grey-purple after 22 hours. UV/Vis (THF; λ_{max}, nm): 575, 486.

MeI: Solution appeared to be a darker purple after 2 hours and much darker grey-purple after 20 hours. UV/Vis (THF; λ_{max}, nm): 579, 488.

EY42 $CpCr(NHC)I_2$ + Mn + MeI

Mn powder (36.1 mg, 0.657 mmol) and iodomethane (0.34 mL, 2.0 M in THF, 0.64 mmol) were added to a stirring green solution of $CpCr(NHC)I_2$ (31.7 mg, 0.0679 mmol) in THF (8 mL, anhydrous "sure-seal"). After 5 days, the resulting intense red-purple solution was filtered through Celite in a pipette and diluted with THF (7 mL) for UV-vis spectroscopy. UV/Vis (THF; λ_{max}, nm): 488.

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