

**Striking the right balance: An exploration of novel
protonolysis precursors for CpCr(LX) complexes**

by

Jeffrey A. Therrien

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Abstract

Directed ortho-metallation is a convenient route to $\text{Li}(\text{Ar-L})$ salts (where Ar is an aryl group), which may be used to synthesize $\text{CpCr}(\text{Ar-L})$ complexes by salt metathesis with chromium dichloride and sodium cyclopentadienylide. Some of these complexes have precedent as effective protonolysis precursors to $\text{CpCr}(\text{LX})$ complexes (where LX is a bidentate monoanionic ligand), providing a clean and direct synthetic pathway to the exploration of various anionic, bidentate ligand sets. Through the course of this investigation several new $\text{CpCr}(\text{Ar-L})$ complexes were rationally designed and synthesized, revealing unanticipated and undesired reactivity modes regarding the targeted protonolysis reactions. This discovery, by providing insight into the protonolysis reaction mechanism, led to the development of new $\text{CpCr}(\text{L})(\text{X})$ complexes (where L is a neutral monodentate ligand, and X is an anionic monodentate ligand) through a number of synthetic routes. X-ray diffraction analysis of single crystals obtained from the attempted synthesis of $\text{CpCr}(\text{Mes})(\text{L})$ (where Mes is 2,4,6-trimethylphenyl) derivative revealed a dimerized structure, suggesting that the complex contains the sought-after property of neutral ligand lability. These complexes have shown promise as a protonolysis precursor to $\text{CpCr}(\text{LX})$ compounds previously found unobtainable by less subtle salt metathesis pathways.

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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.

ne	valence electrons
Å	angstrom, 10^{-10} m
Ar	aryl
atm	atmosphere
<i>t</i> Bu	<i>tert</i> -butyl, Me ₃ C-
°C	degree Celsius
Cp	cyclopentadienyl, η^5 -C ₅ H ₅
Cp*	pentamethylcyclopentadienyl, η^5 -(CH ₃) ₅ C ₅ H ₅
Col	2,4,6-trimethylpyridine
D	deuterium, ² H
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
Dpp	2,6-diisopropylphenyl
equiv	equivalents
Et	ethyl, CH ₃ CH ₂
¹ H	proton
hppH	1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2,a]-pyrimidine
<i>i</i> Pr	isopropyl, (CH ₃) ₂ CH-
K	degree Kelvin
L	neutral, 2-electron-donor ligand; or litre, 10^{-3} m ³
M	metal; or molar, mol L ⁻¹
Me	methyl, CH ₃ -
Mes	mesityl, 2,4,6-trimethylphenyl
min	minutes
mmol	millimole, 10^{-3} mole
mol	mole, $6.022 \cdot 10^{23}$ particles
mL	millilitre, 10^{-3} L
NHC	<i>N</i> -heterocyclic carbene
NMR	nuclear magnetic resonance
no.	number
OTs	tosylate, CH ₃ C ₆ H ₄ SO ₃ ⁻
Ph	phenyl, C ₆ H ₅ -
ppm	parts per million
R	alkyl
THF	tetrahydrofuran, C ₄ H ₄ O
X	halide or other anionic 1-electron-donor ligand
Xyl	xylyl, 2,6-dimethylphenyl

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Introduction

Paramagnetic organochromium complexes have shown promising abilities in catalytic carbon-carbon bond-forming reactions, with important applications in alkene polymerization¹ and organic synthesis.² The presence of unpaired electrons in these complexes, however, renders routine characterization methods by NMR spectroscopy both inconvenient and often uninformative.³ This, coupled with the extreme air and moisture sensitivity of many Cr(II) complexes, makes understanding the fundamental nature of these reactions and catalytic cycles difficult. Therefore, the development of organometallic chemistry has focused largely on more accessible diamagnetic complexes, which most often behave according to the 18-electron rule, undergoing 2-electron reactions such as reductive eliminations, oxidative additions, and neutral ligand coordination and dissociation.

In contrast, the single electron transfer (SET) reactivity common among the less explored paramagnetic organochromium complexes enables novel and interesting radical chemistry.⁴ This is demonstrated by the reactivity of a number of CpCr(LX) (where LX is a bidentate mono-anionic ligand) complexes with organic halides, where the organic halide undergoes homolytic bond cleavage to form Cr(III) alkyl and Cr(III) halide complexes. The rate of this reactivity may be easily studied using UV-Vis spectroscopy as the alkyl and halide complexes display wildly different colours.⁵ In general, modifications to the number and type of ligands in organochromium complexes leads to conspicuous colour changes.⁶

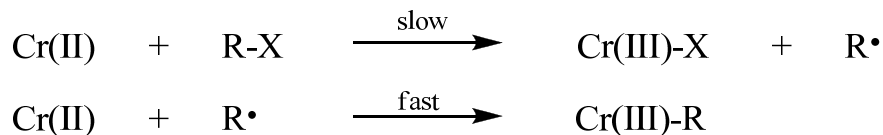


Figure 1 – Reaction scheme for the homolytic bond cleavage of organic halides by various CpCr(LX) complexes.

The Cr-X and Cr-R bond dissociation energies (BDEs) can be adjusted by altering the steric and electronic properties of the bidentate ligand, providing a means of investigating the fundamental factors controlling these reactivity modes.⁷ Increased understanding of these SET reactivity modes will help lead to the rational design of well-defined complexes for both catalytic and stoichiometric applications. Substantial improvements in x-ray diffraction technology since the mid-1990's has allowed these first row transition metal complexes to be more easily explored.⁸

There are a number of attractive classes of CpCr(LX) complexes which have not been explored due to the difficulty of their synthesis. Typically, complexes of this type are synthesized by the introduction of the ligands to Cr(II) chloride via salt metathesis. This multi-step process, however, results in the formation of ionic byproducts which can hinder crystallization and isolation, and in the occasional formation of unsolicited bis(ligand) and “ate” complexes.

Protonolysis is a gentler alternative to salt metathesis which has the advantages of being a simple one-step, “one pot” procedure resulting in neutral byproducts, though it is often slower and potentially reversible as it lacks the thermodynamic driving force of LiX or NaX formation.

The salicylaldiminato, or phenol-imine, class of monoanionic bidentate ligands is easily synthesized by Schiff base chemistry between salicylaldehydes and anilines, which are commercially available with many various substituents and otherwise amenable to variation at key

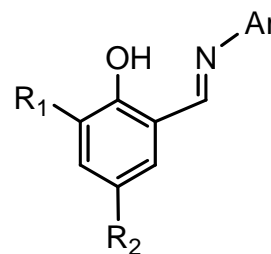


Figure 2 - The tunable phenol-imine ligand.

substitution positions.⁹ In addition, this ligand set has found use in homogeneous and highly active CpCr(LX)X ethylene polymerization catalysts.^{10,11} The ability to easily modify the steric and electronic properties of the ligand make it a promising candidate for investigating structure-activity relationships in SET reactivity.

My previous summer research attempted to synthesize a set of well-defined Cr(II) phenol-imine CpCr(LX) complexes (CpCr[PI], in general) to test SET reactivity with organic halides, but was largely unsuccessful as x-ray quality crystals of the mono-ligated complex were difficult to obtain. Synthetic routes using protonolysis were explored, with some success in making the characteristically green/yellow-green CpCr[PI] complex *in situ* using CpCr(C₆H₄CH₂NMe₂) as a protonolysis precursor. Two major shortcomings were clear, however: the protonolysis precursor had poor solubility and the reaction was too slow. In particular, the slow reactivity allowed bimolecular decomposition side reactions to dominate the reaction, forming a characteristically brown/red mixture of Cp₂Cr and bis(ligand) complexes.

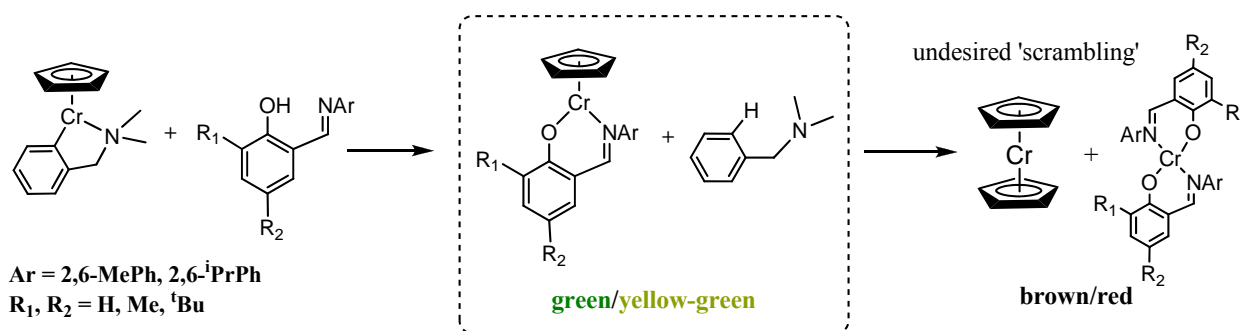


Figure 3 - Scheme for the synthesis of a CpCr[PI] complex by protonolysis, with subsequent 'scrambling' to chromocene and the bis(ligand) complex.

In cases where the slow protonolysis reaction yielded an initial green/yellow-green solution, the concentrated reaction solution, when left to stand at -35°C, yielded crystals of the more

crystalline $\text{Cr}[\text{PI}]_2$ complex. Research in phenol-imine nickel ethylene polymerization catalysts has supported this notion, where the mono-ligated phenol-imine complex has been formed only to react further to yield the bis(ligand) complex. In that case, only when the ligand was sufficiently bulky did the compounds remain mono-ligated.¹² The same tactic was undertaken with these Cr complexes, but without success.

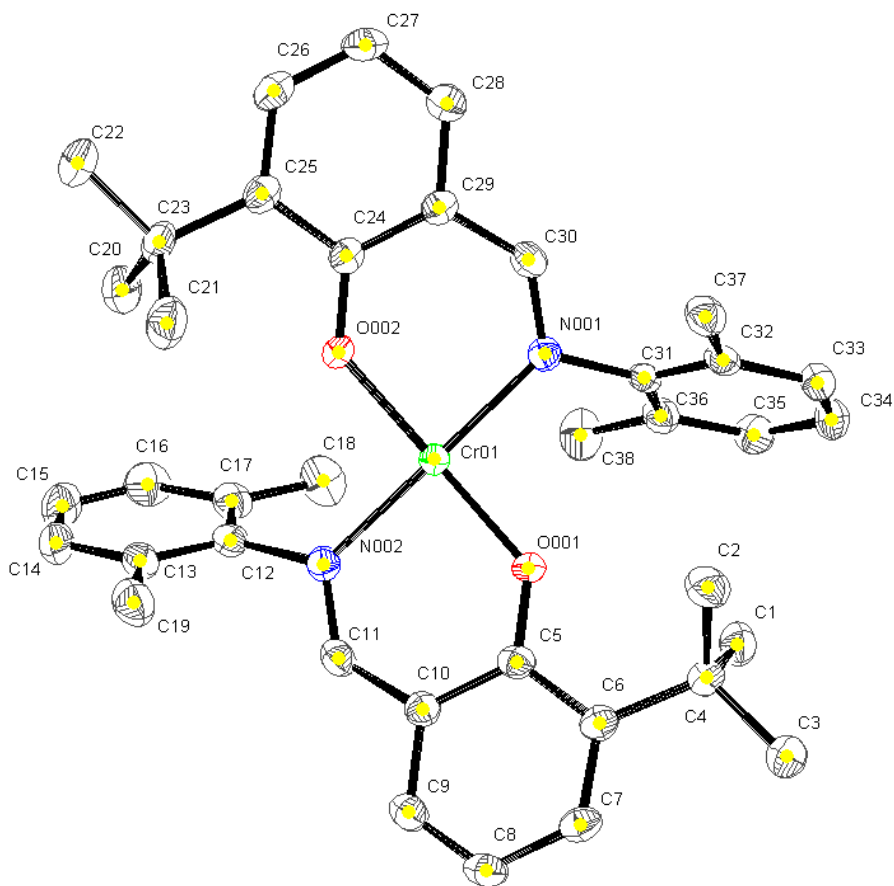


Figure 4 - ORTEP diagram of $\text{Cr}[\text{XylNCH}(2\text{-}^t\text{BuC}_6\text{H}_3\text{O})]_2$.

Protonolysis reactivity using the precursor $[\text{Cp}_2\text{Cr}][\text{I}]$ in the more stable Cr(III) oxidation state resulted in a much more stable $\text{CpCr}(\text{LX})\text{I}$ product, thereby preventing decomposition by loss of

the second Cp ring and making the well-defined product isolable. Further alkylation reactions were able to yield well-defined CpCr(PI)(R) alkyl complexes.

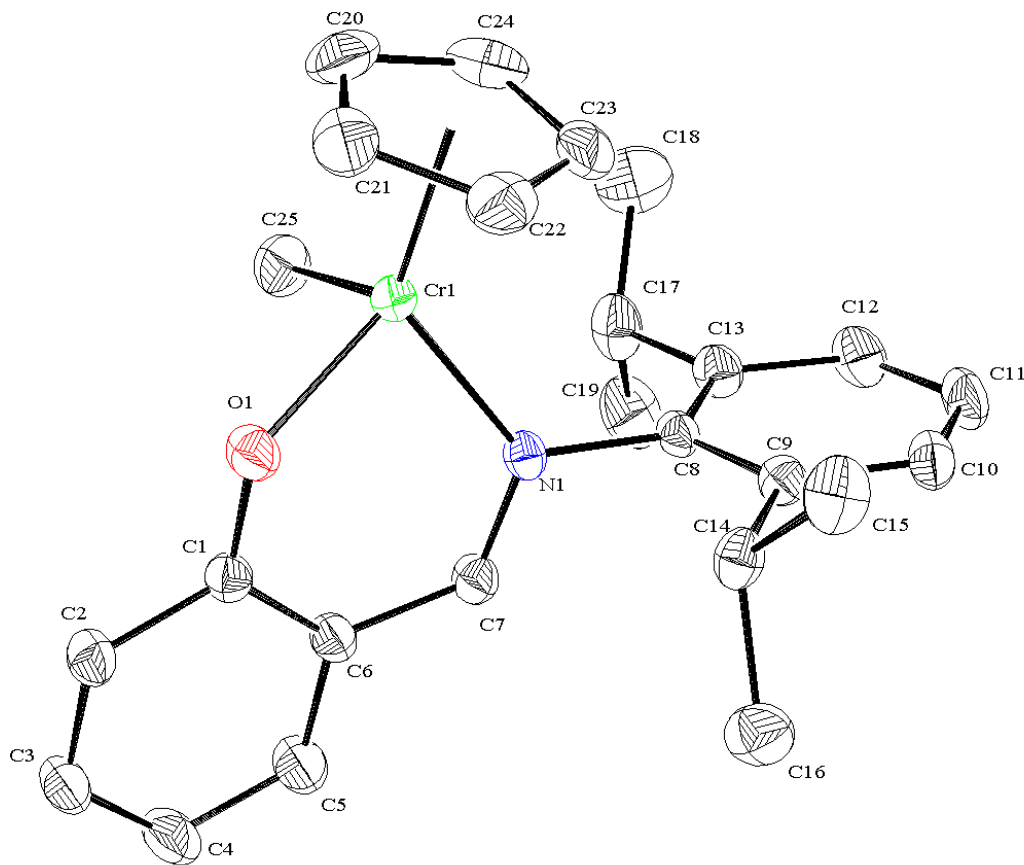


Figure 5 - ORTEP diagram of CpCr[PI-H/Dpp](Me), synthesized *via* protonolysis from [Cp₂Cr][I].

Improved synthetic methodologies are required to enable further investigation of ligand sets, especially in the reactive Cr(II) oxidation state where a fine-tuned selectivity is required to avoid removal of the second Cp ring and formation of bis(ligand) or other undesired complexes. It is from this starting point that the development and design of an improved protonolysis precursor was pursued. With a reliable synthetic route to generating CpCr(LX) complexes *in situ*, a better

understanding of the fundamental structure-activity relationships of paramagnetic organochromium complexes in SET reactions can be attained.

Results and Discussion

The complex previously sampled as a protonolysis precursor, $\text{CpCr}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)$, showed some promise but was never made with protonolysis reactivity in mind.¹³ For an enhanced $\text{CpCr}(\text{LX})$ protonolysis precursor, both good solubility and quick reactivity are desired properties. Solubility in non-polar solvents may be enhanced by the presence of non-interfering alkyl substituents, whereas the key to a reactive complex is an accessible Cr-C bond. Following the same synthetic methods used to create $\text{CpCr}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)$, an improved variation was pursued.

Directed *ortho*-metallation (DoM) is a well-known technique for synthesizing salts of bidentate ligands with anionic carbon and neutral donor atoms which can be used to synthesize $\text{CpCr}(\text{LX})$ complexes by salt metathesis. The presence of a directed metalation group (DMG) guides alkyllithium bases to regioselectively deprotonate at a site *ortho* to the heteroatom-containing DMG, producing an *ortho*-lithiated species.¹⁴ The use of benzenoids, common in DoM reactions, is advantageous because of the corresponding $\text{CpCr}(\text{LX})$ precursor complex having a ligand where a strong, aromatic C-H bond may be formed in the protonolysis reaction, serving as a thermodynamic driving force. In addition, Cr-aryl bonds are typically decomposition resilient.¹⁵

The dialkyl amide group (CONR_2) is a strong DMG,¹⁴ and was used in the directed *ortho*-metallation of diisopropylbenzamide. The metalated ligand was reacted with CrCl_2 and NaCp *in*

situ to produce a purple/purple solution of $\text{CpCr}[\text{C}_6\text{H}_4\text{C}(\text{O})\text{N}^i\text{Pr}_2]$, which was worked up and crystallized from hexanes at -35°C to produce dark violet crystals in 36% yield. This complex contains isopropyl groups directed away from the metal center for added solubility, and an accessible Cr-C bond primed for protonolysis.

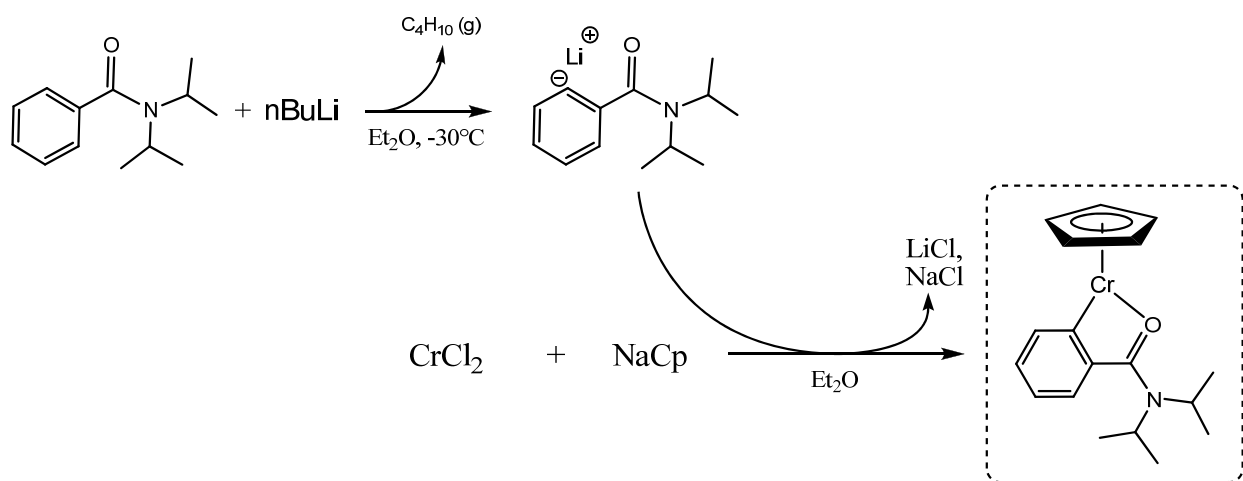


Figure 6 - Synthetic route to $\text{CpCr}[\text{C}_6\text{H}_4\text{C}(\text{O})\text{N}^i\text{Pr}_2]$ using directed *ortho*-metallation.

The protonolysis reactivity of $\text{CpCr}[\text{C}_6\text{H}_4\text{C}(\text{O})\text{N}^i\text{Pr}_2]$ was tested by reaction with one equivalent of $\text{H}[\text{PI-H/Dpp}]$ in hexanes at varying concentrations. A colour change to green/yellow-green is characteristic of a solution of $\text{CpCr}[\text{PI-H/Dpp}]$, whereas brown/red is characteristic of the formation of Cp_2Cr and $\text{Cp}[\text{PI-H/Dpp}]_2$ by the ‘scrambling’ decomposition reaction (Figure 3). These reactions are, respectively, first-order and second-order with respect to the $\text{CpCr}[\text{PI-H/Dpp}]$ target molecule.

$\text{CpCr}[\text{C}_6\text{H}_4\text{C}(\text{O})\text{N}^i\text{Pr}_2]$ was found to be significantly more soluble than $\text{CpCr}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)$ in the non-coordinating, non-polar solvent, as expected, with the non-dilute solution (0.01 M) reacting slowly to display a colour change to green-brown/red-orange and then brown/red over four days, whereas the dilute solutions maintained an increased proportion of green to incident

light as the concentration decreased. All of the solutions were brown/red in varying intensities according to their concentrations after one week.

The increased proportion of green colour in the less concentrated solutions suggests that the desired CpCr[PI-H/Dpp] complex was made *in situ* in some proportion, but was overcome by the bimolecular scrambling side-reaction which became increasingly dominant at higher concentrations due to its second-order relationship to the phenol-imine intermediate.

Solvent effects were also investigated, with the reaction tested in THF, toluene, and hexanes at the same concentration (0.01M). Each of the reactions resulted in a colour change from purple/purple to orange-red/red over one day, with the THF solution reacting most quickly, and the hexanes and toluene solutions reacting moderately more slowly at about the same rate.

Overall, the protonolysis reactivity of CpCr[C₆H₄C(O)NⁱPr₂] with phenol-imines was found to lead primarily to bimolecular decomposition products.

In addition, the use of a carbonyl donor may have favoured decomposition of the complex due to the lone pairs of the carbonyl O-atom attracting the acidic phenol proton towards the Cp ring at the region *trans* to the Cr-C σ -bond, thus weakened by the *trans* effect.¹⁶ Protonation of the Cp ring will lead to its displacement, and then to Cr(LX)(L'X') complexes.

The development of another protonolysis precursor was therefore attempted. The desired complex would be similar to before with an accessible Cr-C bond, but without the potentially perilous lone pairs on the neutral donor. Again, the use of DoM was a guiding factor, selecting 4,4-dimethyl-2-phenyl-2-oxazoline as the ligand backbone as it contains the strong oxazoline DMG with an imine moiety as a neutral donor, and methyl groups for sufficient solubility.

Synthesis of the CpCr[C₆H₄-oxazoline] complex was carried out according to the same synthetic scheme used for CpCr[C₆H₄C(O)NⁱPr₂].

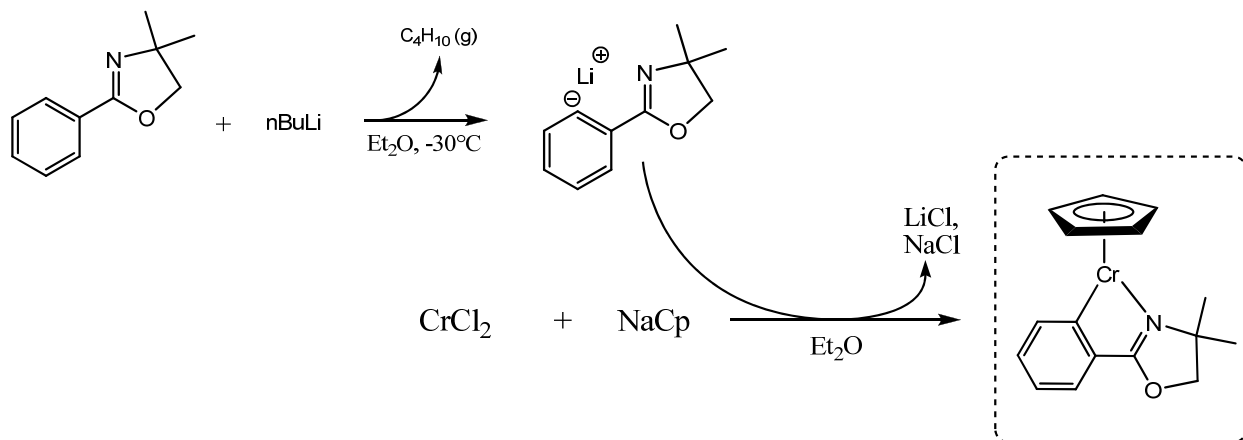


Figure 7 - Synthetic route to CpCr[C₆H₄-oxazoline] using directed *ortho*-metallation.

The metalated ligand was reacted with CrCl₂ and NaCp *in situ* to produce an intensely dark orange-brown/red solution of CpCr[C₆H₄-oxazoline], which was subsequently worked up and crystallized from a concentrated hexanes solution at -35°C to produce dark brown crystals in 31% yield.

Protonolysis reactivity was tested by reaction with one equivalent of H[PI-H/Dpp] in hexanes, resulting in no significant colour change at all. After two days, the solution became cloudy, suggesting decomposition. As the characteristic green/yellow-green colour of the CpCr[PI-H/Dpp] was not observed in any proportion after a week of reaction time, it was speculated that the CpCr[C₆H₄-oxazoline] was too stable, thereby making the Cp ring a better target for protonolysis than the Ph-oxazoline due to the *trans*-effect of the Cr-C bond.

This result suggested that the mechanism of the protonolysis reaction may have been different than expected. The reaction was implicitly assumed to go through an associative substitution,

where the phenol proton of the phenol-imine ligand was transferred to simultaneously form an aromatic C-H bond and break the Cr-C bond, with the neutral imine donor undergoing substitution with the neutral O-donor to result in the dissociation of the protonated diisopropylbenzylamide, no longer experiencing the chelate effect. A dissociative protonolysis mechanism, on the other hand, would require dissociation of the neutral donor of the bidentate ligand as a first step, opening up a coordination site for the neutral donor of the phenol-imine ligand which would then guide the phenol proton to the Cr-C bond, resulting in proton transfer to the carbon and complete dissociation of the diisopropylbenzylamide ligand.

If, instead, the protonolysis reaction proceeds through a dissociative mechanism, the amide isopropyl groups of $\text{CpCr}[\text{C}_6\text{H}_4\text{C}(\text{O})\text{N}^i\text{Pr}_2]$ may have, in an unanticipated manner, hampered the reaction by inhibiting dissociation of the carbonyl O-donor due to inward steric pressure from the bulky isopropyl groups.

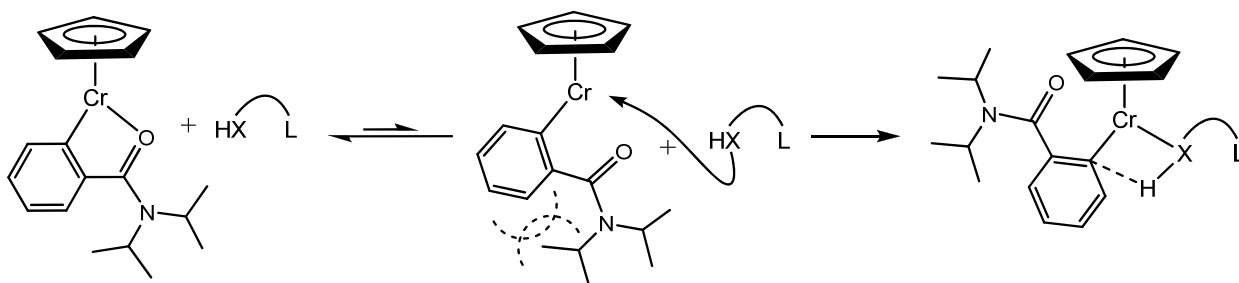


Figure 8 – Inward steric repulsion of the ^iPr groups may inhibit hemilability of the carbonyl donor.

Due to these unsuccessful attempts, a new approach was taken. The dissociation or hemilability of the neutral donor can be encouraged if the chelate effect is removed. In addition, with the neutral and anionic ligands separated, the dissociation reaction becomes concentration dependent. A synthetic strategy to prepare a viable $\text{CpCr}(\text{Ar})(\text{L})$ complex, however, needed to be

developed.

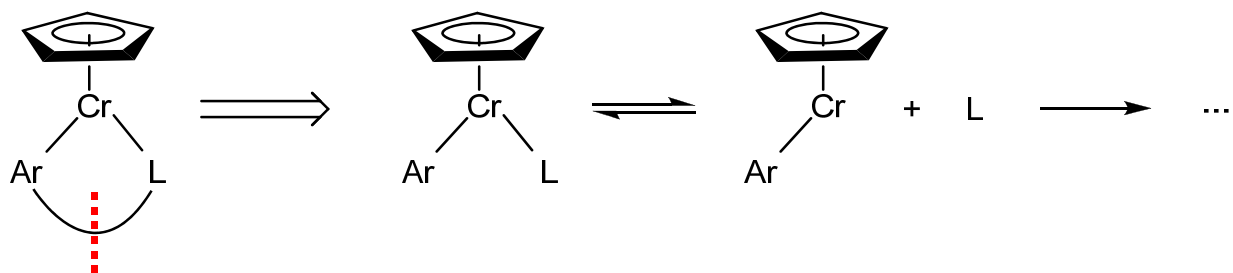


Figure 9 – Without the chelate effect, dissociation of the neutral donor is encouraged.

The most direct synthetic route to $\text{CpCr}(\text{Ar})(\text{L})$ would be the sequential addition of the neutral ligand then the ArMgBr reagent to a mono-Cp Cr(II) precursor. The related reaction of NaCp^* and CrCl_2 yields a $[\text{Cp}^*\text{Cr}(\mu\text{-Cl})]_2$ dimer which can be alkylated to yield $[\text{Cp}^*\text{Cr}(\mu\text{-R})]_2$.

Subsequent reaction with a neutral donor, in order to make the monomer, is possible in some cases, but very slow.¹⁷ Unfortunately, the same reactivity does not occur in Cp systems, where the reaction of NaCp and CrCl_2 simply yields a mixture of Cp_2Cr and CrCl_2 .

Another approach to this type of chromium complex has a single example in the literature, where Cp_2Cr undergoes a reaction where both the neutral and anionic ligands are added to the complex in one step, with simultaneous protonation of the Cp ring, to yield a $\text{CpCr}(\text{L})(\text{X})$ complex. The protonolysis reaction utilizes protonated halide salts of a neutral ligand (HX-L salts). This type of chemistry has been used with the strong σ -donating *N*-heterocyclic carbene (NHC) ligand to synthesize $\text{CpCr}(\text{NHC})(\text{Cl})$, which has been shown to yield the Ph complex upon subsequent alkylation.¹⁸

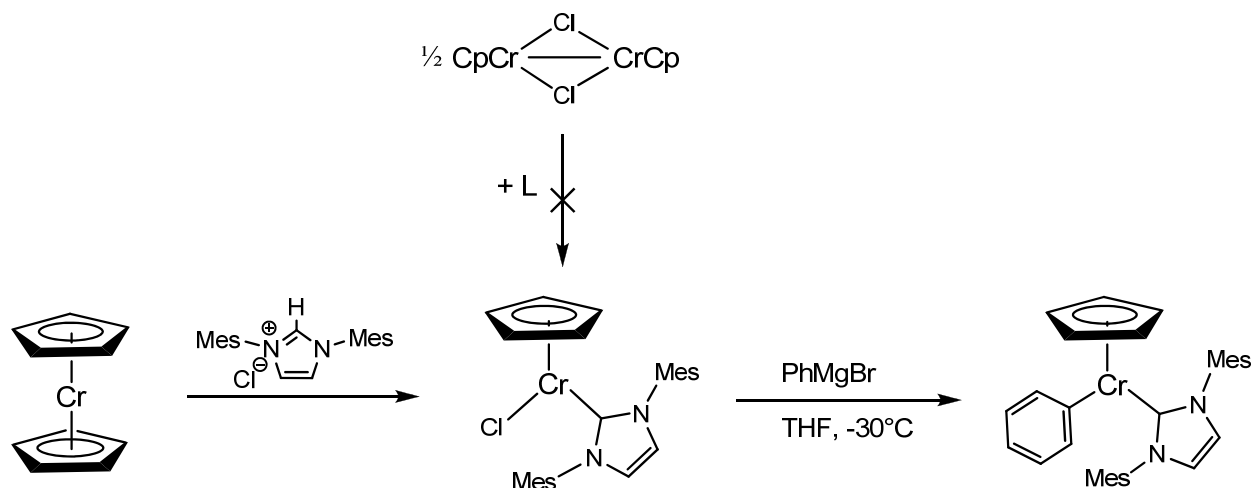


Figure 10 - Synthesis of CpCr(Ph)(NHC) by Voges et al.¹⁸

A variety of related nickel complexes have been explored, providing guidance into the details of what makes the reaction successful.¹⁹⁻²⁰ In each case, the synthesis proceeds by protonolysis of the metallocene using an imidazolium halide salt, resulting in simultaneous addition of both the NHC and X ligands.

Reactions with only the neutral NHC ligand and Cp_2Cr , on the other hand, lead to either an $(\eta^1\text{-Cp})(\eta^5\text{-Cp})\text{Cr(NHC)}$ complex or else a cationic bis(NHC) complex with an outer sphere Cp anion, depending on the substituents of the NHC ligand.²¹ In any case, a successful synthetic route must selectively displace only one Cp ring of Cp_2Cr .

The use of an HX-L salt narrows the range of potential ligands by requiring them to be sufficiently basic in order to make the salt. The acidity of the protonolysis proton is also required to fall into a certain range. If too acidic, the Cr metal center itself will be protonated and oxidized to Cr(III), with the release of hydrogen gas.²² The upper limit of this effect can be seen by the oxidation of decamethylchromocene (Cp^*Cr) by 2,6-dimethylpyridinium borate, whereas Cp_2Cr

is not oxidized in the same reaction.²³ The Cp*₂Cr complex is slightly more oxidizable due to the increased electron donation at the metal center from the additional alkyl groups, thereby stabilizing the Cr(III) oxidation state. On the opposite end of the spectrum, ^tBuOH is only acidic enough to protonate a single Cp ring, producing a [CpCr(μ-^tBuO)]₂ dimer, whereas a less bulky ROH gives the non-Cp Cr(OR)₂ complexes.²⁴ The species of counterion used in the HX-L salt has also been shown to be an important factor, where reactions with Cp₂Ni have displayed a keen specificity for the Cl⁻ anion.¹⁹

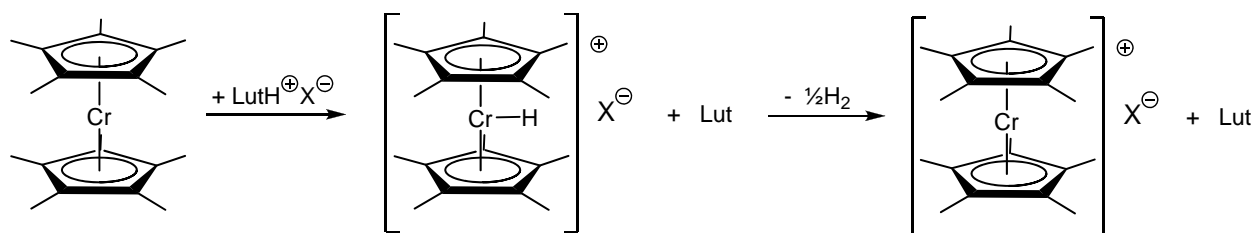


Figure 11 - Oxidation of Cp*₂Cr by [LutH][X].

Knowing these properties, the commercially available 2,4,6-trimethylpyridinium tosylate (HOTs-Col) and 1,8-diazabicyclo[5.4.0]undec-7-ene with p-toluenesulfonic acid (HOTs-DBU) were selected as possible candidates for the protonolysis of Cp₂Cr to form CpCr(L)(X), where the reactions would be carried out with and without the presence of the Cl⁻ counterion source [NEt₄][Cl], and with and without the presence of the neutral PPh₃ ligand.

The reaction using HOTs-DBU with 1 equivalent of [NEt₄][Cl] stood out amongst the others, as it resulted in a colour change from chromocene orange/orange to a deep, clean purple/purple with a white precipitate (which is presumably [NEt₄][OTs]). The same reaction without the presence of the Cl⁻ source resulted in a dark-brown/orange solution with no precipitate. With the

alternate neutral ligand PPh₃, the solution became a lighter orange/orange colour and contained a pink precipitate, indicating unreacted Cp₂Cr and formation of an undesired ionic byproduct.

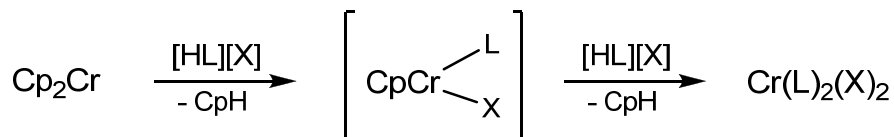


Figure 12 - A lack of 1st vs. 2nd Cp ring selectivity may lead to non-Cp products and unreacted Cp₂Cr.

The reaction using HOTS-Col resulted in a colour change from chromocene orange/orange to yellow-orange/yellow-orange. With 1 equivalent of [NEt₄][Cl], the resulting solution was brown/light-brown with a pale green precipitate, and with 1 equivalent of PPh₃, it was orange/orange with a white precipitate.

	Without Addition	1 equiv. [NEt ₄][Cl]	1 Equiv. PPh ₃
HOTS-Col	✗	✗	✗
HOTS-DBU	✗	✓	✗

Figure 13 – Results of Cp₂Cr + HX-L reactivity with/without Cl⁻ and PPh₃ sources.

The reaction with HOTS-DBU and [NEt₄][Cl] was clearly the most promising, as it produced a distinctive purple/purple solution which is similar to the reported violet colours of CpCr(NHC)(Cl) solutions. Chloride counterion specificity was also observed, as the reaction with solely HOTS-DBU yielded a dubious brown/orange solution. Just the presence of an external chloride source was enough to alter the reactivity. While Nolan et al. suggest this specificity to be due to the formation of a strong M-Cl bond which acts as a strong

thermodynamic driving force,¹⁹ this may also be due to the nucleophilic ability of the chloride. In this explanation, though speculative, it may be that the nucleophilic ability of chloride over the tosylate allows formation of a reactive η^1 -Cp anionic intermediate, attracting the proton to the vulnerable η^1 -Cp which is then completely displaced by protonolysis, leading to the product. Attempts to use fluoride as an alternative counterion seemed to react, though yielding a black, oily, insoluble residue.

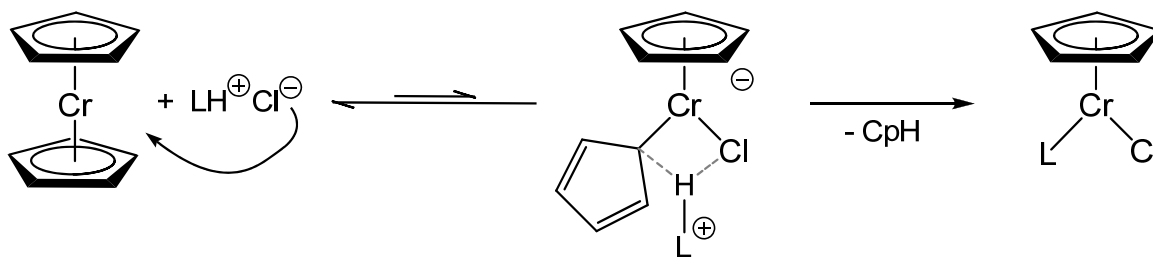


Figure 14 - Speculative reaction mechanism, showing the importance of the nucleophilic ability of the counterion.

A subsequent set of reactions looked at the protonolysis of Cp_2Cr with $[\text{HNEt}_3][\text{Cl}]$ alone, and with $[\text{HNEt}_3][\text{Cl}]$ along with one of 2,6-di-*tert*-butyl-4-methylphenol (BHT), PPh_3 , or $\text{H}[\text{PI-H/Dpp}]$. The reaction is assumed to proceed as in the figure below, where the NEt_3 ligand may be displaced by a better neutral ligand if available.

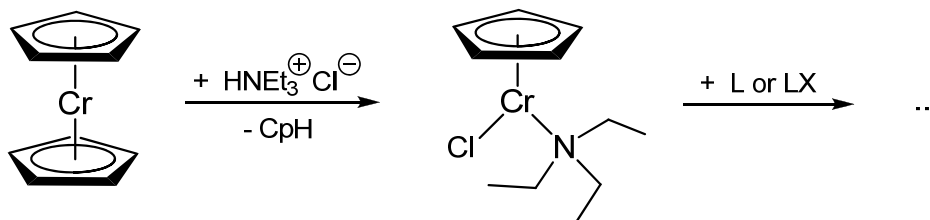


Figure 15 – Speculative formation of a $\text{CpCr}(\text{NEt}_3)(\text{Cl})$ intermediate, able to be trapped by a better L.

The reactions using $[\text{HNEt}_3][\text{Cl}]$ with and without either BHT and PPh_3 resulted in identical looking clear, light yellow-orange/yellow-orange solutions, not characteristic of $\text{CpCr}(\text{L})(\text{X})$ complexes. The reaction with $[\text{HNEt}_3][\text{Cl}]$ and $\text{H}[\text{PI-H/Dpp}]$ resulted in an initial colour change to a very dark green-brown/red-orange which became brown/red over 10 minutes, not characteristic of green/yellow-green $\text{CpCr}[\text{PI}]$ complexes. Thus, the combination of the neutral DBU ligand with the chloride counterion was found to be very specific. The DBU ligand has found limited application in organometallic chemistry, with the most notable example being a $(\text{DBU})_2[\text{Ni}]$ metallacycle catalyst with some specific reactivity related to ethylene.²⁵

The reaction was performed on a larger scale using the authentic HCl-DBU salt, resulting in a dark purple/purple solution, and the isolation of a dark purple powder from a concentrated toluene solution at -35°C in 50% yield.

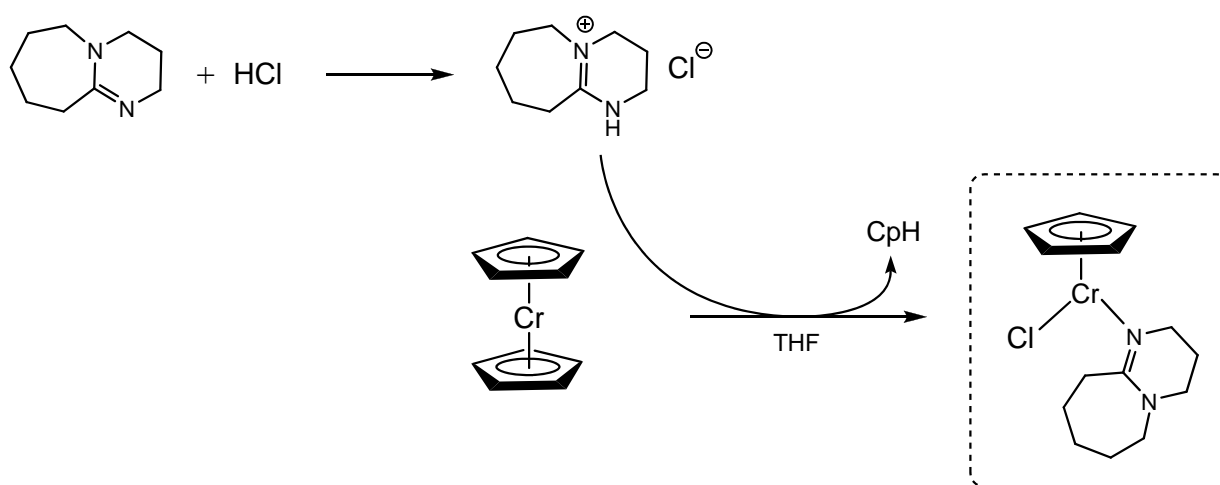


Figure 16 – Synthetic route to $\text{CpCr}(\text{Cl})(\text{DBU})$ by protonolysis of Cp_2Cr with HCl-DBU .

The same reaction was attempted using the protonated chloride salt of 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2,a]-pyrimidine (hppH, for good reason),²⁶ resulting in an instant colour change from chromocene red-orange/red-orange to dark red/red upon addition of the white powder. A teal

precipitate formed over time. While the hppH ligand is very similar to DBU,²⁷ the additional amine-H may act as a proton source for protonolysis of the Cp ring, turning hpp into a bidentate, anionic ligand, and leading to an unexpected product. Again, this highlights the specificity of the DBU ligand.

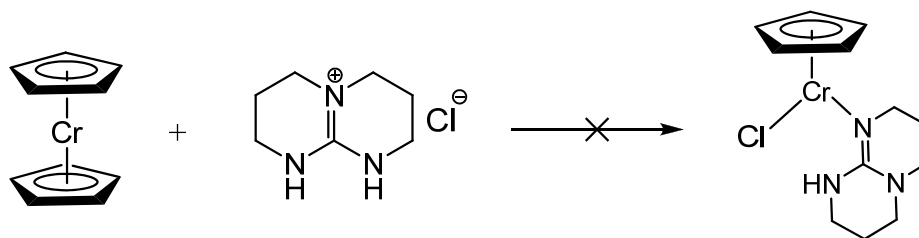


Figure 17 - Protonolysis of Cp₂Cr with HCl-hppH did not show similar reactivity to DBU-HCl.

A similar reaction with 1,3-dimethylimidazolium iodide ([Me₂(NHC)][I]), analogous to the nickel NHC chemistry of Ritleng et al.,²⁰ was also attempted. The reaction of Cp₂Cr with [Me₂(NHC)][I] resulted in a colour change to brown-red/orange with a beige-coloured precipitate, however, which is inconsistent with a CpCr(NHC)(X) complex. Though similar to the successful chemistry of Voges et al.,¹⁸ where a stable CpCrCl(1,3-dimesitylimidazoline-2-ylidene) complex was synthesized and isolated by protonolysis of Cp₂Cr with 1,3-dimesitylimidazolium chloride, the NHC ligand used here contained less bulky methyl substituents as an iodide salt instead. This was due primarily to the ease of the synthesis of [Me₂(NHC)][I], made by the reaction of 1-methylimidazole and methyl iodide at reflux in toluene, whereas the synthetic procedure for 1,3-dimesitylimidazolium chloride (and related) is a more complicated multi-step procedure.²⁸

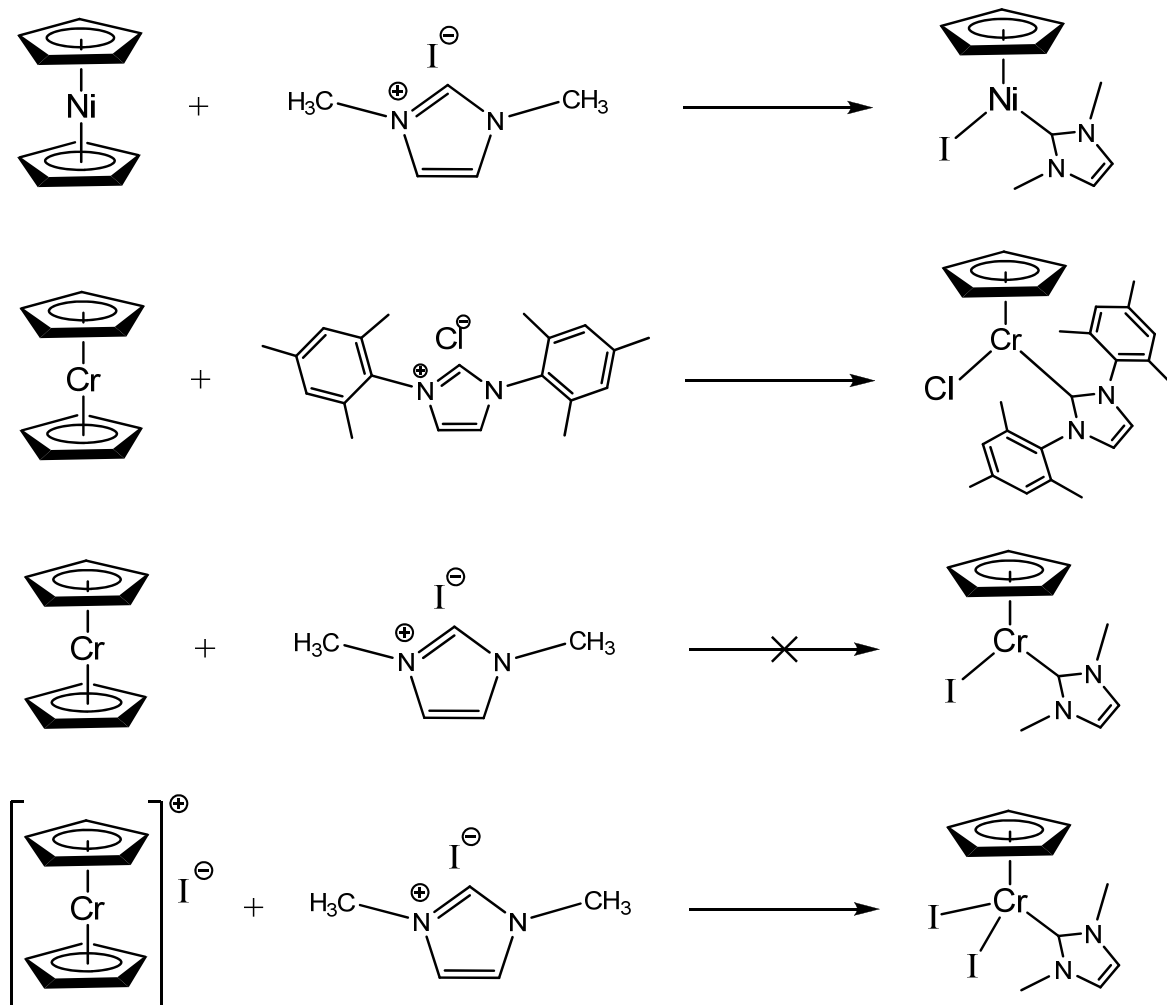


Figure 18 – The reaction of Cp₂M + [Me₂(NHC)]I works with M = Ni, and not M = Cr.

The same protonolysis reaction was also attempted with [Cp₂Cr][I], taking advantage of the greater selectivity between protonation of the first versus second Cp ring in [Cp₂Cr][I] and the greater stability of the Cr(III) product. The CpCr(NHC)(I)₂ product may be able to be reduced to yield the desired Cr(II) CpCr(NHC)I complex. This reaction was investigated in order to determine whether the CpCr(NHC)I complex is inherently unstable, or merely unstable under the given protonolysis reaction conditions where the complex may be made as an intermediate to a

decomposition product due to the fine level of selectivity between protonation of the first and second Cp rings.

The addition of $[\text{Me}_2(\text{NHC})][\text{I}]$ to a suspension of the insoluble $[\text{Cp}_2\text{Cr}][\text{I}]$ in THF resulted in a colour change from cloudy orange-brown to a dark, clear, and intense teal/teal solution. Black needle-like crystals and powder of $\text{CpCr}(\text{NHC})(\text{I})_2$ were collected in 44.3% yield from a concentrated THF solution at -35°C . An analogous reaction with HOTs-DBU and $[\text{Cp}_2\text{Cr}][\text{I}]$ produced a similar colour change to dark teal/teal, though only a few small navy blue crystals were formed amid a black oil.

Before attempting to see if the Cr(II) NHC complex could be obtained by reduction of the Cr(III) NHC di-iodide complex, similar chemistry was explored with $\text{CpCr}(\text{DBU})(\text{Cl})$ as it was a more well-characterized Cr(II)/Cr(III) system. A qualitative amount of $\text{CpCr}(\text{DBU})(\text{Cl})$ in THF was oxidized by addition of CDCl_3 , resulting in an instant colour change from purple/purple to blue/violet-blue. The blue/violet-blue colour is highly characteristic of a CpCrLCl_2 compound,^{22,29} thus indicating oxidation to the Cr(III) $\text{CpCr}(\text{DBU})(\text{Cl})_2$ complex. The resulting solution was evaporated to dryness to remove any lingering CDCl_3 , with the residue re-dissolved in THF and split into three separate vials. One of Mg turnings, Zn powder, or Mn powder was added to each of the vials. The reaction with Zn resulted in a colour change to dark purple/purple after 2 days, and the reaction with Mn resulted in a slower colour change to dark purple/purple (identical) after 7 days. The reaction with Mg resulted in a very slow colour change to orange/brown, not indicative of a solution of $\text{CpCr}(\text{DBU})(\text{Cl})$. From this data, Zn was selected as a suitable reductant for $\text{CpCr}(\text{NHC})(\text{I})_2$.

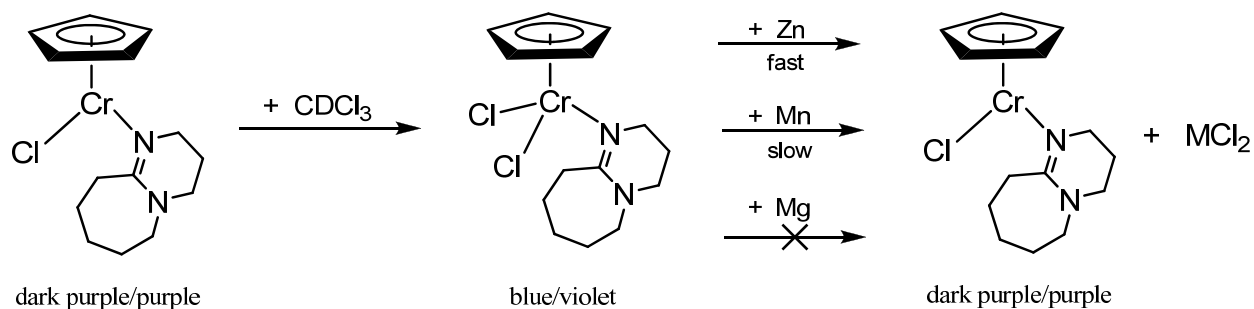


Figure 19 – Scheme for the oxidation/reduction of $CpCr(DBU)(Cl)$ *in situ*.

A spatula tip of Zn was added to a dark teal/teal solution of $CpCr(NHC)(I)_2$ in THF and left to stir. No immediate colour change was observed. After 2 days, however, the solution had clearly changed to become a pale peach-colour. A UV-Vis spectrum of the reduced product was obtained, and then a further oxidation reaction was performed in order to see if the addition of I_2 would reproduce the initial $CpCr(NHC)(I)_2$ compound. The addition of a sub-stoichiometric amount of I_2 resulted in an instant colour change to dark teal/teal, and a UV-Vis spectrum was collected. While the spectrum was similar to that of isolated $CpCr(NHC)(I)_2$ in THF, showing strong absorbance across the spectrum with a minimum at 510 nm, it lacked a strong absorbance at 696 nm. The intense peak at 607 nm is consistent with the presence of a remaining Cp ligand coordinating to chromium, however, with the overall shape of the spectrum similar to related $CpCrX_2L$ complexes.^{22,29} It may be the case that the use of a sub-stoichiometric amount of I_2 resulted in the formation of a $[CpCr(NHC)I_2(\mu-I)]$ complex, but more data is required to support this speculation.

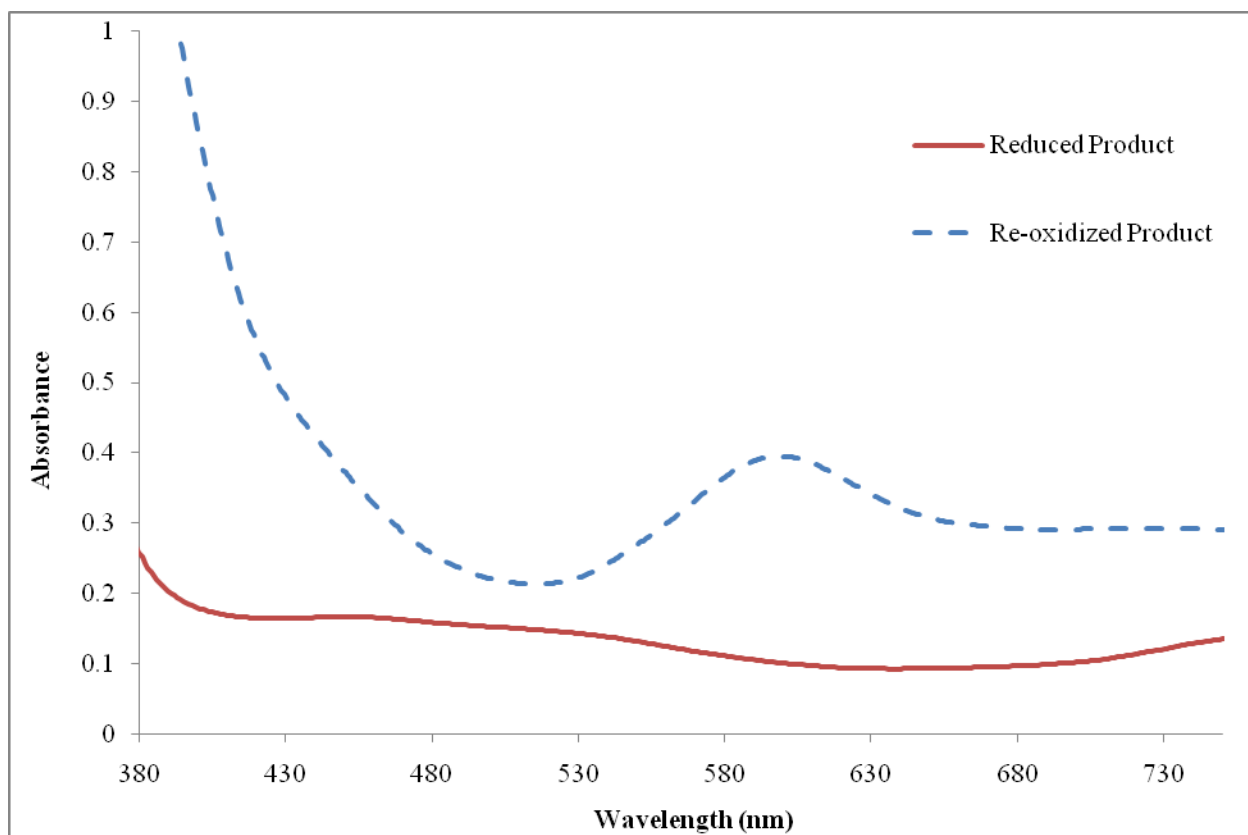


Figure 20 - UV-Vis spectra of the reduced and re-oxidized products of CpCr(NHC)(I)_2 , as well as an isolated sample.

The identity of these complexes as Cr(II) and Cr(III), however, is supported by their relative air stabilities. The Cr(II) pale peach-coloured solution turned black upon contact with oxygen, whereas the Cr(III) teal/teal solution displayed no colour change, even upon dissolution in acetone. This result supports the notion that CpCr(NHC)(I) may not itself be inherently unstable, but merely unstable and unattainable given the protonolysis reaction conditions of the addition of the imidazolium halide salt to Cp_2Cr .

Once these CpCr(L)(X) complexes had been further investigated, the alkylation of CpCr(DBU)(Cl) was attempted using each the Grignard reagents PhMgBr, (4-^tBuPh)MgBr, and MesMgBr. Upon addition of the Grignard reagent, an instant colour change to dark orange/orange was observed. Following work-up, the concentrated Et₂O solutions were left to stand at -35°C and black crystals were formed in each solution. Crystals of the mesityl product were analyzed by x-ray diffraction, revealing an unexpected arrangement. The structure was dimeric, with two crystallographically independent molecules in the unit cell.

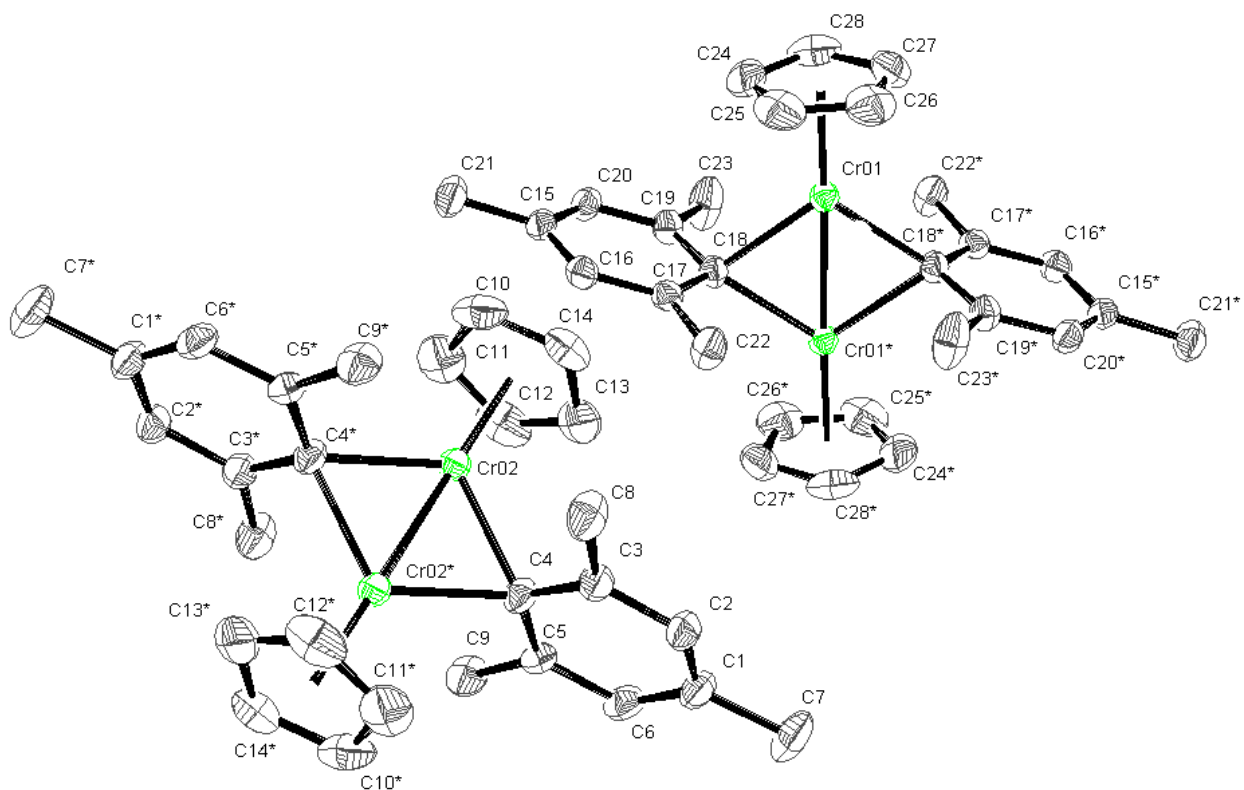


Figure 21 – ORTEP diagram of [CpCr(μ-Mes)]₂. See Appendix for more data.

This structure suggests lability of the neutral DBU ligand, a property advantageous to a dissociative protonolysis mechanism. With a labile DBU, the transient CpCrMes + DBU

intermediate may react to yield the highly crystalline $[\text{CpCr}(\mu\text{-Mes})_2]$ complex, which crystallizes out of solution to drive the equilibrium towards further formation of the dimer.

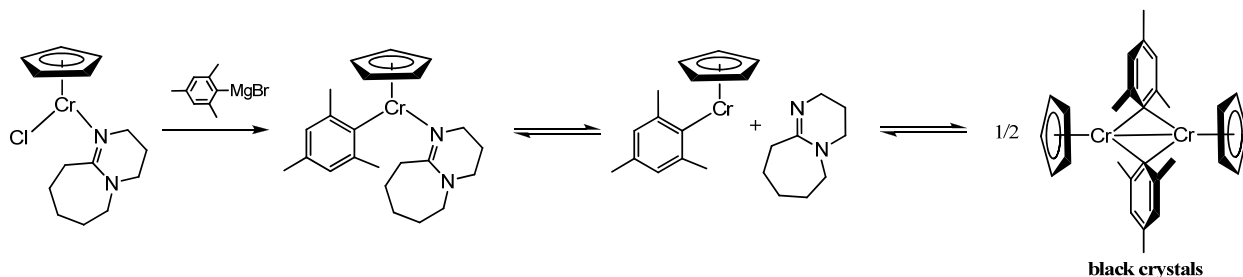


Figure 22 - Reaction scheme for the formation of $[\text{CpCr}(\mu\text{-Mes})_2]$.

Unit Cell Molecule	Cr-Cr Bond Length (Å)	Cr-Cntr.-Cr Angle	$\text{C}_{\text{para}}\text{-C}_{\text{ipso}}\text{-Cr Angles}$
Cr01/Cr01*	2.550	177.65°	125.93°/162.40°
Cr02/Cr02*	2.530	179.00°	138.47°/150.31°

Table 1 - Crystal structure data for $[\text{CpCr}(\mu\text{-Mes})_2]$.

The crystal structures of a variety of Cr-Cr complexes have been investigated in the literature, but not that of $[\text{CpCr}(\mu\text{-Mes})_2]$. The molecule displays a high level of symmetry and is extremely linear,

Molecule	Cr-Cr Distance (Å)	Geometry
$[\text{CpCr}(\mu\text{-O}^t\text{Bu})_2]$ ²⁴	2.632(5)	Sl. Bent
$[\text{CpCr}(\mu\text{-N}^i\text{Pr}_2)_2]$ ³⁰	2.7287(5)	Linear
$[\text{CpCr}(\mu\text{-I})_2]$ ³¹	2.4921(7)	Bent
$[\text{Cp}^*\text{Cr}(\mu\text{-Cl})_2]$ ¹⁷	2.642(2)	Bent
$[\text{Cp}^*\text{Cr}(\mu\text{-CH}_3)_2]$ ¹⁷	2.263(3)	Bent
$[\text{Cp}^*\text{Cr}(\mu\text{-Et})(\mu\text{-Ph})_2]$ ¹⁷	2.289(4)	Bent

Table 2 - Cr-Cr bond lengths in $[\text{CpCr}(\mu\text{-O}^t\text{Bu})_2]$, $[\text{CpCr}(\mu\text{-N}^i\text{Pr}_2)_2]$, $[\text{CpCr}(\mu\text{-I})_2]$, and various $[\text{Cp}^*\text{Cr}(\text{X})_2]$ complexes.

with Cr-center-Cr angles of 177.65° and 179.00° for the two crystallographically independent molecules in the unit cell, respectively. By contrast, related Cr(II) dimers such as $[\text{CpCr}(\mu\text{-I})_2]$,³¹ $[\text{Cp}^*\text{Cr}(\mu\text{-Cl})_2]$, $[\text{Cp}^*\text{Cr}(\mu\text{-CH}_3)_2]$, and $[\text{Cp}^*\text{Cr}(\mu\text{-Et})(\mu\text{-Ph})_2]$ show bent structures.¹⁷

The Cr-Cr bond length of 2.550/2.530 Å is shorter than that of [CpCr(μ-O^tBu)]₂ at 2.632(5) Å,²⁴ which is only slightly bent, and [CpCr(μ-NⁱPr₂)]₂ at 2.7287(5) Å, which is linear.³⁰ This is due to a minimal amount of steric bulk between the Cr atoms. Compared to dimers such as the bridging tetracarboxylate Cr₂(O₂CR)₄ “paddle-wheel” complexes, which routinely display bond lengths less than 2.000 Å, the Cr-Cr bond length is fairly long.³² The angles through the plane of the bridging mesityl ligands to the chromium atoms are 125.93°/162.40° and 138.47°/150.31° for the molecules in the unit cell, respectively, indicating flexibility in the bond angle.

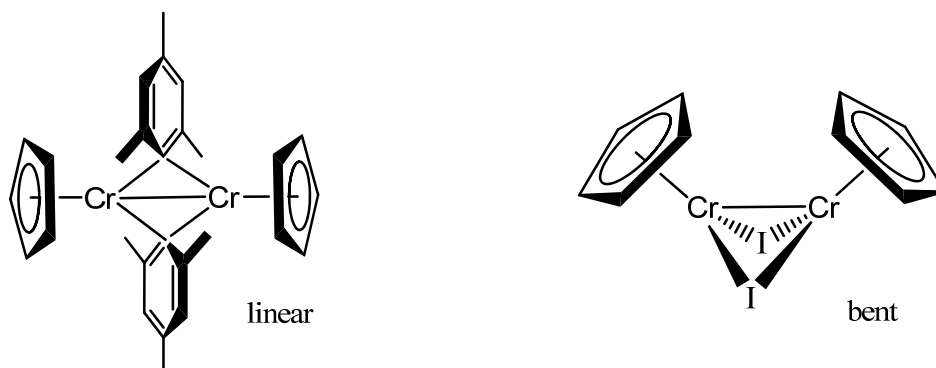


Figure 23 - Linear and bent geometries for dimeric Cr complexes.

Ongoing research in the Smith group is investigating the effects of increased steric bulk on the bridging aryl groups in the attempt to hinder stability of the dimer and obtain a monomeric and isolable CpCr(Ar)(L) complex.

In the absence of a well-defined CpCr(DBU)(Ph) complex, the reactivity of CpCr(DBU)(Cl) was investigated with regard to protonolysis with phenol-imine, β-diketiminato (NacNac), and anilido-imine ligands, and salt metathesis with phenol-imines and β-ketiminatos (AcNac). Anilido-imine complexes, in addition to the phenol-imines, have proven difficult to synthesize.

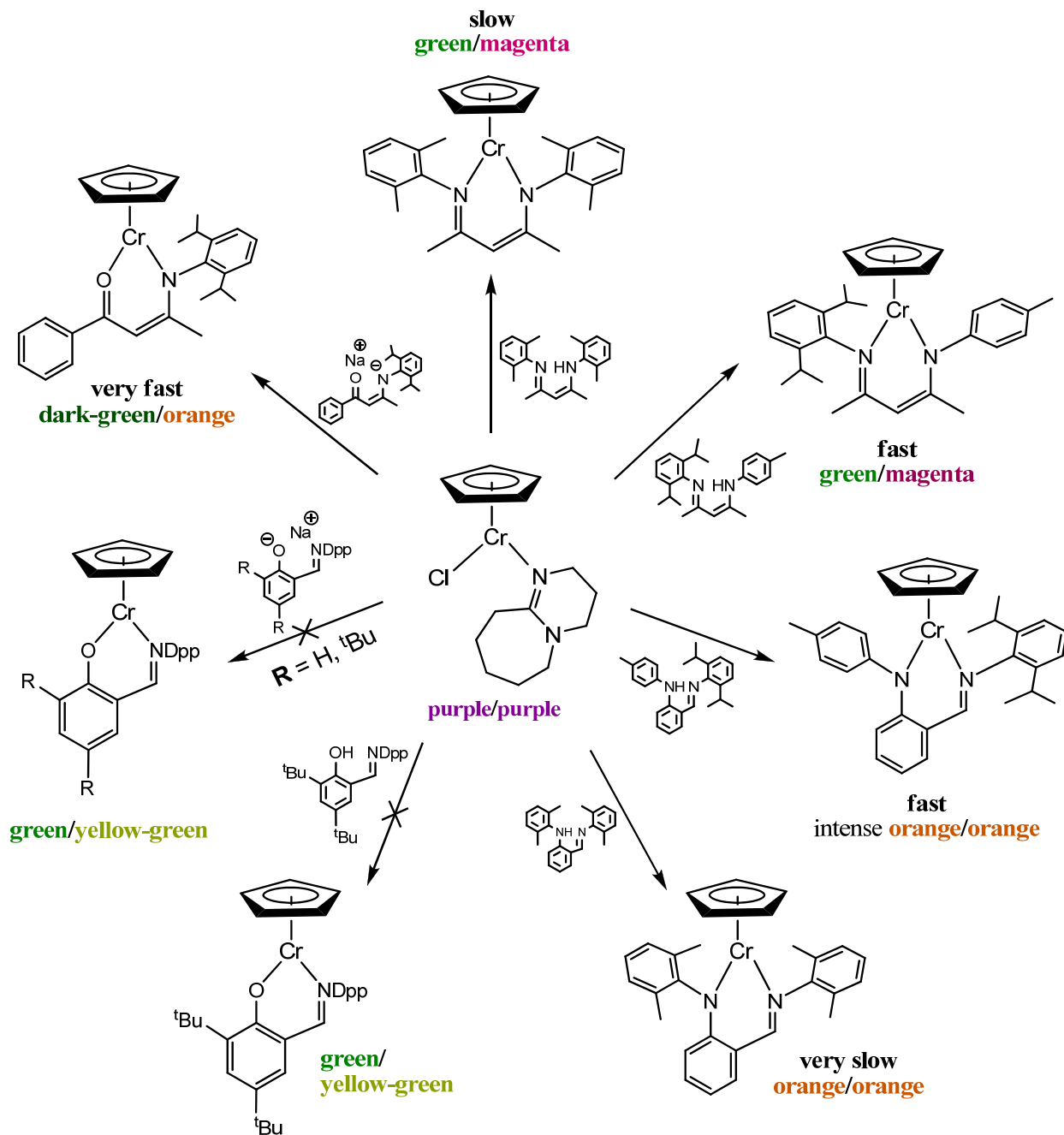


Figure 24 - Reaction scheme for protonolysis and salt metathesis routes to CpCr(LX) complexes from CpCr(DBU)(Cl).

The protonolysis reaction of CpCr(DBU)(Cl) with 1 equivalent of the symmetric NacNac ligand H[(Xyl)NCMe]₂CH in THF resulted in a slow colour change from purple/purple to green/magenta, characteristic of CpCr(NacNac) complexes,⁵ over 6 days. The same reaction

using 1 equivalent of the asymmetric NacNac ligand $\text{H}[\text{DppNC}(\text{Me})\text{CHC}(\text{Me})\text{N}(4\text{-MePh})]$ resulted in a faster colour change to a comparable green/magenta colour over 3 days.³³ Upon work-up, where a precipitate was filtered from each reaction solution, large black crystals of both NacNac complexes were formed from a concentrated hexanes solution at -35°C . Synthetic routes to $\text{CpCr}(\text{NacNac})$ complexes had previously proceeded by salt metathesis, only.^{5,33}

The protonolysis reaction with 1 equivalent of the symmetric anilido-imine $[\text{XylNHC}_6\text{H}_4(\text{CH}=\text{NXyl})]$ in THF resulted in a very slow colour change from purple/purple to red-orange/red-orange over 3 weeks. The same reaction using 1 equivalent of the asymmetric anilido-imine $[(4\text{-MePh})\text{NHC}_6\text{H}_4(\text{CH}=\text{NDpp})]$ resulted in a fast colour change over 18 hours to an intensely dark orange/orange solution with a precipitate. These colour changes were promising as $\text{CpCr}(\text{anilido-imine})$ complexes had not previously been synthesized, but crystallization and further characterization was not pursued.

In both sets of protonolysis reactions, the asymmetric ligand was observed to react more quickly. This is due to reduced steric hindrance around the amine proton, allowing easier proton transfer to occur. The precipitate that formed was presumably that of $[\text{H}(\text{DBU})][\text{Cl}]$, which is a relatively insoluble powder.

Protonolysis with $\text{H}[\text{PI-}^t\text{Bu}/\text{Dpp}]$ was also attempted, resulting in an instant colour change from purple/purple to brown/red. This is indicative of a mixture of the bis(ligand) complex with Cp_2Cr .

The synthesis of $\text{CpCr}[\text{PI-H}/\text{Dpp}]$ and $\text{CpCr}[\text{PI-}^t\text{Bu}/\text{Dpp}]$ from $\text{CpCr}(\text{DBU})(\text{Cl})$ were attempted by salt metathesis, trying to take advantage of the chloride in creating a NaCl byproduct. One equivalent of each of the ligands were deprotonated by reaction with NaH and then introduced to

CpCr(DBU)(Cl). The reaction with [Na][PI-H/Dpp] resulted in an instant colour change to dark brown/red-orange, whereas the reaction with [Na][PI-^tBu/Dpp] resulted in an instant colour change to intense red/red. In either case, the desired CpCr[PI] complexes were not made.

A similar reaction of [Na][PhC(O)CHC(Me)NDpp] with CpCr(DBU)(Cl) displayed more promising results, however, showing an instant colour change from purple/purple to dark green/orange. The reaction mixture was worked up, filtered through Celite, and left to stand as a concentrated hexanes solution at -35°C. Isolable crystals did not form from the green/orange solution. Like the CpCr(anilido-imine) complexes, this complex has not previously been synthesized, though the Cr(III) chloride species has.¹¹

Conclusion

Following the pattern of the earlier complex CpCr(C₆H₄CH₂NMe₂), which showed some promise as a protonolysis precursor to Cr(II) mono-Cp phenol-imine complexes, an improved protonolysis precursor to CpCr(LX) complexes was pursued to solve the issues of slow reactivity and poor solubility. Two related complexes, CpCr[C₆H₄C(O)NⁱPr₂] and CpCr[C₆H₄-oxazoline], were synthesized using directed *ortho*-metallation methodology, with each showing poor protonolysis reactivity with phenol-imines. The new motif of a CpCr(L)(Ar) precursor was investigated in order to encourage high rates of reactivity by dissociative protonolysis mechanisms. Following related work with CpCr(NHC)(Ph), various protonated halide salts were screened for reactivity with Cp₂Cr, with the neutral donor DBU and the anionic donor Cl found to be highly specific in producing CpCr(DBU)(Cl), but not other CpCr(L)(X) complexes. Subsequent alkylation reactions with PhMgBr, (4-^tBuPh)MgBr, and MesMgBr produced distinctive colour changes, with the crystal structure of the CpCr(DBU) + MesMgBr product

revealing a $[\text{CpCr}(\mu\text{-Mes})]_2$ dimer, suggesting the desired property of hemilability of the DBU ligand. The $\text{CpCr}(\text{DBU})(\text{Cl})$ complex showed good reactivity in protonolysis reactions with *NacNac* and anilido-imine ligands, and also by salt metathesis with β -ketiminatos. Though not providing a synthetic route to well-defined Cr(II) mono-Cp phenol-imine complexes, this research has produced increased understanding of the protonolysis mechanism, overall.

Experimental

General Methods

All reactions, with the exception of the synthesis of 1,3-dimethylimidazolium iodide, were performed under 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.³⁴ Anhydrous “sure-seal” grade reagents, such as NaCp in THF, PhMgBr in Et_2O , MesMgBr in Et_2O , (4-^tBuPh)MgBr in Et_2O , and *n*-butyllithium in hexanes, were purchased from Aldrich and used as received. Other liquid reagents were purchased from Aldrich and free-pump-thaw degassed before being brought into the glovebox. If not otherwise stated, the reagent was purchased from Aldrich.

Anhydrous amine hydrochloride salts were prepared by Dr. Kevin Smith by reaction of the neutral amines (DBU, NEt_3 , hppH) in dry Et_2O under N_2 with anhydrous HCl (1.0 M solution in Et_2O , Aldrich), followed by isolation in the glovebox.

UV-Vis spectra were collected using a VARIAN Cary 50 Bio UV-Vis spectrophotometer with air-tight UV cells. All colours are reported as X/Y where the X is the colour to incident light and Y is the colour to transmitted light.

General Syntheses

Cp₂Cr was synthesized from CrCl₂ (anhydrous powder, 99.99% trace metals basis, Aldrich) and 2 equivalents NaCp (Aldrich).³⁵ The phenol-imine ligands were synthesized by condensation of the benzaldehyde with the aniline at reflux in EtOH using a catalytic amount of p-toluenesulfonic acid.⁹

JT50 CpCr[C₆H₄CH₂NMe₂] + H[PI-^tBu/Dpp] - Concentration Effects

Dissolved CpCr[C₆H₄CH₂NMe₂] (24.9 mg, 0.0991 mmol) in hexanes, added H[PI-^tBu/Dpp] (39.5 mg, 0.100 mmol) and made up to 100 mL. The pale yellow-orange solution was diluted by a factor of 10, and 1.0 mL of the dilute solution was further diluted by factors of 10, 25, and 50 in separate containers. No colour changes were visible after 3 hours. After 3 days, the undiluted solution displayed a green/yellow colour.

JT51 CpCr[C₆H₄C(O)NⁱPr₂]

A solution of NaCp (3.5 mL, 2.0 M solution in THF, 7.0 mmol) was added dropwise to a stirring suspension of CrCl₂ (0.8643 g, 7.033 mmol) in THF (25 mL), resulting in an immediate colour change from teal to red-orange. Meanwhile, *n*-butyllithium (4.4 mL, 1.6 M solution in hexanes, 7.0 mmol) was slowly added to a chilled solution of N,N-diisopropylamide (1.437 g, 7.000 mmol) in Et₂O (15 mL). After 3 hours, the resultant yellow *ortho*-lithiated amide solution was added dropwise to the stirring red-orange reaction mixture, resulting in a quick colour change

from red-orange to dark purple/purple-brown. The reaction was left to stir overnight. Afterward, the solvent was removed *in vacuo* and the residue extracted with hexanes (5x5 mL) and filtered through a Celite pad on a glass frit, with the filtrate concentrated *in vacuo*. The resulting dark violet/ violet solution was placed in the freezer (-35°C) and left to stand, affording blocky, dark-violet crystals which were collected in three fractions (808.8 mg, 35.8% yield).

JT52 **CpCr[C₆H₄C(O)NⁱPr₂] + H[PI-H/Dpp]** - **Concentration Effects**

A hexanes solution of H[PI-H/Dpp] (24.9 mg, 0.0885 mmol, pale yellow) was added to a stirring hexanes solution of CpCr[C₆H₄C(O)NⁱPr₂] (29.2 mg, 0.0909 mmol, purple/purple), and the total volume was made up to 10.0 mL. Of the resulting pale purple/purple solution, 1.0 mL aliquots were diluted by factors of 10, 25, and 50 and the solutions left to react. After one day, colour changes to green-brown/red-orange in the undiluted solution, and pale green-brown in the dilute solutions were observed. After 4 days, the undiluted solution was red-brown/red, with the diluted solutions displaying colours of green-red/red, green-orange/pale-red, and green-yellow/pale-red from the least dilute to most dilute, respectively. After 7 days, each of the diluted solutions were orange/red.

JT54 **CpCr[C₆H₄C(O)NⁱPr₂] + H[PI-H/Dpp]** - **Solvent Effects**

Both CpCr[C₆H₄C(O)NⁱPr₂] (60.2 mg, 0.187 mmol) and H[PI-H/Dpp] (52.6 mg, 0.187 mmol) were dissolved separately in hexanes (3.0 mL each). Subsequently, 1.0 mL of each solution were mixed together and made up to 10.0 mL with one of hexanes, toluene, and THF. The

resulting solutions were purple/purple. After 10 minutes, the THF solution was noticeably red to incident. After 1 hour, the toluene and hexanes solutions were noticeably red to incident, with the THF solution orange-red/purple-red. After 1 day, all of the solutions were a dark orange-red/pink-red.

JT56 CpCr[C₆H₄-oxazoline]

A solution of NaCp (3.5 mL, 2.0 M solution in THF, 7.0 mmol) was added dropwise to a stirring suspension of CrCl₂ (0.8652 g, 7.040 mmol) in THF (15 mL), resulting in an immediate colour change from teal to orange-brown. Meanwhile, *n*-butyllithium (4.4 mL, 1.6 M solution in hexanes, 7.0 mmol) was slowly added to a chilled solution of freeze/pump/thaw de-gassed 4,4-dimethyl-2-phenyl-2-oxazoline (1.2325 g, 7.033 mmol) in Et₂O (8 mL). A colour change from colourless, to yellow, to dark red-brown was observed as the *n*-BuLi was added. The resultant red-brown *ortho*-lithiated oxazoline solution was added to the orange-brown reaction mixture dropwise over 5 minutes, resulting in a quick colour change from orange-brown to a cloudy, dark orange-brown/red. The reaction was left to stir overnight. Subsequently, the solvent was removed *in vacuo* with the residue extracted with hexanes and filtered through a Celite pad on a glass frit, with the filtrate concentrated *in vacuo*. The resulting peach-brown/red solution was placed in the freezer (-35°C) and left to stand, affording dark brown powder (633.5 mg, 31% yield).

JT57 CpCr[C₆H₄-oxazoline] + H[PI-H/Dpp]

The protonated ligand H[PI-H/Dpp] (56.24 mg, 0.1999 mmol) was dissolved in hexanes and added dropwise to a stirring orange-brown/red solution of CpCr[C₆H₄-oxazoline] (58.4 mg, 0.200 mmol) in hexanes (10 mL). No significant colour change was observed after 2 days. After a week, the solution was orange-brown/orange-red.

JT58 Screening of Potential CpCr(L)(X) Complexes

Cp₂Cr (106 mg, 0.581 mmol) was dissolved in 7.0 mL THF and divided evenly into 7 separate vials using a 1.0 mL volumetric pipette, with each solution made up to 4.0 mL with THF. To these orange/orange stock solutions of chromocene was added one of 2,4,6-trimethylpyridinium p-toluenesulfonate (HOTs-Col, 24.2 mg, 0.0825 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene with p-toluenesulfonic acid (HOTs-DBU, 26.6 mg, 0.0820 mmol), or H[PI-^tBu/Ph] (26.8 mg, 0.0828 mmol).

The reactions of Cp₂Cr with HOTs-Col or HOTs-DBU were also performed with the addition of one of [NEt₄][Cl] (13.6 mg, 0.0821 mmol) or PPh₃ (22.2 mg, 0.0837 mmol). The colour changes from the initial orange/orange are noted below:

HOTs-Col : Colour change to cloudy, muddy yellow-green/orange after 20 minutes. After 5 days, green-brown/orange with white precipitate. After 2 weeks, yellow-orange/yellow-orange with white precipitate.

HOTs-Col + [NEt₄][Cl] : After 10 minutes, solution was a clear yellow/yellow colour. After 20 minutes, a pale green precipitate started to form. After 5 days, brown-orange/yellow-brown with a tinge of green and a pale green precipitate.

HOTs-Col + PPh₃: Quick colour change to yellow-brown/orange-yellow. After 5 minutes, the solution became cloudy and remained orange/orange. After 5 days, a white precipitate had settled out from the orange/orange solution.

HOTs-DBU : No initial colour change over 30 minutes. After 1 day, a clear brown/orange with no precipitate. Over 2 more weeks, no further changes were detected.

HOTs-DBU + [NEt₄][Cl] : No initial colour change. After 15 minutes, the incident colour was more pink-red. After 2 hours, a cloudy purple/red-purple. After 1 day, the solution was purple/purple with a white precipitate settled out. The solution did not experience further changes over the next 2 weeks.

HOTs-DBU + PPh₃: No noticeable colour change over 2 hours. After 1 day, the solution was a less intense and cloudy orange/orange colour. After 5 days, the solution was orange/orange with a pale pink precipitate.

H[PI-^tBu/Ph]: No initial colour change evident over the first 30 minutes. After 1 day, the solution was a darker orange. After 5 days, the solution was a clear brown/orange.

JT59 Additional Screening of Potential CpCr(L)(Cl) Complexes

Cp₂Cr (106 mg, 0.581 mmol) was dissolved in THF (7.0 mL) and divided evenly into 4 separate vials (0.0831 mmol each) and made up to 6 mL with THF. To each orange/orange solution was

added 1 equivalent of $[\text{HNEt}_3][\text{Cl}]$ (11-13 mg, ~ 0.085 mmol). To three of the vials was added one of 2,6-di-*tert*-butyl-4-methylphenol (BHT, 18.5 mg, 0.0838 mmol), PPh_3 (22.1 mg, 0.0833 mmol), and $\text{H}[\text{PI-H/Dpp}]$ (23.3 mg, 0.0828 mmol). The observed colour changes from the initial orange/orange chromocene solution are noted below:

Only $[\text{HNEt}_3][\text{Cl}]$: The solution initially became darker with a yellow-orange/yellow-brown colour, turning to yellow-orange/brown over 5 minutes. No further colour changes were observed.

With BHT: The solution quickly became darker with a yellow-orange/yellow-orange colour. No further colour changes were observed.

With PPh_3 : The solution had an initial colour change to a slightly darker yellow-orange/yellow-orange than the other similarly-coloured solutions, but after 5 minutes they were indistinguishable. No further colour changes were observed.

With $\text{H}[\text{PI-H/Dpp}]$: An initial colour change to a very dark green-brown/red-orange was observed, where the solution was much darker than the other solutions. Over 5 minutes, the solution turned brown/red. No further colour changes were observed.

JT70 $\text{CpCr}(\text{DBU})(\text{Cl})$ - Preparative Scale

The white powder HCl-DBU (505.8 mg, 2.680 mmol, prepared by Dr. Smith) was added in one portion to a vibrant orange-red/orange-red stirring solution of Cp_2Cr (487.8 mg, 2.678 mmol) dissolved in 50 mL THF. The solution quickly became darker upon addition of HCl-DBU , gaining a purple colour to incident light as the HCl-DBU powder dissolved. After leaving to stir

overnight, the solution was purple/purple. The solvent was removed *in vacuo*, with the residue washed in Et₂O and then the solvent again removed *in vacuo*. The residue was dissolved in toluene, filtered through Celite on a glass frit, and then concentrated in vacuo. The deep purple/purple solution was left to stand in the freezer at -35°C, affording a dark purple powder which became lighter in colour as it was left to dry under an inert atmosphere (458.0 mg, 56.1% yield). The extreme oxygen sensitivity was evidenced by residue of the powder gradually turning black upon exposure to only 0.8 ppm O₂ in the glove box. Elemental analysis Calculated for C₁₄H₂₁ClCrN₂: C, 55.17; H, 6.95; N, 9.19. Found: C, 55.17; H, 6.64; N, 8.90.

JT61 **Cp₂Cr + H[PI-^tBu/Dpp] (+ cat. PhCH₂NMe₂)**

Yellow crystals of H[PI-^tBu/Dpp] (108.2 mg, 0.2749 mmol) were dissolved in 4 mL THF and added dropwise to a stirring solution of Cp₂Cr (50.1 mg, 0.275 mmol) in 10 mL THF. Half of the resulting solution was transferred to another vial, and a pipette-tip of *N,N*-dimethylbenzylamine was added. There was no immediate colour change from chromocene orange/orange. After 2 days, both solutions were dark brown/orange-red, where the solution lacking the *N,N*-dimethylbenzylamine addition was slightly darker.

JT62 **Cp₂Cr + 1) HCl-DBU + 2) MesMgBr → [CpCr(μ-Mes)]₂**

DBU-HCl (207.2 mg, 1.098 mmol) was added to a stirring solution of Cp₂Cr (200.4 mg, 1.100 mmol), resulting in colour change from red-orange/red-orange to purple-red/red after 5 minutes, and then to purple/purple after 15 minutes. The solution was left to stir over the weekend,

remaining a clear, dark purple/purple with a small amount of purple precipitate. The solvent was removed *in vacuo*, with the resulting residue washed with toluene and then dried *in vacuo* again. The washed residue was dissolved in a mixture of 20 mL THF and 10 mL toluene, though a small amount of pale purple powder remained insoluble, and left to stir. MesMgBr (1.0 M in Et₂O, 1.1 mL, 1.1 mmol) was added to the cloudy purple/purple solution slowly via syringe, resulting in a quick colour change to dark brown-black/orange with no evidence of cloudiness or precipitate. The solvent was removed *in vacuo* with the residue taken up in THF (as it was insoluble in hexanes or Et₂O) and filtered through Celite on a glass frit. The black/orange filtrate was concentrated to dryness *in vacuo*, taken up in a minimum of Et₂O, and left to stand at -35°C resulting in the growth of some small, blocky, black crystals which sent away for analysis by x-ray diffraction.

JT64 1-Methylimidazole + MeI → 1,3-dimethylimidazolium iodide, (NHC)-I

Toluene (4 mL) was added to a solution of MeI (2.0 M in ^tBuOMe, 5.0 mL, 10.0 mmol) and let stir. 1-Methylimidazole (99% pure, 0.795 mL, 10.0 mmol) was added to the solution, resulting in a change from clear and colourless to cloudy white. The reaction solution was diluted by the addition of 20 mL toluene, left to stir for 5 minutes, and then sealed and taken out of the glovebox. The solution was heated to reflux and the now-clear solution was left to stir overnight. Upon cooling, a white solid formed. The white solid was washed with hexanes, left to dry, and then isolated as yellow-white blocks (0.9365 g, 41.8% yield). After continued exposure to air, the solid changed to pure white. The ¹H NMR spectrum was collected in D₂O, showing high purity.

JT65 **Cp₂Cr + (NHC)-I**

White crystals of (NHC)-I (123.4 mg, 0.5510 mmol) were added to a stirring solution of Cp₂Cr (101.5 mg, 0.5570 mmol) in one portion, resulting in a noticeable colour change from orange-red/orange-red to darker brown-red/orange-red after 1 minute. After 2 hours, the solution was dark brown-red/orange with a beige precipitate. The reaction solution was discarded after an addition 3 days of reaction time with no further changes.

JT66 **Cp₂Cr + HCl-hppH**

The white powder HCl-hppH (97.7 mg, 0.556 mmol) was added in one portion to a stirring solution Cp₂Cr (100.9 mg, 0.5540 mmol), resulting in an instant colour change from orange-red/orange-red to dark red/red. Within 10 minutes, all of the powder was dissolved. The solution was left to stir overnight, with the solution remaining red/red and containing a teal powder precipitate.

JT79 **[Cp₂Cr][I] + (NHC)-I**

The orange powder of [Cp₂Cr][I] (414.6 mg, 1.341 mmol) was suspended in 30 mL THF, resulting in a cloudy brown mixture. White flakes of (NHC)-I (299.4 mg, 1.336 mmol) were added to the stirring mixture, resulting in no quick colour change as both reactants are insoluble. After 40 minutes, the mixture was darker with a green tint to transmitted light. The solution was left to stir for 3 days, after which it was a dark, clear teal/teal solution. The solution was concentrated in vacuo and then filtered through Celite in a pipette. The resulting filtrate was a

strong, deep teal/teal colour, and was left to stand in the freezer at -35°C . Black needle-like crystals and powder were collected in 3 fractions (277 mg, 44.3% yield). Some of the crystals were mounted and were submitted for by x-ray crystallography, but did not diffract. Elemental analysis Calculated for $\text{C}_{10}\text{H}_{13}\text{CrI}_2$: C, 25.72; H, 2.81; N, 6.00. Found: C, 26.10; H, 2.45; N, 5.72.

JT68 $\text{Cp}_2\text{Cr} + [\text{NBu}_4][\text{Ph}_3\text{SiF}_2] + \text{HOTs-DBU}$

HOTs-DBU (89.8 mg, 0.277 mmol) was added to a stirring solution of Cp_2Cr (50.1 mg, 0.275 mmol) in 10 mL THF. After 5 minutes, a solution of $[\text{NBu}_4][\text{Ph}_3\text{SiF}_2]$ (148.4 mg, 0.2749 mmol) in 2 mL THF was slowly added dropwise to the stirring reaction solution. No sudden colour change was observed. After 30 minutes, the reaction mixture appeared less bright and still contained some undissolved HOTs-DBU. After 2 days, the yellow-orange/yellow-orange solution was concentrated to dryness *in vacuo*, with the residue dissolved in Et_2O and filtered through Celite on a glass frit. A lot of insoluble black residue was removed. The solvent was again removed *in vacuo*, with the residue taken up in a minimum of hexanes and left to stand at -35°C . The orange/orange solution produced red-orange needle-like crystals, typical of Cp_2Cr .

JT71 $\text{CpCr}(\text{DBU})(\text{Cl})$ Oxidation and Reduction

A qualitative amount of $\text{CpCr}(\text{DBU})(\text{Cl})$ in toluene was diluted into 2 mL THF. CDCl_3 (5 drops) was added to the dark purple/purple solution, resulting in an instant colour change to blue/violet-blue. The solvent was removed *in vacuo* and then dissolved in 36 mL THF, with the blue/violet-

blue solution split into three separate vials. A spatula tip of either Mg turnings, Zn powder, or Mn powder was added to each vial, with the mixtures left to stir overnight. After 1 day, the Zn solution was purple/purple like CpCr(DBU)(Cl), whereas the Mg and Mn reaction solutions displayed no colour change. After 5 days, the Mn solution had slowly turned to purple/purple, matching the Zn solution. The Mg solution had turned orange/red-brown.

JT72 CpCr(NHC)(I)₂ Reduction and Oxidation

A spatula tip of Zn powder was added to a dark teal/teal solution of CpCr(NHC)(I)₂ (24.8 mg, 0.0531 mmol), resulting in no instant colour change. After stirring for 2 days, the solution was a light peach/peach colour. The sample was diluted up to 25 mL with THF, and then analyzed by UV-Vis spectroscopy. A fleck of I₂ was added to the remaining peach/peach, resulting in an instant colour change to a darker green-teal/green-teal solution. The sample was analyzed by UV-Vis spectroscopy. The teal/teal solution displayed no evident colour change upon exposure to oxygen and acetone, whereas the reduced peach/peach solution instantly turned black.

JT78 [Cp₂Cr][I] + HOTs-DBU

White crystals of HOTs-DBU (106.8 mg, 0.3290 mmol) were added to an orange-brown suspension of [Cp₂Cr][I] (100.1 mg, 0.3239 mmol) in 15 mL THF and left to stir. After 3 days, the reaction mixture was a dark, clear teal/teal solution. The solution was concentrated in vacuo and filtered through Celite in a pipette. The dark teal/teal filtrate was left to stand in the freezer at -35°C, resulting in the formation of microcrystals. Hexanes was added to the solution, resulting

in the formation of a black oil. The solvent was removed in vacuo with the residue dissolved in a minimum of toluene. The solution was left to stand in the freezer at -35°C over 2 weeks, resulting in the formation of a few small navy blue crystals.

JT80 **CpCr(DBU)(Cl) (*in situ*) + H[PI-^tBu/Dpp]**

The white powder DBU-HCl (44.1 mg, 0.234 mmol) was added to a stirring solution of Cp₂Cr (42.8 mg, 0.235 mmol) in 8 mL THF, resulting in a colour change from orange-red/orange-red to dark purple/purple over 30 minutes. Yellow crystals of H[PI-^tBu/Dpp] (92.2 mg, 0.234 mmol) were dissolved in 2 mL THF and added dropwise to the stirring solution, resulting in an instant colour change from purple/purple to dark brown/red.

JT81 **Cp₂Cr + H[PI-^tBu/Dpp] (+ cat. DBU)**

A solution of H[PI-^tBu/Dpp] (54.1 mg, 0.137 mmol) in 2 mL THF was added dropwise to a solution of Cp₂Cr (25.1 mg, 0.138 mmol) in 10 mL THF, resulting in no colour change. The solution was stirred, and then split into two separate vials. In one of the vials, a drop of DBU was added, resulting in an instant colour change to red-brown/red. The solution without DBU did not display any evident colour change. A drop of the solution with DBU was added to the solution without, though no colour change was observed after 1 hour. After 1 month, the separate solutions were observed, where the “non-DBU” (actually has a small amount from the other reaction) reaction was green/yellow-brown, and the DBU reaction remained red-brown/red.

JT82 **Cp₂Cr + DBU**

A drop of DBU was added to a solution of Cp₂Cr (8.9 mg, 0.049 mmol) in 4 mL THF, resulting in no noticeable colour change over 1 week.

JT84A **CpCr(DBU)(Cl) + H[(XylNCMe)₂CH]**

The protonated ligand H[(XylNCMe)₂CH] (182.2 mg, 0.5946 mmol) was dissolved in 2 mL THF and added dropwise to a stirring solution of CpCr(DBU)(Cl) (10 mL, 0.61 mmol) generated *in situ*. No immediate colour change was observed. After 1 day, the previously purple/purple solution was brown-purple/red-purple, and slowly turned to green/red-pink by 6 days. After 10 days, the solvent was removed *in vacuo* with the residue dissolved in a minimum of hexanes and filtered through Celite in a pipette, removing some brown precipitate. The green/magenta solution was left to stand at -35°C in the freezer, and large black crystals quickly formed.

JT84B **CpCr(DBU)(Cl) + H[DppNC(Me)CHC(Me)N(4-MePh)]**

The protonated ligand H[DppNC(Me)CHC(Me)N(4-MePh)] (213.6 mg, 0.6129 mmol) was dissolved in 2 mL THF and added dropwise to a stirring solution of CpCr(DBU)(Cl) (10 mL, 0.61 mmol) generated *in situ*. A quick colour change was observed, where the previously purple/purple solution became darker and the transmitted colour became cherry red. After 30 minutes, the solution was brown-purple/red and slowly turned to a very dark green/cherry-red by 3 days. After 10 days, the solvent was removed *in vacuo* with the residue dissolved in a minimum of hexanes and filtered through Celite in a pipette, removing some brown precipitate.

The green/magenta solution was left to stand at -35°C in the freezer, and dark-red crystals quickly formed.

JT84Y CpCr(DBU)(Cl) + [XylNHC₆H₄(CH=NXyl)]

The protonated ligand [XylNHC₆H₄(CH=NXyl)] (201.3 mg, 0.6129 mmol) was dissolved in 2 mL THF and added dropwise to a stirring solution of CpCr(DBU)(Cl) (10 mL, 0.61 mmol) generated *in situ*. No initial colour change was observed. After 1 day, the previously purple/purple solution had become slightly darker, with a stronger red colour to transmitted light. No significant changes were observed after 1 week. After 3 weeks, the solution was a darker red-orange/red-orange.

JT84Z CpCr(DBU)(Cl) + [(4-MePh)NHC₆H₄(CH=NDpp)]

The protonated ligand [(4-MePh)NHC₆H₄(CH=NDpp)] (227.0 mg, 0.6126 mmol) was dissolved in 2 mL THF and added dropwise to a stirring solution of CpCr(DBU)(Cl) (10 mL, 0.61 mmol) generated *in situ*. A quick colour change was observed, where the previously purple/purple solution became darker. After 20 minutes, the solution was brown-orange/red and turned to a very dark orange/orange-red by 2 hours, and an intensely dark orange/orange by 18 hours. No further colour changes were observed, and after 10 days the solvent was removed *in vacuo* with the residue dissolved in a minimum of hexanes/Et₂O and filtered through Celite in a pipette, removing some violet precipitate. The orange/orange solution was left to stand at -35°C in the freezer, and a mixture of dark crystals and clear crystals formed over 2 weeks.

JT85A CpCr(DBU)(Cl) + [Na][PI-^tBu/Dpp]

The protonated ligand H[PI-^tBu/Dpp] (241.8 mg, 0.6143 mmol) was dissolved in 2 mL THF and added dropwise to a suspension of NaH (27.8 mg, 1.16 mmol) in 4 mL THF, resulting in a cloudy bright yellow mixture. The mixture was filtered through Celite in a pipette and added dropwise to a stirring purple/purple solution of CpCr(DBU)(Cl) (0.61 mmol) generated *in situ* which had its solvent removed *in vacuo* and was then re-dissolved in 12 mL THF. An instant colour change to dark orange/orange-red was observed. After 2 hours, the solution was dark, intense cherry-red/red. No further colour changes were observed over 1 week. The solvent was removed *in vacuo* with the residue dissolved in 15 mL hexanes and filtered through Celite in a pipette to produce a dark orange/red solution which was left to stand at -35°C. A portion of the solution was removed from the glovebox and exposed to oxygen, remaining a strong orange-red colour even upon contact with acetone.

JT85B CpCr(DBU)(Cl) + [Na][PI-H/Dpp]

The protonated ligand H[PI-H/Dpp] (171.9 mg, 0.6109 mmol) was dissolved in 2 mL THF and added dropwise to a suspension of NaH (29.5 mg, 1.23 mmol) in 4 mL THF, resulting in a cloudy bright yellow mixture. The mixture was filtered through Celite in a pipette and added dropwise to a stirring purple/purple solution of CpCr(DBU)(Cl) (0.61 mmol) generated *in situ* which had its solvent removed *in vacuo* and was then re-dissolved in 12 mL THF. An instant colour change to dark orange/orange-red was observed. After 2 hours, the solution was a dark brown/red-orange colour. No further colour changes were observed over 1 week. The solvent

was removed *in vacuo* with the residue dissolved in a minimum of hexanes and filtered through Celite in a pipette to produce a dark orange/orange solution which was left to stand at -35°C. Large black crystals were isolated (176.6 mg), but have not been characterized.

JT85C CpCr(DBU)(Cl) + [Na][PhC(O)CHC(Me)NDpp]

The protonated ligand [PhC(O)CHC(Me)NHDpp] (197.3 mg, 0.6118 mmol) was dissolved in 2 mL THF and added dropwise to a suspension of NaH (28.4 mg, 1.18 mmol) in 4 mL THF, resulting in a cloudy peach-coloured mixture. The mixture was filtered through Celite in a pipette and added dropwise to a stirring purple/purple solution of CpCr(DBU)(Cl) (0.61 mmol) generated *in situ* which had its solvent removed *in vacuo* and was then re-dissolved in 12 mL THF. An instant colour change to dark green/yellow-orange was observed. After 1 day, the solution had become dark green/orange. No further colour changes were observed over 1 week. The solvent was removed *in vacuo* with the residue dissolved in a minimum of hexanes and filtered through Celite in a pipette, removing a gray-brown powder. The dark green/orange solution was left to stand at -35°C with a non-isolable amount of powder coming out of solution over 1 week.

JT86A CpCr(DBU)(Cl) + PhMgBr

A THF solution of CpCr(DBU)(Cl) generated *in situ* (10 mL, 0.61 mmol) had the solvent removed *in vacuo*, with the residue dissolved in 12 mL THF. The Grignard reagent PhMgBr (3.0 M in Et₂O, 0.21 mL, 0.063 mmol) was added dropwise by syringe to a solution the stirring

purple/purple solution of CpCr(DBU)(Cl), resulting in an instant colour change to an intensely dark orange/orange solution. The solution was left to stir overnight, and then the solvent was removed *in vacuo*. The residue was dissolved in a minimum of Et₂O and filtered through Celite in a pipette. The resulting dark orange/orange was left to stand at -35°C in the freezer, resulting in the formation of a black oil embedded with small black crystals.

JT86B CpCr(DBU)(Cl) + MesMgBr

A THF solution of CpCr(DBU)(Cl) generated *in situ* (10 mL, 0.61 mmol) had the solvent removed *in vacuo*, with the residue dissolved in 12 mL THF. The Grignard reagent MesMgBr (1.0 M in Et₂O, 0.62 mL, 0.062 mmol) was added dropwise by syringe to a solution the stirring purple/purple solution of CpCr(DBU)(Cl), resulting in an instant colour change to an intensely dark orange/orange solution. The solution was left to stir overnight, and then the solvent was removed *in vacuo*. The residue was dissolved in a minimum of Et₂O and filtered through Celite in a pipette. The resulting dark orange/orange was left to stand at -35°C in the freezer, resulting in the formation some blocky black crystals, which were isolated and sent away for analysis by x-ray crystal diffraction.

JT86C CpCr(DBU)(Cl) + (4-^tBuPh)MgBr

A THF solution of CpCr(DBU)(Cl) generated *in situ* (10 mL, 0.61 mmol) had the solvent removed *in vacuo*, with the residue dissolved in 12 mL THF. The Grignard reagent MesMgBr (2.0 M in Et₂O, 0.31 mL, 0.062 mmol) was added dropwise by syringe to a solution the stirring

purple/purple solution of CpCr(DBU)(Cl), resulting in an instant colour change to an intensely dark orange/orange solution. The solution was left to stir overnight, and then the solvent was removed *in vacuo*. The residue was dissolved in a minimum of Et₂O and filtered through Celite in a pipette. The resulting dark orange/orange was left to stand at -35°C in the freezer, resulting in the formation some black crystals.

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Appendix – Crystallographic Data for [CpCr(μ -Mes)]₂

EXPERIMENTAL

Data Collection

A black tablet crystal of C₅₆H₆₄Cr₄ having approximate dimensions of 0.16 X 0.35 X 0.40 mm was mounted on a glass fiber. All measurements were made on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-K α radiation.

The data were collected at a temperature of $-100.0 \pm 0.1^\circ\text{C}$ to a maximum 2θ value of 56.14° . Data were collected in a series of ϕ and ω scans in 0.50° oscillations with 5.0 second exposures. The crystal-to-detector distance was 36.00 mm.

Data Reduction

Of the 16929 reflections that were collected, 5590 were unique ($R_{\text{int}} = 0.0235$); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT¹ software package. The linear absorption coefficient, μ , for Mo-K α radiation is 9.37 cm^{-1} . Data were corrected for absorption effects using the multi-scan technique (SADABS²), with minimum and maximum transmission coefficients of 0.797 and 0.861, respectively. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods³. The material crystallizes on a mirror plane, with one half-molecule in the asymmetric unit. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions but were not refined. The material crystallizes with two independent molecules in the asymmetric unit. The final cycle of full-matrix least-squares refinement⁴ on F^2 was based on 5590 reflections and 275 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.0466$$

$$wR2 = [\sum (w (F_o^2 - F_c^2)^2) / \sum w(F_o^2)^2]^{1/2} = 0.1025$$

The standard deviation of an observation of unit weight⁵ was 1.186. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.394 and $-0.318 \text{ e}^-/\text{\AA}^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber⁶. Anomalous dispersion effects were included in F_{calc} ⁷; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley⁸. The values for the mass attenuation coefficients are those of Creagh and Hubbell⁹. All refinements were performed using the SHELXTL¹⁰ crystallographic software package of Bruker-AXS.

References

(1) SAINT. Version 7.46A. Bruker AXS Inc., Madison, Wisconsin, USA. (1997-2007).

(2) SADABS. Bruker Nonius area detector scaling and absorption correction - V2.10, Bruker AXS Inc., Madison, Wisconsin, USA (2003).

(3) SIR92 - Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. J. Appl. Crystallogr. 1993, 26, 343-350.

(4) Least Squares function minimized:

$$\sum w(F_o^2 - F_c^2)^2$$

(5) Standard deviation of an observation of unit weight:

$$[\sum w(F_o^2 - F_c^2)^2 / (N_o - N_v)]^{1/2}$$

where: N_o = number of observations
 N_v = number of variables

(6) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(7) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(8) Creagh, D. C. & McAuley, W.J.; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(9) Creagh, D. C. & Hubbell, J.H.; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(10) SHELXTL Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA. (1997).

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula $C_{56}H_{64}Cr_4$
Formula Weight 945.12g/mol
Crystal Color, Habit black, irregular
Crystal Dimensions 0.16 X 0.35 X 0.40 mm
Crystal System triclinic
Lattice Type primitive
Lattice Parameters $a = 8.3398(8) \text{ \AA}$
 $b = 11.8870(12) \text{ \AA}$
 $c = 12.6085(12) \text{ \AA}$
 $\alpha = 94.928(5)^\circ$
 $\beta = 93.544(4)^\circ$
 $\gamma = 108.619(5)^\circ$
 $V = 1174.86(23) \text{ \AA}^3$

Space Group P -1 (#1)

Z value 2

D_{calc} 1.34 g/cm³

F000 495.9

$\mu(\text{MoK}\alpha)$ 9.37 cm^{-1}

B. Intensity Measurements

Diffractometer Bruker X8 APEX II
Radiation MoK α ($\lambda = 0.71073 \text{ \AA}$)
graphite monochromated

Data Images 1559 exposures @ 5.0 seconds
Detector Position 36.00 mm
 $2\theta_{\max}$ 56.14. $^{\circ}$
No. of Reflections Measured Total: 16929
Unique: 5590 ($R_{\text{int}} = 0.0235$)

Corrections Absorption ($T_{\min} = 0.797$, $T_{\max} = 0.861$)
Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution Direct Methods (SIR92)
Refinement Full-matrix least-squares on F^2
Function Minimized $\sum w (F_o^2 - F_c^2)^2$
Least Squares Weights $w = 1/(\sigma^2(F_o^2) + (0.0190P)^2 + 1.7798P)$
Anomalous Dispersion All non-hydrogen atoms
No. Observations ($I > 0.00\sigma(I)$) 5590
No. Variables 275
Reflection/Parameter Ratio 20.33
Residuals (refined on F^2 , all data): R1; wR2 0.0466; 0.1025
Goodness of Fit Indicator 1.186
No. Observations ($I > 2.00\sigma(I)$) 4831
Residuals (refined on F): R1; wR2 0.0394; 0.0996
Max Shift/Error in Final Cycle 0.00
Maximum peak in Final Diff. Map 0.394 e $^-/\text{\AA}^3$
Minimum peak in Final Diff. Map -0.318 e $^-/\text{\AA}^3$

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ks112. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)		
C(1)			6375(4)	3894(2)	-787(2)	34(1)
C(2)			7546(4)	3502(2)	-240(2)	30(1)
C(3)			7178(3)	2321(2)	-33(2)	27(1)
C(4)			5566(3)	1461(2)	-383(2)	26(1)
C(5)			4386(3)	1880(2)	-965(2)	26(1)
C(6)			4807(4)	3066(2)	-1156(2)	32(1)
C(7)			6782(5)	5185(3)	-965(3)	52(1)
C(8)			8550(4)	2000(3)	575(3)	40(1)
C(9)			2632(4)	1052(3)	-1385(2)	37(1)
C(10)			4079(5)	276(3)	2625(2)	48(1)
C(11)			2452(4)	-94(3)	2068(3)	50(1)
C(12)			2281(4)	885(4)	1600(3)	49(1)
C(13)			3816(5)	1826(3)	1829(3)	47(1)
C(14)			4909(4)	1457(3)	2498(2)	44(1)
C(15)			-1816(3)	920(2)	4423(2)	29(1)
C(16)			-482(3)	1593(2)	3902(2)	29(1)
C(17)			-36(3)	2832(2)	3965(2)	26(1)
C(18)			-941(3)	3465(2)	4553(2)	26(1)
C(19)			-2346(3)	2750(2)	5040(2)	29(1)
C(20)			-2739(3)	1515(2)	4979(2)	30(1)
C(21)			-2247(4)	-413(2)	4395(3)	40(1)
C(22)			1450(4)	3477(3)	3385(3)	39(1)
C(23)			-3478(4)	3289(3)	5645(3)	51(1)
C(24)			1069(5)	3308(3)	6837(3)	48(1)
C(25)			2597(5)	3778(3)	6407(3)	51(1)
C(26)			3296(4)	4979(4)	6798(3)	53(1)
C(27)			2201(5)	5256(3)	7488(3)	51(1)
C(28)			849(5)	4215(3)	7540(3)	50(1)
Cr(01)			784(1)	4753(1)	5801(1)	24(1)
Cr(02)			4432(1)	337(1)	833(1)	22(1)

Table 2. Bond lengths [Å] and angles [deg] for ks112.

C(1)-C(2)	1.382(4)
C(1)-C(6)	1.386(4)
C(1)-C(7)	1.503(4)
C(2)-C(3)	1.390(4)
C(2)-H(2)	0.9500
C(3)-C(4)	1.420(4)
C(3)-C(8)	1.504(4)
C(4)-C(5)	1.429(3)
C(4)-Cr(02)#1	2.165(2)
C(4)-Cr(02)	2.181(3)
C(5)-C(6)	1.386(4)
C(5)-C(9)	1.512(4)
C(6)-H(6)	0.9500
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-C(14)	1.381(5)
C(10)-C(11)	1.405(5)
C(10)-Cr(02)	2.301(3)
C(10)-H(10)	0.9500
C(11)-C(12)	1.392(5)
C(11)-Cr(02)	2.308(3)
C(11)-H(11)	0.9500
C(12)-C(13)	1.400(5)
C(12)-Cr(02)	2.330(3)
C(12)-H(12)	0.9500
C(13)-C(14)	1.399(5)
C(13)-Cr(02)	2.291(3)
C(13)-H(13)	0.9500
C(14)-Cr(02)	2.326(3)
C(14)-H(14)	0.9500
C(15)-C(20)	1.383(4)
C(15)-C(16)	1.387(4)
C(15)-C(21)	1.506(4)
C(16)-C(17)	1.392(4)
C(16)-H(16)	0.9500
C(17)-C(18)	1.422(3)
C(17)-C(22)	1.503(4)
C(18)-C(19)	1.420(3)
C(18)-Cr(01)#2	2.166(3)
C(18)-Cr(01)	2.189(3)
C(19)-C(20)	1.392(4)
C(19)-C(23)	1.509(4)
C(20)-H(20)	0.9500
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800

C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-C(25)	1.383(5)
C(24)-C(28)	1.400(5)
C(24)-Cr(01)	2.307(3)
C(24)-H(24)	0.9500
C(25)-C(26)	1.391(5)
C(25)-Cr(01)	2.312(3)
C(25)-H(25)	0.9500
C(26)-C(27)	1.393(5)
C(26)-Cr(01)	2.301(3)
C(26)-H(26)	0.9500
C(27)-C(28)	1.393(5)
C(27)-Cr(01)	2.302(3)
C(27)-H(27)	0.9500
C(28)-Cr(01)	2.338(3)
C(28)-H(28)	0.9500
Cr(01)-C(18)#2	2.166(3)
Cr(01)-Cr(01)#2	2.5496(8)
Cr(02)-C(4)#1	2.165(2)
Cr(02)-Cr(02)#1	2.5301(8)

C(2)-C(1)-C(6)	118.2(2)
C(2)-C(1)-C(7)	120.9(3)
C(6)-C(1)-C(7)	120.9(3)
C(1)-C(2)-C(3)	122.0(3)
C(1)-C(2)-H(2)	119.0
C(3)-C(2)-H(2)	119.0
C(2)-C(3)-C(4)	120.9(2)
C(2)-C(3)-C(8)	117.2(2)
C(4)-C(3)-C(8)	121.9(2)
C(3)-C(4)-C(5)	116.2(2)
C(3)-C(4)-Cr(02)#1	115.81(18)
C(5)-C(4)-Cr(02)#1	118.28(18)
C(3)-C(4)-Cr(02)	114.11(18)
C(5)-C(4)-Cr(02)	113.20(17)
Cr(02)#1-C(4)-Cr(02)	71.21(8)
C(6)-C(5)-C(4)	121.0(2)
C(6)-C(5)-C(9)	117.6(2)
C(4)-C(5)-C(9)	121.4(2)
C(1)-C(6)-C(5)	121.7(3)
C(1)-C(6)-H(6)	119.2
C(5)-C(6)-H(6)	119.2
C(1)-C(7)-H(7A)	109.5
C(1)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(1)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(3)-C(8)-H(8A)	109.5
C(3)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(3)-C(8)-H(8C)	109.5

H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(5)-C(9)-H(9A)	109.5
C(5)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(5)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(14)-C(10)-C(11)	109.4(3)
C(14)-C(10)-Cr(02)	73.66(18)
C(11)-C(10)-Cr(02)	72.52(18)
C(14)-C(10)-H(10)	125.3
C(11)-C(10)-H(10)	125.3
Cr(02)-C(10)-H(10)	120.2
C(12)-C(11)-C(10)	107.0(3)
C(12)-C(11)-Cr(02)	73.40(18)
C(10)-C(11)-Cr(02)	71.97(18)
C(12)-C(11)-H(11)	126.5
C(10)-C(11)-H(11)	126.5
Cr(02)-C(11)-H(11)	120.0
C(11)-C(12)-C(13)	108.0(3)
C(11)-C(12)-Cr(02)	71.68(18)
C(13)-C(12)-Cr(02)	70.86(17)
C(11)-C(12)-H(12)	126.0
C(13)-C(12)-H(12)	126.0
Cr(02)-C(12)-H(12)	123.1
C(12)-C(13)-C(14)	108.5(3)
C(12)-C(13)-Cr(02)	73.88(17)
C(14)-C(13)-Cr(02)	73.75(17)
C(12)-C(13)-H(13)	125.8
C(14)-C(13)-H(13)	125.8
Cr(02)-C(13)-H(13)	118.5
C(10)-C(14)-C(13)	107.0(3)
C(10)-C(14)-Cr(02)	71.61(18)
C(13)-C(14)-Cr(02)	70.98(17)
C(10)-C(14)-H(14)	126.5
C(13)-C(14)-H(14)	126.5
Cr(02)-C(14)-H(14)	122.6
C(20)-C(15)-C(16)	117.8(2)
C(20)-C(15)-C(21)	120.8(3)
C(16)-C(15)-C(21)	121.4(3)
C(15)-C(16)-C(17)	121.5(2)
C(15)-C(16)-H(16)	119.2
C(17)-C(16)-H(16)	119.2
C(16)-C(17)-C(18)	121.7(2)
C(16)-C(17)-C(22)	117.2(2)
C(18)-C(17)-C(22)	121.1(2)
C(19)-C(18)-C(17)	115.6(2)
C(19)-C(18)-Cr(01)#2	120.96(18)
C(17)-C(18)-Cr(01)#2	119.37(18)
C(19)-C(18)-Cr(01)	108.05(17)
C(17)-C(18)-Cr(01)	110.01(17)
Cr(01)#2-C(18)-Cr(01)	71.67(8)
C(20)-C(19)-C(18)	121.2(2)
C(20)-C(19)-C(23)	117.0(2)
C(18)-C(19)-C(23)	121.7(2)
C(15)-C(20)-C(19)	122.1(2)

C(15)-C(20)-H(20)	119.0
C(19)-C(20)-H(20)	119.0
C(15)-C(21)-H(21A)	109.5
C(15)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(15)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(17)-C(22)-H(22A)	109.5
C(17)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(17)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(19)-C(23)-H(23A)	109.5
C(19)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(19)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(25)-C(24)-C(28)	107.6(3)
C(25)-C(24)-Cr(01)	72.79(19)
C(28)-C(24)-Cr(01)	73.67(18)
C(25)-C(24)-H(24)	126.2
C(28)-C(24)-H(24)	126.2
Cr(01)-C(24)-H(24)	119.3
C(24)-C(25)-C(26)	108.5(3)
C(24)-C(25)-Cr(01)	72.37(18)
C(26)-C(25)-Cr(01)	72.02(19)
C(24)-C(25)-H(25)	125.7
C(26)-C(25)-H(25)	125.7
Cr(01)-C(25)-H(25)	121.6
C(25)-C(26)-C(27)	108.0(3)
C(25)-C(26)-Cr(01)	72.88(19)
C(27)-C(26)-Cr(01)	72.40(19)
C(25)-C(26)-H(26)	126.0
C(27)-C(26)-H(26)	126.0
Cr(01)-C(26)-H(26)	120.5
C(28)-C(27)-C(26)	107.7(3)
C(28)-C(27)-Cr(01)	73.97(19)
C(26)-C(27)-Cr(01)	72.38(19)
C(28)-C(27)-H(27)	126.1
C(26)-C(27)-H(27)	126.1
Cr(01)-C(27)-H(27)	119.4
C(27)-C(28)-C(24)	108.0(3)
C(27)-C(28)-Cr(01)	71.11(18)
C(24)-C(28)-Cr(01)	71.25(18)
C(27)-C(28)-H(28)	126.0
C(24)-C(28)-H(28)	126.0
Cr(01)-C(28)-H(28)	123.3
C(18)#2-Cr(01)-C(18)	108.33(8)
C(18)#2-Cr(01)-C(27)	98.08(11)
C(18)-Cr(01)-C(27)	151.94(11)
C(18)#2-Cr(01)-C(26)	105.30(12)
C(18)-Cr(01)-C(26)	137.92(12)
C(27)-Cr(01)-C(26)	35.22(13)
C(18)#2-Cr(01)-C(24)	156.57(11)

C(18)-Cr(01)-C(24)	94.12(11)
C(27)-Cr(01)-C(24)	58.73(12)
C(26)-Cr(01)-C(24)	58.49(13)
C(18)#2-Cr(01)-C(25)	137.98(13)
C(18)-Cr(01)-C(25)	104.16(12)
C(27)-Cr(01)-C(25)	58.42(13)
C(26)-Cr(01)-C(25)	35.10(13)
C(24)-Cr(01)-C(25)	34.84(13)
C(18)#2-Cr(01)-C(28)	123.24(12)
C(18)-Cr(01)-C(28)	118.13(12)
C(27)-Cr(01)-C(28)	34.92(13)
C(26)-Cr(01)-C(28)	58.00(13)
C(24)-Cr(01)-C(28)	35.08(12)
C(25)-Cr(01)-C(28)	57.77(13)
C(18)#2-Cr(01)-Cr(01)#2	54.58(7)
C(18)-Cr(01)-Cr(01)#2	53.76(7)
C(27)-Cr(01)-Cr(01)#2	151.29(9)
C(26)-Cr(01)-Cr(01)#2	149.46(10)
C(24)-Cr(01)-Cr(01)#2	147.27(9)
C(25)-Cr(01)-Cr(01)#2	147.26(9)
C(28)-Cr(01)-Cr(01)#2	150.52(9)
C(4)#1-Cr(02)-C(4)	108.79(8)
C(4)#1-Cr(02)-C(13)	156.54(12)
C(4)-Cr(02)-C(13)	94.54(11)
C(4)#1-Cr(02)-C(10)	100.76(11)
C(4)-Cr(02)-C(10)	145.22(12)
C(13)-Cr(02)-C(10)	58.27(12)
C(4)#1-Cr(02)-C(11)	98.22(12)
C(4)-Cr(02)-C(11)	148.04(12)
C(13)-Cr(02)-C(11)	58.82(13)
C(10)-Cr(02)-C(11)	35.51(13)
C(4)#1-Cr(02)-C(14)	130.97(11)
C(4)-Cr(02)-C(14)	110.60(11)
C(13)-Cr(02)-C(14)	35.27(12)
C(10)-Cr(02)-C(14)	34.72(12)
C(11)-Cr(02)-C(14)	58.77(12)
C(4)#1-Cr(02)-C(12)	126.81(12)
C(4)-Cr(02)-C(12)	113.12(12)
C(13)-Cr(02)-C(12)	35.26(13)
C(10)-Cr(02)-C(12)	58.10(12)
C(11)-Cr(02)-C(12)	34.93(13)
C(14)-Cr(02)-C(12)	58.38(12)
C(4)#1-Cr(02)-Cr(02)#1	54.68(7)
C(4)-Cr(02)-Cr(02)#1	54.11(7)
C(13)-Cr(02)-Cr(02)#1	148.56(9)
C(10)-Cr(02)-Cr(02)#1	150.18(9)
C(11)-Cr(02)-Cr(02)#1	148.60(9)
C(14)-Cr(02)-Cr(02)#1	149.80(9)
C(12)-Cr(02)-Cr(02)#1	148.33(9)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y,-z #2 -x,-y+1,-z+1

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ks112. The anisotropic displacement factor exponent takes the form: $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12		
C(1)	45(2)		24(1)		35(1)	10(1)	12(1)	11(1)
C(2)	32(1)		23(1)		33(1)	5(1)	7(1)	3(1)
C(3)	28(1)		25(1)		28(1)	4(1)	1(1)	8(1)
C(4)	26(1)		22(1)		29(1)	6(1)	-1(1)	9(1)
C(5)	28(1)		27(1)		24(1)	8(1)	2(1)	11(1)
C(6)	38(2)		32(1)		31(1)	12(1)	4(1)	18(1)
C(7)	65(2)		28(2)		67(2)	22(2)	14(2)	14(2)
C(8)	28(1)		32(1)		54(2)	7(1)	-10(1)	3(1)
C(9)	32(1)		38(2)		41(2)	10(1)	-9(1)	13(1)
C(10)	59(2)		67(2)		28(2)	14(2)	12(1)	33(2)
C(11)	45(2)		55(2)		46(2)	2(2)	23(2)	10(2)
C(12)	40(2)		77(2)		40(2)	-8(2)	1(1)	37(2)
C(13)	71(2)		42(2)		39(2)	-2(1)	12(2)	34(2)
C(14)	46(2)		52(2)		29(2)	-9(1)	0(1)	16(2)
C(15)	32(1)		24(1)		30(1)	4(1)	-6(1)	9(1)
C(16)	34(1)		28(1)		28(1)	0(1)	1(1)	16(1)
C(17)	29(1)		27(1)		23(1)	2(1)	3(1)	12(1)
C(18)	26(1)		23(1)		27(1)	1(1)	4(1)	7(1)
C(19)	26(1)		27(1)		33(1)	1(1)	5(1)	7(1)
C(20)	28(1)		25(1)		33(1)	7(1)	2(1)	4(1)
C(21)	43(2)		25(1)		51(2)	6(1)	-4(1)	10(1)
C(22)	47(2)		30(1)		44(2)	4(1)	23(1)	15(1)
C(23)	42(2)		33(2)		79(3)	4(2)	36(2)	8(1)
C(24)	58(2)		37(2)		50(2)	12(1)	-15(2)	18(2)
C(25)	59(2)		66(2)		44(2)	2(2)	-9(2)	45(2)
C(26)	34(2)		68(2)		50(2)	16(2)	-10(1)	9(2)
C(27)	74(2)		42(2)		35(2)	-3(1)	-16(2)	22(2)
C(28)	58(2)		71(2)		33(2)	23(2)	10(2)	32(2)
Cr(01)	26(1)		22(1)		25(1)	3(1)	3(1)	10(1)
Cr(02)	23(1)		22(1)		23(1)	3(1)	2(1)	10(1)

Table 5. Torsion angles [deg] for ks112.

C(6)-C(1)-C(2)-C(3)	-1.5(4)
C(7)-C(1)-C(2)-C(3)	177.8(3)
C(1)-C(2)-C(3)-C(4)	0.1(4)
C(1)-C(2)-C(3)-C(8)	-179.7(3)
C(2)-C(3)-C(4)-C(5)	1.0(4)
C(8)-C(3)-C(4)-C(5)	-179.2(3)
C(2)-C(3)-C(4)-Cr(02)#1	146.6(2)
C(8)-C(3)-C(4)-Cr(02)#1	-33.6(3)
C(2)-C(3)-C(4)-Cr(02)	-133.5(2)
C(8)-C(3)-C(4)-Cr(02)	46.3(3)

C(3)-C(4)-C(5)-C(6)	-0.8(4)
Cr(02)#1-C(4)-C(5)-C(6)	-145.5(2)
Cr(02)-C(4)-C(5)-C(6)	134.1(2)
C(3)-C(4)-C(5)-C(9)	179.7(2)
Cr(02)#1-C(4)-C(5)-C(9)	35.0(3)
Cr(02)-C(4)-C(5)-C(9)	-45.4(3)
C(2)-C(1)-C(6)-C(5)	1.7(4)
C(7)-C(1)-C(6)-C(5)	-177.6(3)
C(4)-C(5)-C(6)-C(1)	-0.5(4)
C(9)-C(5)-C(6)-C(1)	178.9(3)
C(14)-C(10)-C(11)-C(12)	-0.6(4)
Cr(02)-C(10)-C(11)-C(12)	-65.6(2)
C(14)-C(10)-C(11)-Cr(02)	64.9(2)
C(10)-C(11)-C(12)-C(13)	2.7(4)
Cr(02)-C(11)-C(12)-C(13)	-61.9(2)
C(10)-C(11)-C(12)-Cr(02)	64.6(2)
C(11)-C(12)-C(13)-C(14)	-3.7(4)
Cr(02)-C(12)-C(13)-C(14)	-66.2(2)
C(11)-C(12)-C(13)-Cr(02)	62.5(2)
C(11)-C(10)-C(14)-C(13)	-1.7(4)
Cr(02)-C(10)-C(14)-C(13)	62.5(2)
C(11)-C(10)-C(14)-Cr(02)	-64.2(2)
C(12)-C(13)-C(14)-C(10)	3.3(4)
Cr(02)-C(13)-C(14)-C(10)	-63.0(2)
C(12)-C(13)-C(14)-Cr(02)	66.3(2)
C(20)-C(15)-C(16)-C(17)	2.3(4)
C(21)-C(15)-C(16)-C(17)	-177.2(3)
C(15)-C(16)-C(17)-C(18)	-0.9(4)
C(15)-C(16)-C(17)-C(22)	179.0(3)
C(16)-C(17)-C(18)-C(19)	-1.7(4)
C(22)-C(17)-C(18)-C(19)	178.4(3)
C(16)-C(17)-C(18)-Cr(01)#2	-159.3(2)
C(22)-C(17)-C(18)-Cr(01)#2	20.8(3)
C(16)-C(17)-C(18)-Cr(01)	121.0(2)
C(22)-C(17)-C(18)-Cr(01)	-58.9(3)
C(17)-C(18)-C(19)-C(20)	2.9(4)
Cr(01)#2-C(18)-C(19)-C(20)	160.1(2)
Cr(01)-C(18)-C(19)-C(20)	-120.8(2)
C(17)-C(18)-C(19)-C(23)	-177.0(3)
Cr(01)#2-C(18)-C(19)-C(23)	-19.8(4)
Cr(01)-C(18)-C(19)-C(23)	59.3(3)
C(16)-C(15)-C(20)-C(19)	-1.1(4)
C(21)-C(15)-C(20)-C(19)	178.5(3)
C(18)-C(19)-C(20)-C(15)	-1.6(4)
C(23)-C(19)-C(20)-C(15)	178.3(3)
C(28)-C(24)-C(25)-C(26)	-2.6(4)
Cr(01)-C(24)-C(25)-C(26)	63.4(2)
C(28)-C(24)-C(25)-Cr(01)	-66.0(2)
C(24)-C(25)-C(26)-C(27)	0.7(4)
Cr(01)-C(25)-C(26)-C(27)	64.4(2)
C(24)-C(25)-C(26)-Cr(01)	-63.6(2)
C(25)-C(26)-C(27)-C(28)	1.4(4)
Cr(01)-C(26)-C(27)-C(28)	66.1(2)
C(25)-C(26)-C(27)-Cr(01)	-64.7(2)
C(26)-C(27)-C(28)-C(24)	-2.9(4)
Cr(01)-C(27)-C(28)-C(24)	62.1(2)
C(26)-C(27)-C(28)-Cr(01)	-65.0(2)

C(25)-C(24)-C(28)-C(27)	3.4(4)
Cr(01)-C(24)-C(28)-C(27)	-62.0(2)
C(25)-C(24)-C(28)-Cr(01)	65.4(2)
C(19)-C(18)-Cr(01)-C(18)#2	-117.52(19)
C(17)-C(18)-Cr(01)-C(18)#2	115.42(19)
Cr(01)#2-C(18)-Cr(01)-C(18)#2	0.0
C(19)-C(18)-Cr(01)-C(27)	42.0(3)
C(17)-C(18)-Cr(01)-C(27)	-85.1(3)
Cr(01)#2-C(18)-Cr(01)-C(27)	159.5(2)
C(19)-C(18)-Cr(01)-C(26)	101.1(2)
C(17)-C(18)-Cr(01)-C(26)	-26.0(3)
Cr(01)#2-C(18)-Cr(01)-C(26)	-141.42(15)
C(19)-C(18)-Cr(01)-C(24)	55.7(2)
C(17)-C(18)-Cr(01)-C(24)	-71.4(2)
Cr(01)#2-C(18)-Cr(01)-C(24)	173.19(11)
C(19)-C(18)-Cr(01)-C(25)	89.5(2)
C(17)-C(18)-Cr(01)-C(25)	-37.5(2)
Cr(01)#2-C(18)-Cr(01)-C(25)	-152.96(11)
C(19)-C(18)-Cr(01)-C(28)	28.8(2)
C(17)-C(18)-Cr(01)-C(28)	-98.3(2)
Cr(01)#2-C(18)-Cr(01)-C(28)	146.30(11)
C(19)-C(18)-Cr(01)-Cr(01)#2	-117.52(19)
C(17)-C(18)-Cr(01)-Cr(01)#2	115.42(19)
C(28)-C(27)-Cr(01)-C(18)#2	139.8(2)
C(26)-C(27)-Cr(01)-C(18)#2	-105.1(2)
C(28)-C(27)-Cr(01)-C(18)	-20.6(4)
C(26)-C(27)-Cr(01)-C(18)	94.5(3)
C(28)-C(27)-Cr(01)-C(26)	-115.1(3)
C(28)-C(27)-Cr(01)-C(24)	-36.6(2)
C(26)-C(27)-Cr(01)-C(24)	78.5(2)
C(28)-C(27)-Cr(01)-C(25)	-77.7(2)
C(26)-C(27)-Cr(01)-C(25)	37.4(2)
C(26)-C(27)-Cr(01)-C(28)	115.1(3)
C(28)-C(27)-Cr(01)-Cr(01)#2	123.4(2)
C(26)-C(27)-Cr(01)-Cr(01)#2	-121.5(2)
C(25)-C(26)-Cr(01)-C(18)#2	-161.9(2)
C(27)-C(26)-Cr(01)-C(18)#2	82.3(2)
C(25)-C(26)-Cr(01)-C(18)	-19.7(3)
C(27)-C(26)-Cr(01)-C(18)	-135.6(2)
C(25)-C(26)-Cr(01)-C(27)	115.9(3)
C(25)-C(26)-Cr(01)-C(24)	36.7(2)
C(27)-C(26)-Cr(01)-C(24)	-79.2(2)
C(27)-C(26)-Cr(01)-C(25)	-115.9(3)
C(25)-C(26)-Cr(01)-C(28)	78.2(2)
C(27)-C(26)-Cr(01)-C(28)	-37.7(2)
C(25)-C(26)-Cr(01)-Cr(01)#2	-117.8(2)
C(27)-C(26)-Cr(01)-Cr(01)#2	126.3(2)
C(25)-C(24)-Cr(01)-C(18)#2	-87.4(4)
C(28)-C(24)-Cr(01)-C(18)#2	27.5(4)
C(25)-C(24)-Cr(01)-C(18)	109.0(2)
C(28)-C(24)-Cr(01)-C(18)	-136.1(2)
C(25)-C(24)-Cr(01)-C(27)	-78.5(2)
C(28)-C(24)-Cr(01)-C(27)	36.4(2)
C(25)-C(24)-Cr(01)-C(26)	-37.0(2)
C(28)-C(24)-Cr(01)-C(26)	78.0(2)
C(28)-C(24)-Cr(01)-C(25)	114.9(3)
C(25)-C(24)-Cr(01)-C(28)	-114.9(3)

C(25)-C(24)-Cr(01)-Cr(01)#2	119.2(2)
C(28)-C(24)-Cr(01)-Cr(01)#2	-125.9(2)
C(24)-C(25)-Cr(01)-C(18)#2	143.6(2)
C(26)-C(25)-Cr(01)-C(18)#2	26.7(3)
C(24)-C(25)-Cr(01)-C(18)	-76.5(2)
C(26)-C(25)-Cr(01)-C(18)	166.5(2)
C(24)-C(25)-Cr(01)-C(27)	79.4(2)
C(26)-C(25)-Cr(01)-C(27)	-37.5(2)
C(24)-C(25)-Cr(01)-C(26)	116.9(3)
C(26)-C(25)-Cr(01)-C(24)	-116.9(3)
C(24)-C(25)-Cr(01)-C(28)	38.0(2)
C(26)-C(25)-Cr(01)-C(28)	-78.9(2)
C(24)-C(25)-Cr(01)-Cr(01)#2	-119.2(2)
C(26)-C(25)-Cr(01)-Cr(01)#2	123.8(2)
C(27)-C(28)-Cr(01)-C(18)#2	-49.8(3)
C(24)-C(28)-Cr(01)-C(18)#2	-167.3(2)
C(27)-C(28)-Cr(01)-C(18)	169.2(2)
C(24)-C(28)-Cr(01)-C(18)	51.7(2)
C(24)-C(28)-Cr(01)-C(27)	-117.5(3)
C(27)-C(28)-Cr(01)-C(26)	38.0(2)
C(24)-C(28)-Cr(01)-C(26)	-79.5(2)
C(27)-C(28)-Cr(01)-C(24)	117.5(3)
C(27)-C(28)-Cr(01)-C(25)	79.7(2)
C(24)-C(28)-Cr(01)-C(25)	-37.8(2)
C(27)-C(28)-Cr(01)-Cr(01)#2	-125.4(2)
C(24)-C(28)-Cr(01)-Cr(01)#2	117.1(2)
C(3)-C(4)-Cr(02)-C(4)#1	-110.6(2)
C(5)-C(4)-Cr(02)-C(4)#1	113.5(2)
Cr(02)#1-C(4)-Cr(02)-C(4)#1	0.0
C(3)-C(4)-Cr(02)-C(13)	71.9(2)
C(5)-C(4)-Cr(02)-C(13)	-64.0(2)
Cr(02)#1-C(4)-Cr(02)-C(13)	-177.49(11)
C(3)-C(4)-Cr(02)-C(10)	36.1(3)
C(5)-C(4)-Cr(02)-C(10)	-99.8(2)
Cr(02)#1-C(4)-Cr(02)-C(10)	146.67(17)
C(3)-C(4)-Cr(02)-C(11)	103.3(3)
C(5)-C(4)-Cr(02)-C(11)	-32.7(3)
Cr(02)#1-C(4)-Cr(02)-C(11)	-146.16(19)
C(3)-C(4)-Cr(02)-C(14)	39.6(2)
C(5)-C(4)-Cr(02)-C(14)	-96.3(2)
Cr(02)#1-C(4)-Cr(02)-C(14)	150.20(10)
C(3)-C(4)-Cr(02)-C(12)	103.0(2)
C(5)-C(4)-Cr(02)-C(12)	-32.9(2)
Cr(02)#1-C(4)-Cr(02)-C(12)	-146.45(10)
C(3)-C(4)-Cr(02)-Cr(02)#1	-110.6(2)
C(5)-C(4)-Cr(02)-Cr(02)#1	113.5(2)
C(12)-C(13)-Cr(02)-C(4)#1	-49.3(4)
C(14)-C(13)-Cr(02)-C(4)#1	66.0(4)
C(12)-C(13)-Cr(02)-C(4)	124.7(2)
C(14)-C(13)-Cr(02)-C(4)	-119.9(2)
C(12)-C(13)-Cr(02)-C(10)	-78.4(2)
C(14)-C(13)-Cr(02)-C(10)	36.9(2)
C(12)-C(13)-Cr(02)-C(11)	-36.5(2)
C(14)-C(13)-Cr(02)-C(11)	78.8(2)
C(12)-C(13)-Cr(02)-C(14)	-115.3(3)
C(14)-C(13)-Cr(02)-C(12)	115.3(3)
C(12)-C(13)-Cr(02)-Cr(02)#1	120.9(2)

C(14)-C(13)-Cr(02)-Cr(02)#1	-123.8(2)
C(14)-C(10)-Cr(02)-C(4)#1	153.8(2)
C(11)-C(10)-Cr(02)-C(4)#1	-89.1(2)
C(14)-C(10)-Cr(02)-C(4)	5.8(3)
C(11)-C(10)-Cr(02)-C(4)	122.9(2)
C(14)-C(10)-Cr(02)-C(13)	-37.5(2)
C(11)-C(10)-Cr(02)-C(13)	79.5(2)
C(14)-C(10)-Cr(02)-C(11)	-117.1(3)
C(11)-C(10)-Cr(02)-C(14)	117.1(3)
C(14)-C(10)-Cr(02)-C(12)	-79.3(2)
C(11)-C(10)-Cr(02)-C(12)	37.8(2)
C(14)-C(10)-Cr(02)-Cr(02)#1	122.3(2)
C(11)-C(10)-Cr(02)-Cr(02)#1	-120.7(2)
C(12)-C(11)-Cr(02)-C(4)#1	-148.3(2)
C(10)-C(11)-Cr(02)-C(4)#1	97.0(2)
C(12)-C(11)-Cr(02)-C(4)	-0.5(3)
C(10)-C(11)-Cr(02)-C(4)	-115.2(3)
C(12)-C(11)-Cr(02)-C(13)	36.8(2)
C(10)-C(11)-Cr(02)-C(13)	-77.9(2)
C(12)-C(11)-Cr(02)-C(10)	114.7(3)
C(12)-C(11)-Cr(02)-C(14)	78.3(2)
C(10)-C(11)-Cr(02)-C(14)	-36.4(2)
C(10)-C(11)-Cr(02)-C(12)	-114.7(3)
C(12)-C(11)-Cr(02)-Cr(02)#1	-120.5(2)
C(10)-C(11)-Cr(02)-Cr(02)#1	124.8(2)
C(10)-C(14)-Cr(02)-C(4)#1	-35.0(3)
C(13)-C(14)-Cr(02)-C(4)#1	-151.2(2)
C(10)-C(14)-Cr(02)-C(4)	-176.47(19)
C(13)-C(14)-Cr(02)-C(4)	67.3(2)
C(10)-C(14)-Cr(02)-C(13)	116.2(3)
C(13)-C(14)-Cr(02)-C(10)	-116.2(3)
C(10)-C(14)-Cr(02)-C(11)	37.2(2)
C(13)-C(14)-Cr(02)-C(11)	-79.0(2)
C(10)-C(14)-Cr(02)-C(12)	78.4(2)
C(13)-C(14)-Cr(02)-C(12)	-37.8(2)
C(10)-C(14)-Cr(02)-Cr(02)#1	-123.3(2)
C(13)-C(14)-Cr(02)-Cr(02)#1	120.5(2)
C(11)-C(12)-Cr(02)-C(4)#1	40.5(3)
C(13)-C(12)-Cr(02)-C(4)#1	157.86(19)
C(11)-C(12)-Cr(02)-C(4)	179.7(2)
C(13)-C(12)-Cr(02)-C(4)	-62.9(2)
C(11)-C(12)-Cr(02)-C(13)	-117.3(3)
C(11)-C(12)-Cr(02)-C(10)	-38.4(2)
C(13)-C(12)-Cr(02)-C(10)	78.9(2)
C(13)-C(12)-Cr(02)-C(11)	117.3(3)
C(11)-C(12)-Cr(02)-C(14)	-79.5(2)
C(13)-C(12)-Cr(02)-C(14)	37.8(2)
C(11)-C(12)-Cr(02)-Cr(02)#1	121.2(2)
C(13)-C(12)-Cr(02)-Cr(02)#1	-121.5(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z #2 -x,-y+1,-z+1