THESIS

INVESTIGATION INTO DISCRETE MOLECULAR CATALYSTS FOR BIOMASS CONVERSION INTO 5-HYDROXYMETHYLFURFURAL

Submitted by

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ABSTRACT

INVESTIGATION INTO DISCRETE MOLECULAR CATALYSTS FOR BIOMASS CONVERSION INTO 5-HYDROXYMETHYLFURFURAL

As part of ongoing research into the conversion of biomass into the platform chemical 5-hydroxymethylfurfural (HMF), two primary investigations have been performed. The first is an exploration of discrete lanthanide complexes as possible catalysts for the conversion of glucose to HMF. Catalysts of the type $Ln(HMDS)_3$, $Ln(MeTMS)_3$, and $Ln(OTf)_3$ have been examined in ionic liquid (IL) for their performance in the glucose-to-HMF conversion. In this study $Sc(OTf)_3$ has been identified as a good catalyst for both glucose (up to 38% HMF yield) and cellulose (up to 19% HMF yield) conversions. The second investigation was concerned with the effect of N-heterocyclic carbenes (NHCs) on the biomass conversion system that containing IL solvents. Since NHC's can be readily formed from deprotonation of ILs, there exists in the literature the hypothesis that an NHC-$CrCl_x$ complex is the true catalyst in these conversion systems. Three sets of experiments are reported herein to test this hypothesis: controls with all additives used by previous investigations purporting an NHC effect, tests of *in situ* generated and discrete preformed NHC-Cr complexes suggested by the hypothesis, and quantitative NHC titration (poisoning) experiments. The combined evidence shows conclusively that the NHC ligand actually serves as a poison to the chromium catalyst system and that a superstoichiometric amount (2 or 3 equiv) of NHC ligand can completely shut down the catalysis.

ACKNOWLEDGEMENTS

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Chapter 1. Introduction

HMF as a Platform Chemical

At present, virtually everything around us is made of petroleum-derived ingredients or involves the expenditure of petroleum fuels for its creation. Everything from paints to plastics to pharmaceuticals is synthesized from a platform of chemicals derived from petroleum sources. Also included in these processes are the fossil fuels burnt to generate electricity and transportation. Indeed, the modern lifestyle is entirely dependent on a limited and unsustainable resource of fossil fuels.

Plant-derived biomass is the best candidate to replace oil because it is abundant and highly sustainable. Specifically, *non-food* biomass has the potential to replace petroleum in many applications without threatening the world's food supply. There is several times more plant biomass on the earth today than there is oil reserves,[1,2] and that biomass is constantly being replenished. Tapping this renewable resource for fuels and materials is a requirement for a sustainable future.

Much research has been directed at finding a method to convert plant biomass into usable chemicals. 5-Hydroxymethylfurfural (HMF) has been recognized as one promising possibility to become the key platform chemical of biomass-derived feedstocks.[3,4] A platform chemical provides a convenient common chemical that can be derivatized into various feedstocks in route to production of other useful chemicals (Figure 1.1). The 6-carbon of HMF structure can potentially be efficiently derived from the common 6-carbon sugar building blocks of biomass resources, and it could be readily transformed into a platform of useful chemicals both for manufacturing and fuel.[5–8]

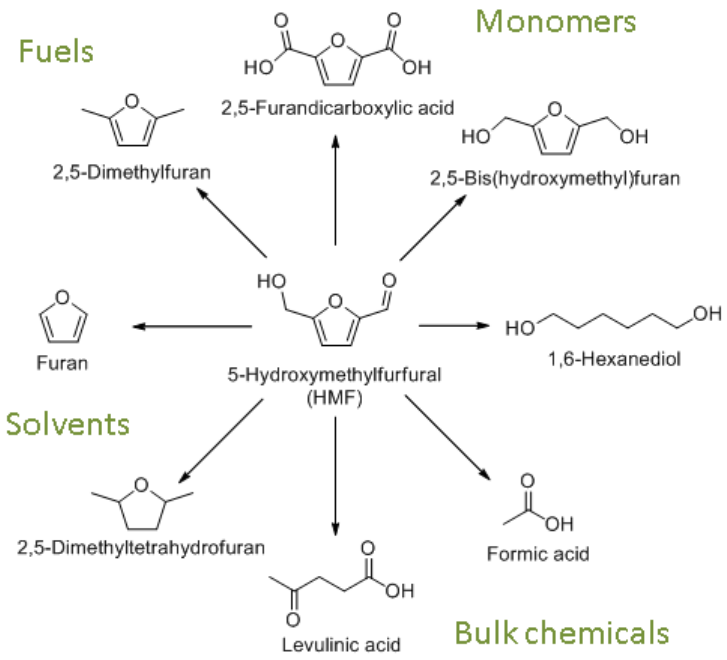

Figure 1.1. HMF as a platform chemical.

Many difficulties are present in the chemical conversion of biomass to fuel. Non-food biomass consists primarily of cellulose and other indigestible and insoluble oligomers.[10] Most chemical studies consider only the conversion of simplified feedstocks such as cellulose, its repeating unit, glucose, or other hexoses. Another problem is creating a homogenous system for the conversion of cellulose, which is virtually insoluble in all common solvents. Outside of a few caustic solvent systems, cellulose can be solvated by many ionic liquids (ILs)[11,12] which have also been shown to enhance the conversion of carbohydrates to HMF.[13–15]

Glucose Conversion by Metal Halide Catalysts

Although facile conversion from fructose was known since the 1980s, Zhao et al.'s seminal work in 2007 demonstrated the promise of metal halide catalysts in the conversion of glucose to HMF. [16] They found that chromium catalysts gave the best yields of those they tested with $CrCl_2$

precatalyst giving a 70% yield of HMF from glucose and $CrCl_3$ precatalyst a slightly lower 45% yield. Since then, numerous studies have investigated the possibility of metal halide catalysts in ionic liquids. Figure 1.2 shows a summary of the best performance for each precatalyst type tested in the literature proceeding from Zhao's 2007 paper until present (early 2013). This summary includes only metal halide catalysts in ionic liquid solvents under thermal conditions with no other additives. Chromium precatalysts are one of the most thoroughly studied catalysts for these conditions and have given the best performance so far with some examples topping 80% conversion.[17] Other precatalysts studied have approached only about 50% conversion even when more thoroughly optimized (cf. $GeCl_4$, $SnCl_4$).[18,19]

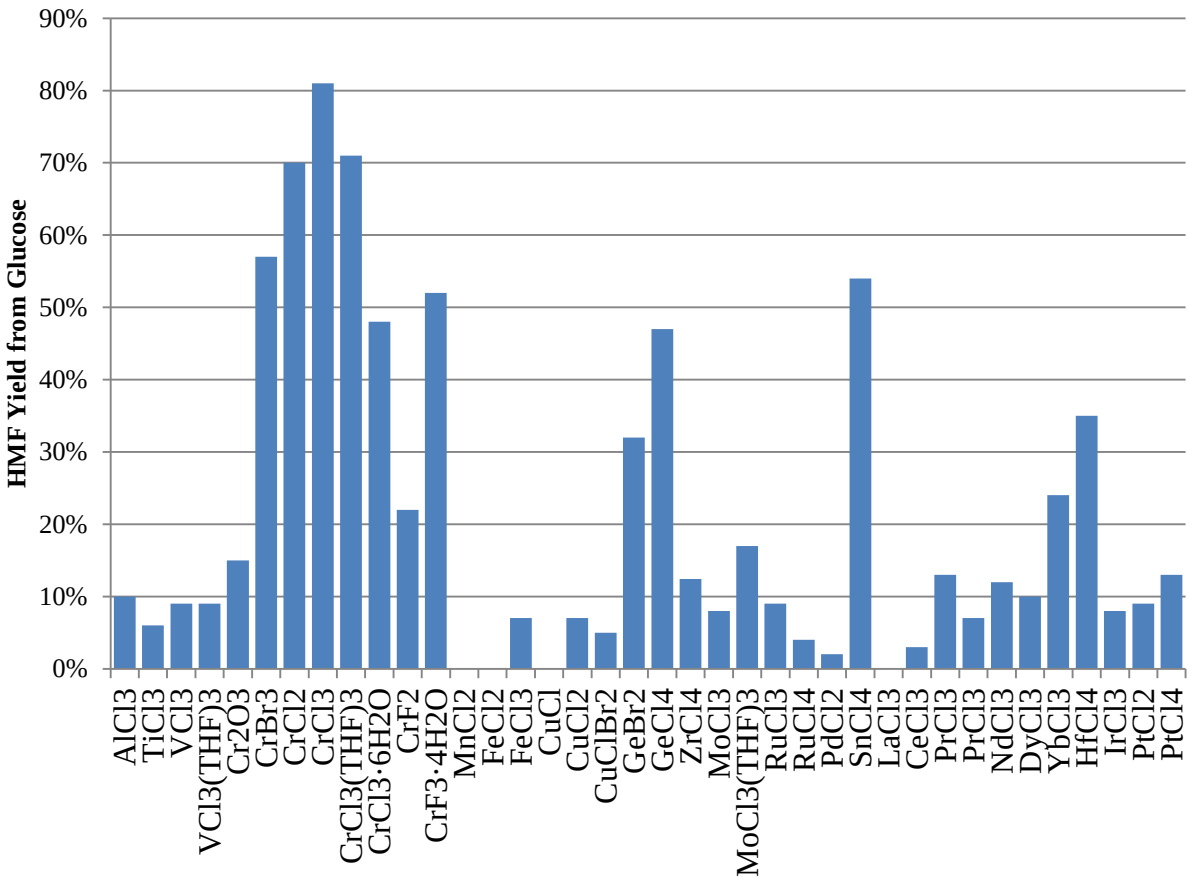

Figure 1.2. Summary of the conversions of glucose to HMF by metal halide catalysts from 2007-2013.[16–26]

Mechanism of Glucose Conversion to HMF

Fructose readily dehydrates to form HMF in a variety of thermal conditions,[27–31] but glucose has only given high yields of HMF under a few conditions with specific catalysts and solvents. For this reason, the glucose conversion mechanism has been hypothesized[16,32–34] to contain at least two steps: 1) isomerization of glucose to fructose, then 2) dehydration of fructose to HMF (Figure 1.3). It has also been suggested that the most effective metal catalysts form different active catalyst species for each of these steps.[32,33] Additionally, the ionic liquid solvent is presumed to become ligated to the active metal center, and sometimes even an N-heterocyclic carbene (NHC) ligand formed from the ionic liquid is coordinated to the active catalyst.[34,35] From these hypotheses, there is a plethora of proposed active catalyst species of mononuclear, dinuclear, or nonmetal composition, all variously supported by DFT calculations or indirect observations.[32–34] Compounding this problem is the apparent sensitivity of the reaction outcome (and mechanism) to temperature, concentration, and ionic liquid type. The result is a poorly understood, complicated system that is very difficult to optimize due to lack of understanding about the true catalyst.

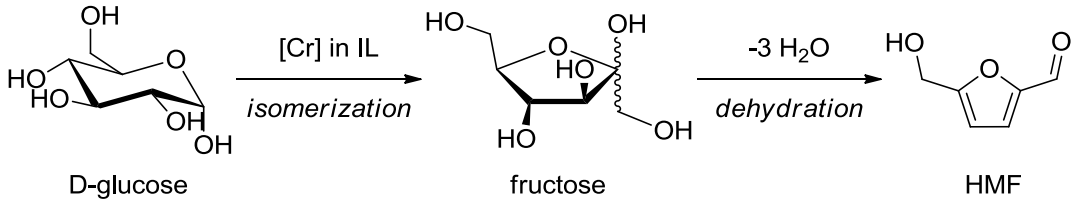

Figure 1.3. Schematic for the conversion of glucose to HMF

Purpose of This Thesis

The intent of this work was to discover new catalysts or catalyst design parameters that would result in an increased yield of HMF from glucose. Previously untested lanthanide catalysts are screened and some optimization in the temperature and solvent parameter space is

also performed in Chapter 2. Also, the NHC hypothesis[35] is closely examined in Chapter 3 toward the end of deducing what, in fact, is the active catalyst species in the glucose to HMF reactions.

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Chapter 2: Non-Halide Lanthanides as Catalysts for the Conversion of Glucose and Cellulose to 5-Hydroxymethylfurfural in Ionic Liquids

Introduction

For the past few decades, 5-hydroxymethylfurfural (HMF) has been studied as a promising key platform chemical for an entirely renewable, biomass-derived chemical platform.[1–7] The conversion of fructose into HMF is quite facile in a variety of solvents,[8–13] but the conversion of other carbohydrates is considerably less effective. This led to the defacto hypothesis that the mechanism for HMF conversion for most carbohydrates (cf. glucose and cellulose) proceeds through a fructose intermediate before dehydration to HMF (Figure 2.1). The innovation of using ionic liquids[14,15] (ILs) as solvents for HMF conversion revolutionized the field,[16,17] allowing higher yields, lower temperatures, and the easy solvation of cellulose.[18–21] These studies also popularized metal-halide catalysts in ionic liquids for highest HMF yield,[16,22–26] such as $CrCl_3$ with a yield over 80%.[27]

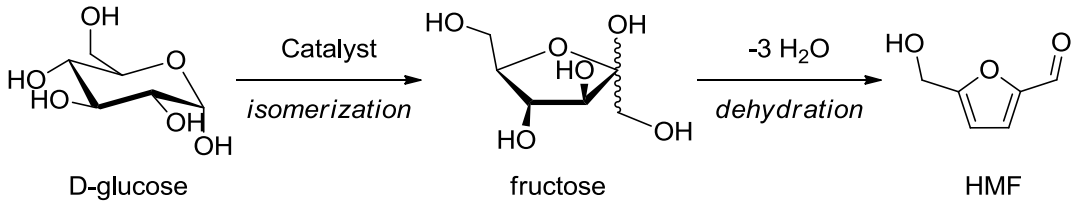

Figure 2.1: Schematic for the conversion of glucose to HMF.

Lanthanides are interesting catalysts because the entire series is electronically similar, but have different ionic radii. Thus, studies of rare-earth metals can sometimes demonstrate the effect of catalyst ionic radius on reaction kinetics. The exploration of lanthanide catalysts for HMF conversion was begun by Seri, et al. in 1996 with a series of lanthanide-chloride precatalysts in supercritical water[28–30] and organic solvents.[31] Their studies using glucose and fructose substrates showed a bimodal trend between metal ionic radius and reaction rate.[28,29]

After Zhang, et al.'s demonstrated the effectiveness of ionic liquids as solvents for these reactions,[16] Ståhlberg, et al. continued the investigation of lanthanide precatalysts in ionic liquid solvents.[32] They obtained only slightly higher HMF yields than the earlier reports, for example $NdCl_3$ showed the greatest improvement but only increased from 5% in water to 12% in ionic liquid. Importantly, Ståhlberg, et al. noticed that $Yb(OTf)_3$ had an enhanced effect over its halogenated analogue, $YbCl_3$, which they attributed to its higher Lewis acidity. Herein, we study a short series of lanthanide triflates among other non-halide lanthanide precatalysts to test if triflates are indeed superior to their chloride analogues. Finally, $Sc(OTf)_3$ is shown to be the best performing catalyst for glucose and cellulose conversion in ionic liquids.

Experimental

Materials, reagents, and methods

All syntheses and manipulations of air- and moisture-sensitive materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line or in an argon or nitrogen-filled glovebox. HPLC-grade organic solvents were sparged for one hour with nitrogen during filling of the solvent reservoir and then dried by passage through activated alumina (for Et_2O, THF, and CH_2Cl_2) followed by passage through Q-5-supported copper catalyst (for toluene and hexanes) in stainless steel columns. Dimethyl sulfoxide (DMSO) was degassed and dried over activated Davison 4-Å molecular sieves overnight. HPLC-grade N,N-dimethylformamide (DMF) was degassed, dried over CaH_2, filtered, and then vacuum-distilled; the dried DMF was stored over activated molecular sieves. NMR spectra were recorded on a Varian Inova 300 (FT 300 MHz, ^1H; 75 MHz, ^{13}C) or a Varian Inova 400 MHz spectrometer. Chemical shifts for ^1H spectra were referenced to internal solvent resonances and are reported as parts per million relative to

tetramethylsilane. The HMF-containing products were analyzed by Agilent 1260 Infinity HPLC system equipped with an Agilent Eclipse Plus C18 Column (100×4.6 mm; 80/20 water/methanol, 0.6 ml/min, 30 °C) and a UV detector (284 nm).

D-Glucose (Granular powder, Fisher Chemical), $CrCl_2$ (Alfa Aesar), $CrCl_3$ (Alfa Aesar), $Sc(OTf)_3$, $Y(OTf)_3$ and $Nd(OTf)_3$ (Aesar) were used as received. $Y(MeTMS)_3$ and $Y(MeTMS)_3$ were prepared by literature procedure.[33] $La(HMDS)_3$, $Nd(HMDS)_3$, $Sm(HMDS)_3$, and $Er(HMDS)_3$ were prepared by literature procedure.[34] $Y(Flu\text{-}NHC)(MeTMS)_2$ was synthesized by literature procedure.[35] Cellulose (Sigma-Aldrich) was dried in a vacuum oven at 120 °C overnight before use, and stored in an argon-filled glovebox. 1-Butanol and benzyl alcohol were degassed, stirred over CaH_2 for 1 hour, then vacuum distilled before use. Ionic liquids (ILs), 1-ethyl-3-methylimidazolium chloride (Fluka), [EMIM]Cl, and 1-butyl-3-methylimidazolium chloride (Fluka), [BMIM]Cl, and 1-Hexyl-3-methyl-imidazolium chloride (Fluka), [HMIM]Cl, were dried under vacuum at 100 °C for 24 h, then further purified by repeated recrystallization from CH_2Cl_2 and hexanes at room temperature. The purified ionic liquids were stored in an argon-filled glovebox.

Conversion of glucose to HMF

In a typical experiment, precatalyst (0.056 mmol, 10 mol% relative to glucose) was premixed with ionic liquid (0.50 g, 5:1 wt. relative to glucose) or 0.5 mL of solvent in a 5 mL vial in the argon-filled glove box, followed by further loading of glucose (0.10 g, 0.56 mmol). Next, 0.5 mL of co-solvent was added when appropriate. The sealed vials were placed in a temperature-controlled orbit shaker (100 or 120 °C, 300 RPM) and heated at the desired temperature for 3 h. The reaction was quenched with ice-water and then diluted with a known amount of deionized water. HMF was quantified via calibration curves generated from the

commercially available standard in distilled water. A typical HPLC chromatogram of the reaction product is shown in Figure 2.2.

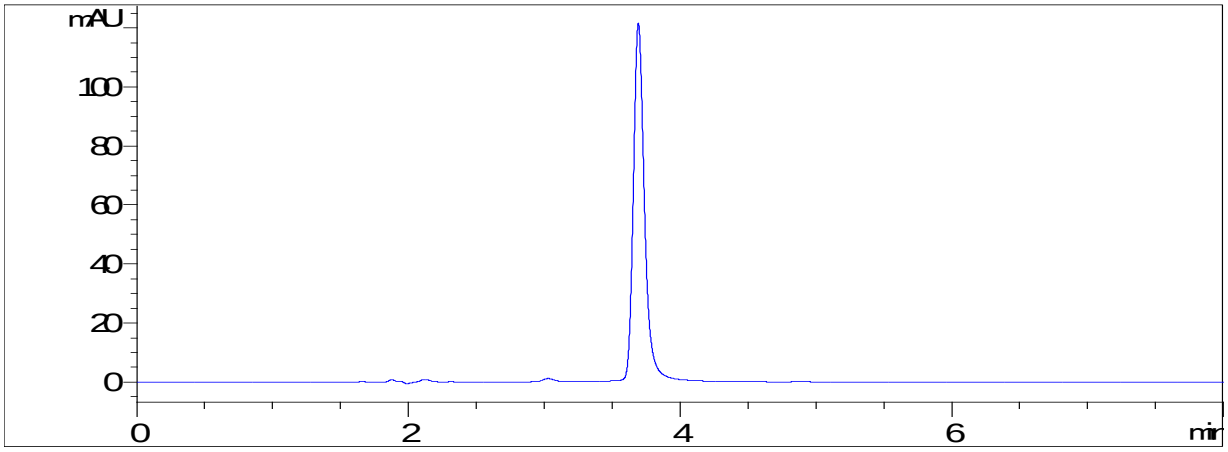

Figure 2.2: Typical chromatogram of $Sc(OTf)_3$ catalyzed conversion of glucose showing HMF response at 3.7 min (UV detector, 284nm).

Conversion of Cellulose to HMF by $Sc(OTf)_3$

$Sc(OTf)_3$ (60.7 mg, 0.123 mmol, 10 mol % relative to cellulose repeating unit) was premixed with [BMIM]Cl (2.0 g, 10:1 wt. relative to cellulose). The mixture was then divided into 4 vials containing 50 mg of cellulose each. The vial was tightly capped and placed in a temperature-controlled orbit shaker at 100 °C and 300 RPM. After the desired reaction time, the reaction mixture was quenched with distilled water and analyzed as above. The water-insoluble portion was filtered with a syringe filter (0.45 μm) and dried thoroughly in a vacuum oven. The dried net weight was compared to the initial cellulose weight to determine the percent conversion of cellulose.

Results and Discussion

Lanthanide Catalyst Screening

A series of homoleptic lanthanide precatalysts (hexamethyldisilazane-, trimethylsilylmethyl-, and triflate-) where screened under standard conditions of 10 wt % glucose in ionic liquid with 10 mol % precatalyst at 120 °C for 6 h (Table 2.1). The triflates $Y(OTf)_3$ and $Nd(OTf)_3$ (runs 2 and 3) did not show improved HMF yields over those reported for lanthanide chlorides, which performed in the range of 3-13%.[32] The amide-ligated and organometallic species tested showed negligible HMF yield (runs 4-7). Of the catalysts studied, only $Sc(OTf)_3$ showed significant glucose conversion. It is interesting to note that $Sc(OTf)_3$ showed much greater conversion than $Y(OTf)_3$ and $Nd(OTf)_3$, suggesting that scandium's smaller ionic radius is beneficial in the glucose conversion process. Also, an NHC tethered, fluorenyl ligated yttrium catalyst was also tested because it contains both a coordinating metal center and a carbene moiety, each hypothesized to play a part either together or separately in the glucose conversion. The result here was poor (run 10), and later studies (Chapter 3)[36] show the carbene to be a deleterious addition.

Table 2.1: Selected results of Lanthanide-catalyzed conversion of glucose

Run	Catalyst	HMF Yield (%)[a]
1	$Sc(OTf)_3$	16
2	$Y(OTf)_3$	3
3	$Nd(OTf)_3$	2
4	$La(HMDS)_3$	0
5	$Nd(HMDS)_3$	0
6	$Sm(HMDS)_3$	1
7	$Er(HMDS)_3$	2
8	$Y(MeTMS)_3$	4
9	$Lu(MeTMS)_3$	0
10	$Y(Flu\text{-}NHC)(MeTMS)_2$	4

[a] Conditions: 50 mg glucose, 10 mol% catalyst, and 500 mg [BMIM]Cl, 6 hours at 120 °C.

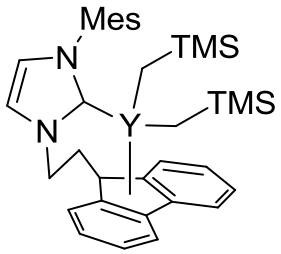

Figure 2.3: Structure of Y(Flu-NHC)(MeTMS)$_2$

Optimization of Scandium Triflate Conversion of Glucose

The conditions using scandium triflate were optimized in an attempt to make it competitive with existing catalysts, especially the chromium chlorides ($CrCl_x$) which can exceed 70% HMF yield from glucose under similar conditions.[16,27,37,38] The first step was to test varying solvent and temperature profiles (Figure 2.4). The higher temperature of 120 °C proved to be superior to the lower temperature 100 °C. Conversion was faster and reached a higher yield, but under these conditions it is known[32,39,40] that HMF will decompose in the timeframe of a few hours. The elevated temperature accelerates the glucose conversion here, outpacing HMF decomposition for the first few hours of the reaction. After this time, the glucose is almost completely consumed and further heating only decomposes the HMF product. Increasing temperature increases the rate of glucose conversion, but accelerates HMF decomposition even more. This tradeoff limits the yield optimization possible by changing the temperature.

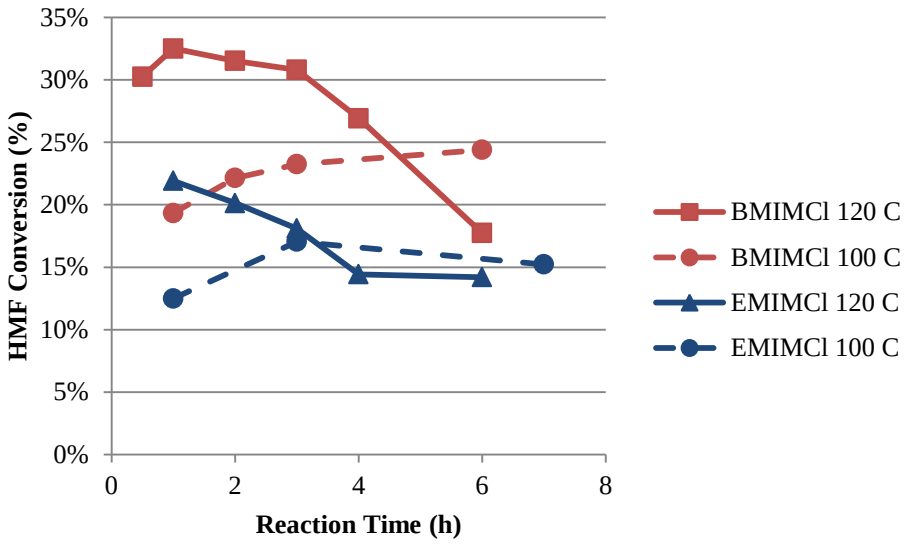

Figure 2.4: Time and temperature profile for HMF Conversion with $Sc(OTf)_3$. Conditions: 50 mg glucose, 500 mg IL, and 10 mol % $Sc(OTf)_3$.

Conversion was also tested in a variety of ionic liquid and organic solvents (Table 2). Whereas the yield in [BMIM]Cl peaked at 120°C (run 4), the yield in [EMIM]Cl peaked at lower temperature of 100°C (run 1), suggesting a different balance between the glucose conversion and HMF decomposition rates in this solvent. The non-ionic-liquid solvents tested—DMSO, acetonitrile, and water—performed poorly with HMF yields always less than 10% (runs 7-11).

Table 2: Effect of solvent on conversion of glucose to HMF with $Sc(OTf)_3$

run	Solvent[a]	Temp (°C)	Time (hr)[b]	HMF Yield[c]
1	[EMIM]Cl	100	6	22
2	[EMIM]Cl	120	1	18
3	[BMIM]Cl	100	3	23
4	[BMIM]Cl	120	3	26
5	[BMIM]Cl	130	1	24
6	[HMIM]Cl	120	1	7
7	DMSO	100	12	4
8	DMSO	120	6	11
9	MeCN	80	12	0
10	H_20	80	12	0
11	H_20	100	12	2

[a] 500 mg IL or 0.5 mL liquid solvent. [b] When maximum yield was obtained. [c] Conditions: 50 mg glucose, 10 mol % $Sc(OTf)_3$.

It was noticed[27,41] that organic cosolvents added to the ionic liquid had the potential to boost the HMF yield, so a variety of protic and aprotic cosolvents were tested with this system (Table 2.3). Surprisingly, all the solvent additives to [BMIM]Cl caused a substantial increase in HMF yield, except for DMSO which reduced yield to 8% (run 1). DMF, o-dichlorobenzene, and butyl alcohol all gave the best yields of 38%, showing that the appropriately selected cosolvent can increase HMF yield by more than 10%.

Table 2.3: Effect of mixed solvents on conversion of glucose to HMF with $Sc(OTf)_3$

Run	IL	Cosolvent	Temp (°C)	Time (hr)	HMF Yield (%)[a]
1	[BMIM]Cl	DMSO	120	3	8
2		DMF	120	3	38
3		o-Dichlorobenzene	120	3	38
4		Toluene	120	3	37
5		Benzene	120	3	35
6		Octane	120	3	31
7	[BMIM]Cl	Water	120	6	28
8		Butyl Alcohol	120	6	38
9		Benzyl Alcohol	120	6	37
10	[EMIM]Cl	Toluene	120	3	23
11	[HMIM]Cl	DMF	120	3	7

[a] Conditions: 50 mg glucose, 500 mg IL, 0.5 mL solvent, and 10 mol % $Sc(OTf)_3$

Scandium Triflate Conversion of Cellulose

The catalytic activity of $Sc(OTf)_3$ towards the conversion of cellulose to HMF was also explored (Figure 2.5). A maximum yield of 19% was obtained after 6 hours at 100°C; selectivity was also high at this time, as approximately all of the converted cellulose produced HMF. After 6 hours, cellulose was still being hydrolyzed, but the HMF yield decreased due to its decomposition. This suggests that the cellulose hydrolysis is the slowest step and becomes outpaced by HMF decomposition later in the reaction. After the 15 hour mark, production of byproducts (humins) is responsible for a majority of the insoluble products and maximum cellulose conversion could not be determined.

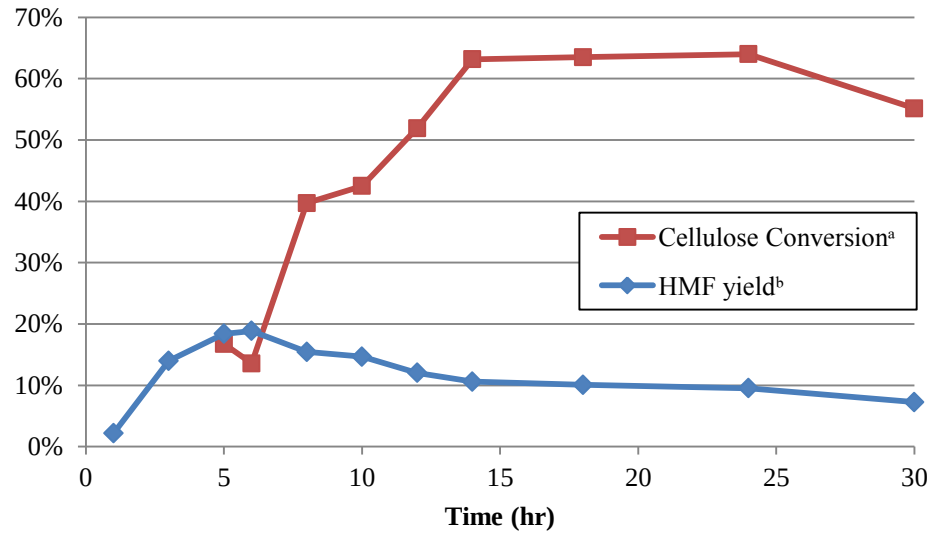

Figure 2.5: Conversion of Cellulose to HMF with $Sc(OTf)_3$. [a] Based on recovered insoluble products. [b] Conditions: 50 mg cellulose, 10 mol% $Sc(OTf)_3$, 500 mg [BMIM]Cl, 100 °C.

Conclusions

Several lanthanide catalysts were screened in this study. Those which were stronger Lewis acids (the triflates) showed higher yields than the rest, but still not higher than previously reported halides.[32] With the exception of $Sc(OTf)_3$, all the lanthanide catalysts tested produced less than 10% HMF yield from glucose. Scandium triflate showed the best-yet HMF yields (up to 38%) from glucose for lanthanide catalysts, and it seems the smaller ionic radius of scandium was beneficial to conversion. In optimizing the system, there is competition between the rate of substrate (glucose) conversion and product (HMF) decomposition, but some enhancement was found by adding cosolvents. The direct conversion of cellulose to HMF using $Sc(OTf)_3$ showed similar conversion to the $LaCl_2$ catalyst,[30] but at a much lower temperature of 100 °C instead of 250 °C.

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Chapter 3. Role of N-Heterocyclic Carbenes in Glucose Conversion into HMF by Cr Catalysts in Ionic Liquids

Introduction

As a part of major on-going efforts to develop effective pathways for the conversion of plant biomass into biofuels and feedstock chemicals, 5-hydroxymethylfurfural (HMF) has received increasing attention and been recognized as the key biomass platform chemical.[1–4] Lignocellulosic materials hold promise to provide humanity with a sustainable source of fuels, materials, and chemicals as they are abundant, inexpensive, and biorenewable. However, the key challenge has been to advance the biorefining of such inedible renewable feedstocks to render them technologically and economically competitive compared to traditional petroleum feedstocks.[5–11] Compared to other pathways, including biological and hydrothermal cellulosic conversion processes, chemical routes utilize more rapid and selective catalytic processes to depolymerize biomass polycarbohydrates into sugars, followed by subsequent chemical transformations into fuels or chemicals, all carried out under mild conditions. In this context, the biomass-derived sugars can be converted into fuels and value-added chemicals by liquid-phase catalytic processing.[9,12] Alternatively, cellulosic materials can be directly converted into the biomass platform chemical HMF, which can, among other things, then be converted into 2,5-dimethylfuran, a promising biofuel[13] or upgraded into C12 intermediates to be used as kerosene or jet fuel.[14]

Fructose can be readily dehydrated into HMF, typically in high selectivity and yield.[15–20] However, glucose, a more desirable feedstock from nonfood cellulosic biomass, has been shown to be resistant to conversion into HMF; yields were typically low (~10%) when catalyzed by a variety of catalyst systems, such as lanthanide halides $LnCl_3$, in water or organic solvents.[21–23]

The use of ionic liquids (ILs)[24–26] as environmentally benign alternatives to the volatile organic solvents, particularly 1-alkyl-3-methylimidazolium chloride salts,[27] which exhibit a unique capability to dissolve biomass materials including cellulose[28,29] and common carbohydrates,[30,31] has brought about spectacular advances, achieving high HMF yields from glucose using simple metal salts as Lewis acid catalysts. The seminal work of Zhang et al. revealed that glucose can be converted into HMF in unprecedented yields of 68–70% with $CrCl_2$ as the precatalyst in 1-ethyl-3-methylimidazolium chloride [EMIM]Cl at 100 °C for 3 h.[32] The conversion process was proposed to proceed via *in situ* glucose-to-fructose isomerization, catalyzed by the anion $CrCl^{3-}$ in the resulting metallate [EMIM]+$CrCl^{3-}$ formed upon mixing $CrCl_2$ and [EMIM]Cl, followed by dehydration of fructose to HMF (Figure 1). [32]

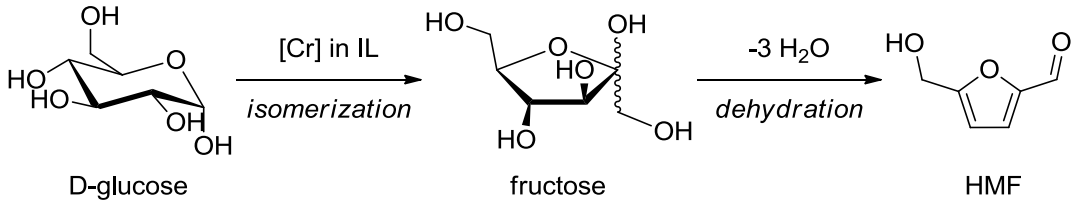

Figure 3.1. General schematic for catalytic conversion of glucose to HMF by Cr catalysts

Interestingly, the HMF yields for many catalyst systems other than $CrCl_x$ were only 10% or less, including a large number of metal (main-group, transition-metal, and rare-earth) halides that were investigated.[32] A subsequent study by Hensen et al.[33] reported a lower HMF yield of 62% under the same conditions ([EMIM]Cl, 6 mol% $CrCl_2$, 100 °C, 3 h) as Zhang et al., but this study provided both experimental evidence and theoretical basis to support the proposed reaction sequence. Since the initial discovery of the $CrCl_2$/IL catalyst system, a large number of other effective metal catalyst systems have been reported for the glucose (or cellulose)-to-HMF conversion in ILs, but they are nearly exclusively halide complexes of metals.[34–46]

Of the catalyst systems reported in the literature, we were particularly intrigued by the report of Ying et al.[47] in which the N-heterocyclic carbene (NHC)-$CrCl_x$ (x = 2 or 3) complex was hypothesized to be the true catalyst responsible for the glucose-to-HMF conversion activity by the the $CrCl_x$/IL (1-butyl-3-methylimidazolium chloride [BMIM]Cl) system. If this hypothesis was true, then rational design of the NHC ligands for the (NHC)-Cr complexes could be achieved to discover more advanced molecular catalysts for this biomass conversion process.

However, the conclusion of Yong et al.'s study was largely based on the observed HMF yield (81%) by the hypothesized (NHC)-$CrCl_2$ complex, which is much higher than a typical HMF yield of 60–70% by the $CrCl_2$/IL system (note that the exact yield depends on the IL structure as well as reaction temperature and time).[33,47] Furthermore, authentic, discrete (NHC)-Cr complexes were not employed to test the hypothesis, nor were other needed controls (e.g., HMF yields by $CrCl_2$ alone and in combination with any of other reagents present in the system) carried out to eliminate alternative hypotheses. These control experiments are particularly important, as the system employed the co-solvent DMF and 5 other different reagents in a one-pot fashion, including an imidazolium salt (the putative NHC precursor), KOtBu (base), $CrCl_2$ (precatalyst), [BMIM]Cl (solvent), and glucose (substrate). The above reagents, once premixed and heated in a stepwise fashion, were proposed to generate the NHC ligand and, subsequently, the corresponding (NHC)-Cr complex that catalyzes the conversion.

Accordingly, the central objective of this work was to address this important mechanistic question: What is the role of an NHC ligand in the glucose conversion reaction by $CrCl_x$ in ILs? Our results herein, obtained from multiple sets of experiments (controls with all additives (reagents) involved in the conversion system, performances of *in situ* generated NHC ligands or Cr complexes as well as discrete NHC ligands and Cr complexes (Figure 3.2), and quantitative

NHC titration (poisoning)[48] experiments) conclusively show that the NHC ligand actually serves as a *poison* to the chromium catalyst system and that a superstoichiometric amount (2 or 3 equiv) of the NHC ligand completely shuts down the catalysis.

Experimental

Materials, reagents, and methods

All syntheses and manipulations of air- and moisture-sensitive materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line or in an argon or nitrogen-filled glovebox. HPLC-grade organic solvents were sparged for at least one hour with nitrogen during filling of the solvent reservoir and then dried by passage through activated alumina (for Et_2O, THF, and CH_2Cl_2) followed by passage through Q-5-supported copper catalyst (for toluene and hexanes) stainless steel columns. Dimethyl sulfoxide (DMSO) and dimethylacetamide (DMA) were degassed and dried over activated Davison 4-Å molecular sieves overnight before use. HPLC-grade N,N-dimethylformamide (DMF) was degassed, dried over CaH_2, filtered, and vacuum-distilled; the dried DMF was stored over activated molecular sieves overnight. NMR spectra were recorded on a Varian Inova 300 (FT 300 MHz, 1H; 75 MHz, 13C) or a Varian Inova 400 MHz spectrometer. Chemical shifts for ^1H spectra were referenced to internal solvent resonances and are reported as parts per million relative to tetramethylsilane. The HMF-containing products were analyzed by Agilent 1260 Infinity HPLC system equipped with an Agilent Eclipse Plus C18 Column (100×4.6 mm; 80/20 water/methanol, 0.6 ml/min, 30 °C) and a UV detector (284 nm). Sugar contents of the products were measured by Agilent 1260 Infinity HPLC system equipped with a Biorad Aminex HPX-87H Column (300 mm ×7.8 mm; water, 0.8 mL/min, 45 °C) and a RI detector (35 °C).

D-Glucose (Granular powder, Fisher Chemical), $CrCl_2$ and $CrCl_3$ (Alfa Aesar), 1-bromobutane, 1-chlorobutane and 1-vinylimidazole (Fisher Chemical), Zn powder (Alfa Aesar), lithium bis(trifluoromethanesulphonyl)imide $LiNTf_2$ (Acros Organics), 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU, Acros Organics), and potassium bis(trimethylsilyl)amide KHMDS (0.5 M solution in toluene, Aldrich), 2,4-pentanedione (Alfa Aesar), 2,5-diisopropyl aniline (Alfa Aesar), glyoxal (40% solution in water, Alfa Aesar), HCl (2.0M solution in Et_2O, Sigma-Aldrich), n-butyllithium (1.6M in hexanes, Aldrich), and sodium bis(trimethylsilyl)amide (Sigma-Aldrich) were used as received. Tert-butanol (Aldrich) was stirred in CaH_2 for 1 h, and then vacuum distilled before use. Imidazolium salts 1,3-bis(2,4,6-trimethyl-phenyl)imidazolium chloride ([IMesH]Cl), 1,3-bis(diisopropylphenyl)imidazolium chloride ([IPrH]Cl), and 1,3-bis(diisopropylphenyl)imidazolinium chloride ([SIPrH]Cl) were purchased from Alfa Aesar and dried in vacuo on a schlenk line for one hour prior to use. Ionic liquids (ILs), 1-ethyl-3-methylimidazolium chloride (Fluka), [EMIM]Cl, and 1-butyl-3-methylimidazolium chloride (Fluka), [BMIM]Cl, and 1-ethyl-3-methylimidazolium acetate (Fluka), [EMIM]OAc, were dried under vacuum at 100 °C for 24 h; [EMIM]Cl and [EMIM]Cl were further purified by repeated recrystallization from CH_2Cl_2 and hexanes at room temperature. The purified ionic liquids were stored in an argon-filled glovebox. The N-heterocyclic carbene (NHC), 1,3-bis(2,4,6-trimethyl-phenyl)imidazol-2-ylidene (IMes), was purchased from Strem Chemical Co and used as received. Literature procedures were employed to prepare the following ligand and metal complexes (see Figure 3.2): 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr),[49] $(IPr)CrCl_2$,[50] $(IPr)_2CrCl_2$ and $(SIPr)_2CrCl_2$,[50,51] $Cr(OtBu)_2(THF)_2$,[52] and $CrCl_3(THF)_3$.[53] The identity of chromium containing compounds were known by appearance of the described literature color, and purified by crystallization.

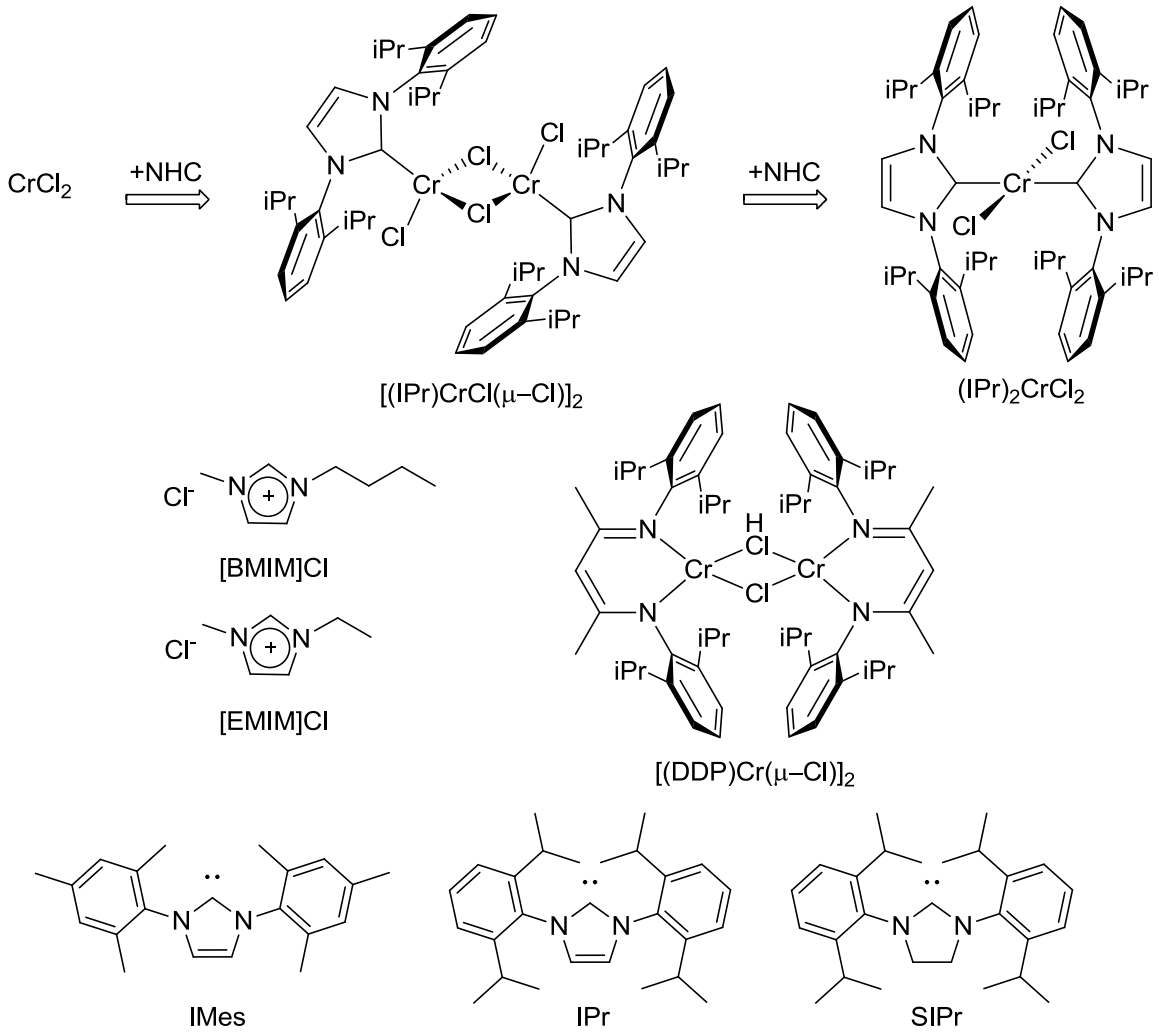

Figure 3.2. Structures of synthesized molecular catalysts and NHC's

The dinuclear chromium complex $[(DDP)Cr(\mu\text{-}Cl)]_2$ was prepared following literature procedures;[54,55] the dimer contained two coordinated THF molecules and its molecular structure was confirmed by single-crystal X-ray diffraction analysis (Figure 3.3). Single crystals obtained from recrystallization in THF were quickly covered with a layer of Paratone-N oil (Exxon, dried and degassed at 120 °C/10-6 Torr for 24 h) after decanting the mother liquor. A crystal was then mounted on a thin glass fiber and transferred into the cold nitrogen stream of a Bruker SMART CCD diffractometer. The structure was solved by direct methods and refined using the Bruker SHELXTL program library.[56] The structure was refined by full-matrix least-squares on F2 for all

reflections. All atoms were located by difference Fourier synthesis and refined anisotropically, whereas hydrogen atoms were included in the structure factor calculations at idealized positions. CCDC-917755 contains the supplementary crystallographic data for this paper. X-ray crystallography data for this structure appear in Appendix 1.

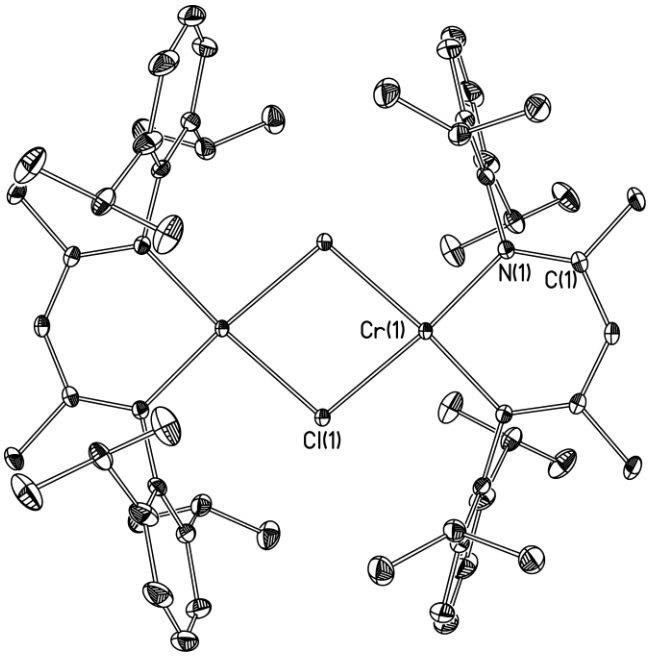

Figure 3.3. X-ray single crystal structure of the dinuclear chromium complex [(DDP)Cr(μ-Cl)]$_2$. H atoms and the coordinated THF molecules were omitted for clarity.

Conversion of glucose to HMF

In a typical experiment, $CrCl_2$ (0.111 mmol, 10 mol% relative to glucose) was premixed with [EMIM]Cl (2.0 g, 10:1 wt. [EMIM]Cl:glucose) in a vial in an argon-filled glove box, then divided into 4 vials each containing a preweighed amount of glucose (50mg x4, 1.11 mmol). Other additives (e.g., co-solvent or NHC) were then added where appropriate. For experiments with added various amounts of NHC, a predetermined amount of IMes (0, 0.5, 1, 2, 3, 5 equiv relative to $CrCl_2$) was added to each of the six parallel vials. The sealed vials were placed in a temperature-controlled orbit shaker (100 or 120 °C, 300 RPM) and heated at the desired

temperature for 3-6 hours. The reaction was quenched and then diluted with a known amount of deionized water. HMF was quantified with calibration curves generated from the commercially available HMF dissolved in water. A typical HPLC chromatogram of the reaction product is shown in Figure 3.4.

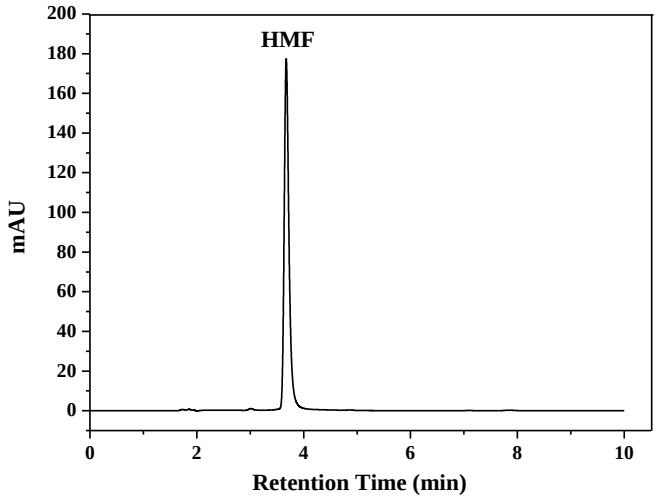

Figure 3.4. Typical chromatogram of Cr catalyzed conversion of glucose showing HMF response at 3.7 min (UV detector, 284 nm).

For conversion experiments with the *in situ* generated NHC, an imidazolium chloride salt (0.056 mmol) and KOtBu (6.2 mg, 0.056 mmol) were weighed into a vial in a glovebox, then 1 mL of DMF was added and the mixture was allowed to react for 1 h. $CrCl_2$ (6.1 mg, 0.050 mmol) was added and the vial was placed on the shaker for 6 h at 80° C. The vial was returned to the glovebox and the solution was divided by 0.5 mL volumes into vials containing 50 mg of glucose and 500 mg [BMIM]Cl. The vial was then returned to the shaker and heated at 100 °C for 6 h. Experiments were also performed to analyze glucose. [EMIM]Cl (0.5 g) and glucose (0.1 g) were charged into a 5 mL vial in a glovebox, followed by further loading of catalysts and NHCs. After the reaction, the resulting mixture was diluted to 25 mL after quenching by ice-water, and 0.5 mL of the supernatant was passed through the cation and anion exchange columns

to remove the IL. A total of 5 mL eluent was collected for HPLC analysis (RI detector). A control experiment showed that glucose recovery was 96.2% after passing through the ions-exchange column.

Results and discussion

Controls with additives and discrete Cr complexes

At the outset, it is important to note that the glucose-to-HMF conversion process, or glucose dehydration, produces 3 equivalents of water per 1 equivalent of HMF formed (cf. Figure 3.1). Therefore, we first investigated the effects of water by varying the amount of water added to the glucose-to-HMF conversion system promoted by two benchmark chromium precatalysts, $CrCl_2$ and $CrCl_3$. Under identical reaction conditions {[EMIM]Cl, 10 mol% Cr (relative to glucose), 100 °C and 3 h}, the glucose conversion system catalyzed by $CrCl_2$ without any added water gave HMF in 60% yield (average values of at least two runs with a standard error of ±1.0 % based on HPLC variance). A gradual increase in the amount of water added to the system from 0.5 to 100 equivalents (relative to Cr) did not significantly alter the HMF yield which remained in a narrow range of 60% to 63%. These results showed the robustness of the chromium catalyst in the presence of a large excess of water. However, it is known that the divalent chromium chloride is rapidly oxidized by air, especially in solution, and traces of water can cause oxidation;[57] in the presence of a trace amount of acid, $CrCl_2$ reacts with water to form the trivalent chromium chloride $CrCl_3$. Hence, $Cr_{(III)}$ should be the true catalyst for systems that employ $CrCl_2$.[58] On the other hand, the system employing $CrCl_3$ directly was noticeably less effective than $CrCl_2$, achieving 53% HMF yield (vs. ~60% by $CrCl_2$); this is largely due to low solubility of $CrCl_3$ in the IL solvent. Upon addition of 6 equivalents of water (to preform the

$CrCl_3$•$6H_2O$ complex that is more readily soluble in [EMIM]Cl), the system based on $CrCl_3$ now experienced a ~4% bump in the HMF yield to 57% .

The highest HMF yield of 81% was reported in the literature by a system comprised of multiple components.[47] Specifically, in addition to the catalyst precursor $CrCl_2$, the IL solvent [BMIM]Cl (solvent), and the substrate glucose, the system also employed the co-solvent DMF as well as two other different reagents, an imidazolium salt such as [IMesH]Cl and the base, KOtBu. The base was hypothesized to generate NHC ligands *in situ* that thereby purportedly formed the (NHC)-$CrCl_2$ complex, which was believed to be the true catalyst for glucose conversion.[47]

As various needed controls were not reported, we also examined the effects of various additives (reagents) involved in the glucose conversion system, using the same conditions (Table 3.1) as those used in the literature. Specifically, control runs with reagents IMes, KOtBu, and IMes + KOtBu gave no formation of HMF. In the absence of an additive, $CrCl_2$ afforded HMF in 46% yield (average value of the two runs with an error of ±1%) under the current standard conditions (9 mol% precatalyst, 100 °C, 6 h). Addition of IMes (1 equiv relative to $CrCl_2$) in DMF lowed the HMF yield to 43%, and the HMF yield was further reduced to only 23% upon addition of IMes + 5 mol% KOtBu (i.e. 0.56 equiv of KOtBu relative to $CrCl_2$). Interestingly, an enhanced HMF yield to 54% was observed with addition of [IMesH]Cl (1 equiv) + DMF (run 5). Addition of 1 equiv of KOtBu (relative to $CrCl_2$) nearly shut down the catalysis (2% yield, run 6), whereas addition of only 0.56 equiv of KOtBu still gave a good HMF yield of 40%. Since KOtBu can convert [EMIM]Cl to the corresponding NHC ligand, this result indicated the inhibiting effect of the *in situ* formed NHC ligand on the catalysis. Lastly, a varied amount of DMF was added (runs 8–10), showing small modulation of the HMF yield ranging from 44% to 48% due to this added solvent.

Table 3.1. Controls with additives used in the glucose conversion system with $CrCl_2$ in [BMIM]Cl[a]

run #	additive	HMF yield (%)
1	none	46
2	IMes	21
3	IMes + DMF	43
4	IMes + 5% KO^{t}Bu	23
5	[IMesH]Cl + DMF	54
6	9% KO^{t}Bu (1 equiv)	2
7	5% KO^{t}Bu (0.56 equiv)	40
8	0.1mL DMF	47
9	0.5mL DMF	48
10	1.0mL DMF	44

[a] Conditions: 50 mg glucose, 500 mg [BMIM]Cl, 9 mol% precatalyst, 100 °C, 6 h.

Next, we investigated various controls using the stepwise procedure used by Ying, et al. to obtain their best HMF yields.[47] This consisted of a premixing step of IL and base, a step 1 heated with added precatalyst, and step 2 heated with the substrate added, the results of which were summarized in Table 3.2. In our hands, the procedure that premixed [IMesH]Cl with KOtBu, followed by the reaction of the resulting species with $CrCl_2$, then addition of [EMIM]Cl and glucose, gave HMF in 46% yield (run 1, Table 2). The same procedure using [IPrH]Cl in place of [IMesH]Cl afforded a lower HMF yield of 40% (run 2). Increasing the amount of the base to 2 equiv in the premixing stage drastically reduced the HMF yield to only 10% (run 3). Ying, et al. also claimed an ~14% increase in HMF yield by running the reactions open to air.[47] Carrying out the conversion in air in both steps 1 and 2 lowered the yield to 38% (run 4). Whereas, operating the second step only in air did not alter the HMF yield (47%, run 5). Using the preformed NHC (IMes) for direct complexation with $CrCl_2$ in step 1 gave HMF in 44% yield (run 6). Replacing IMes with the base KOtBu in step 1 resulted in a lower HMF yield of 40% (run 7). Interestingly, the highest HMF yield of 55% (run 7) was achieved when the imidazolium salt [IMesH]Cl was used, in place of IMes or the *in situ* generated NHC. *Overall, no HMF yield*

enhancement was observed for the system containing an NHC ligand, either generated in situ or introduced externally. Instead, the system with the added imidazolium salt [IMesH]Cl improved the HMF yield by about 10% (run 4, Table 3.1; run 8, Table 3.2) over the original $CrCl_2$ system in [BMIM]Cl under the current conditions.

Table 3.2. Controls with stepwise procedures for conversion of glucose to HMF

run #	premix[a]	step 1[b]	step 2[c]	HMF yield (%)
1	[IMesH]Cl + KO^{t}Bu	$CrCl_2$	[BMIM]Cl	46
2	[IPrH]Cl + KO^{t}Bu	$CrCl_2$	[BMIM]Cl	40
3	[IMesH]Cl + 2 KO^{t}Bu	$CrCl_2$	[BMIM]Cl	10
4	[IMesH]Cl + KO^{t}Bu	$CrCl_2$ (air)	[BMIM]Cl (air)	38
5	[IMesH]Cl + KO^{t}Bu	$CrCl_2$	[BMIM]Cl (air)	47
6	N/A	IMes + $CrCl_2$	[BMIM]Cl	44
7	N/A	KO^{t}Bu + $CrCl_2$	[BMIM]Cl	40
8	N/A	[IMesH]Cl + $CrCl_2$	[BMIM]Cl	55

[a] Reagents were stirred for 1 h in DMF before next step. b Reagents were added to the premix or dissolved in DMF, then heated at 80 °C for 6 h. c Reagents or solvents, along with 50 mg of glucose, were added after step 1, then heated at 100 °C for 6 h.

The next logical step was to use authentic (NHC)-$CrCl_2$ complexes to test if they are the true catalysts and if they are superior to $CrCl_2$ or not. In this context, we employed the discrete mono-NHC complex (IPr)$CrCl_2$, which performed similarly to $CrCl_2$ under the current standard conditions. The bis(NHC) complexes $(IPr)_2CrCl_2$ was a *much poorer catalyst*, affording HMF in ~14% yield. Consistently, the analogous bis(NHC) complexes $(SIPr)_2CrCl_2$ (i.e., the IPr derivative with the saturated backbone) produced HMF in low yield (~13%). The bis(alkoxide) complex $Cr(OtBu)_2(THF)_2$ also afforded HMF in low yield (5%), and the dinuclear complex $[(DDP)Cr(\mu\text{-}Cl)]_2$ gave HMF in 8% yield.

Quantitative NHC titration experiments

To determine *quantitatively* the effects of the NHC ligand on the $CrCl_x$-catalyzed glucose-to-HMF conversion in ILs, we performed titration experiments using two preformed, discrete NHCs, the results of which were summarized in Table 3.3. Two bulky NHC ligands, IMes and

IPr, were chosen for this study, as they were described as the two most effective NHCs for the fructose or glucose conversion into HMF in the *in situ* generated studies.[47] The reaction under our conditions (10 mol% $CrCl_2$, [EMIM]Cl, 100 °C, 3 h) gave an HMF yield of 58%, but the yield was lowered to 57% and 40% upon addition of 0.5 equiv and 1.0 equiv of IMes, respectively. A further increase in the amount of IMes added to the system to 2.0, 3.0, and 5.0 equiv drastically diminished the yield to only 5%, 3%, and 3%, respectively; this level of yield corresponds to the background yield (1–3%) achievable in the absence of the Cr catalyst. The linear, extrapolated portion of the data yielded an intercept of 2.3 (Figure 3.5), which represents the calculated equivalent of the NHC needed to halt the catalysis. This result also indicates that the NHC ligand is a more potent poison than 2,2'-bipyridine, as 5 equivalents of 2,2'-bipyridine were needed to shut down the catalysis by $CrCl_2$ in [EMIM]Cl.[32]

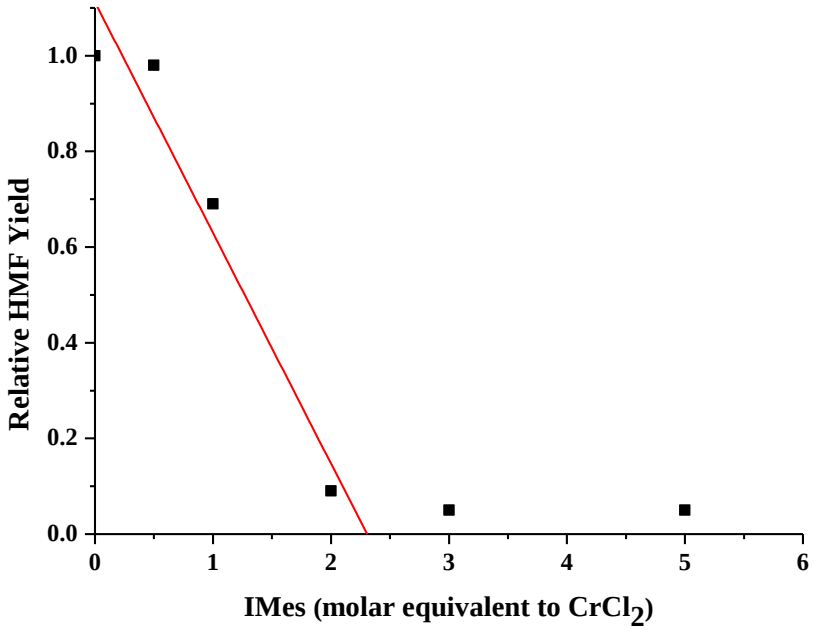

Figure 3.5. Plot of the relative HMF yield vs equiv of the NHC IMes added to the conversion system by $CrCl_2$ in [EMIM]Cl at 100 °C for 3 h.

Table 3.3. NHC effect on HMF yield by Cr catalysts [a]

Cr precatalyst	IL temp, time	NHC	NHC equiv. (relative to Cr)	HMF yield (%)
$CrCl_2$	[EMIM]Cl 100 °C, 3 h	IMes	0	58
			0.5	57
			1	40
			2	5
			3	3
			5	3
$CrCl_2$	[BMIM]Cl 100 °C, 6 h	IPr	0	46
			0.5	47
			1	43
			2	21
			3	2
			5	2
$CrCl_3(THF)_3$	[EMIM]Cl 100 °C, 3 h	IMes	0	57
			0.5	61
			1	56
			2	35
			3	2
			5	2

[a] Carried out at 100 °C for 3 h in [EMIM]Cl or 6 h in [BMIM]Cl with a 10 mol% catalyst loading (relative to glucose); average values based on two runs with an error of ±1.0 %.

Glucose conversion by $CrCl_2$ was typically quantitative under the current conditions in the absence of the NHC ligand or in the presence of up to 1 equiv NHC (IMes). Therefore, the HMF yield reported herein is the same as the HMF selectivity (Table 3.4). On the other hand, the low HMF yield upon addition of 2 or 3 equiv of IMes was due to the low conversion of glucose and poor selectivity to HMF (Runs 4 and 5, Table 3.4). Also noteworthy is when the catalysis for HMF formation was shut down by 2 equivalents of IMes, the glucose conversion rendered was

also significantly suppressed (only 46 %), considering that 20 % glucose conversion or degradation is achieved in IL without any precatalyst added under the same conditions (Run 7, Table 4). When an additional equivalent of IMes was added, the glucose conversion increased to 63 %. This is consistent with the result of the control runs (Table 3.1), which showed that the NHC ligand alone (IMes, 10 mol% loading) promoted higher glucose conversion or degradation (83 %, Table 4) but did not form HMF. Hence, having an active form of the Cr catalyst is critical to achieve high HMF yield or selectivity.

Table 3.4. Effect of NHC (IMes) on glucose conversion and HMF selectivity [a]

Run	Cr precatalyst	NHC	NHC equiv. (relative to Cr)	Glucose conversion (%)	HMF yield (%)	HMF selectivity(%)
1	$CrCl_2$	-	0	>99	58	58
2	$CrCl_2$	IMes	0.5	>99	57	57
3	$CrCl_2$	IMes	1	97	40	41
4	$CrCl_2$	IMes	2	46	5	11
5	$CrCl_2$	IMes	3	63	3	5
6	-	IMes	0.1[b]	83	0	0
7	-	-	-	20	0	0

[a] Carried out at 100 °C for 3 h in [EMIM]Cl with a 10 mol% precatalyst loading (relative to glucose); [b] 0.1 equiv (10 mol %) of IMes loading relative to glucose.

A similar trend was also observed for the glucose-to-HMF conversion system with $CrCl_2$ in [BMIM]Cl (100 °C, 6 h) when titrated using IPr as the discrete NHC source (Table 3.3). The linear, extrapolated portion of the data yielded an intercept of 3.1 (Figure 3.6), suggests that approximately 3 equiv of IPr can shut down the catalysis. Finally, the same titration experiment performed on the Cr(III) precatalyst $CrCl_3(THF)_3$ ([EMIM]Cl, 100 °C, 3 h) using IMes as the NHC also yielded similar results (Table 3.3) and the same intercept (3.2, Figure 3.7). The THF

adduct, $CrCl_3(THF)_3$, is used for this study instead of anhydrous $CrCl_3$ because $CrCl_3$ has limited solubility in [EMIM]Cl.

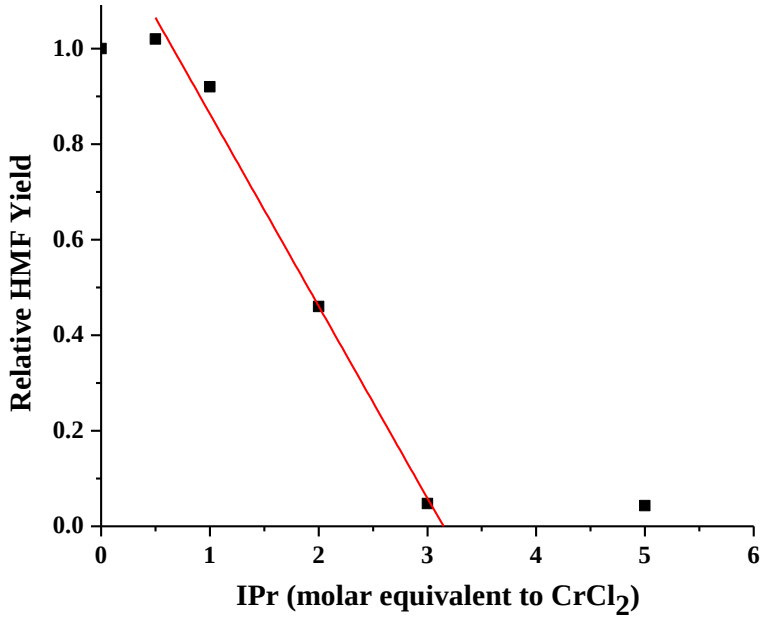

Figure 3.6. Plot of the relative HMF yield vs equiv of the NHC IPr added to the conversion system by $CrCl_2$ in [BMIM]Cl at 100 °C for 6 h.

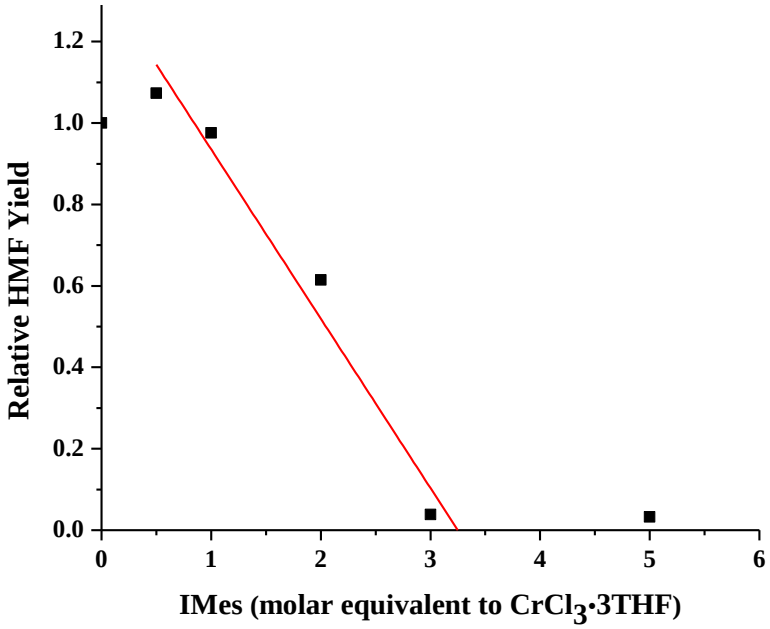

Figure 3.7. Plot of the relative HMF yield vs equiv of the NHC IMes added to the conversion system by $CrCl_3(THF)_3$ in [EMIM]Cl at 100 °C for 3 h.

Overall, the above results consistently and conclusively showed that the *NHC ligand actually serves as a poison to the chromium catalyst system* and a superstoichiometric amount (2 or 3 equiv) of the NHC can completely shut down the catalysis. Since both sets of control experiments with discrete Cr-complexes and added authentic carbenes showed the same activity trend, it is reasonable to assume that the NHC ligand is interacting with the Cr catalyst in the latter experiments to cause this effect. In this case, it is reasoned that strongly donating, largely non-labile NHC ligands render the Cr center coordinatively saturated, thereby negatively impacting or even completely shutting down the catalyst activity.

Conclusions

This study, through three different sets of experiments, has addressed the role of the NHC ligand in the glucose-to-HMF conversion system with $CrCl_x$ in ILs. It is conclusively shown that the NHC ligand serves as a poison to the chromium catalyst system based on controls with all additives (reagents) involved in the conversion system, performance of *in situ* generated and discrete NHC ligands and Cr complexes that were proposed to be the true catalyst, and quantitative NHC titration (poisoning) experiments. Additionally, a superstoichiometric amount (2 or 3 equiv) of the NHC ligand can completely shut down the catalysis. It is reasoned that strongly σ-donating, largely non-labile NHC ligands render the Cr center coordinatively saturated, thereby negatively impacting or even completely shutting down the catalyst activity. On the other hand, the free NHC ligand present in the system can promote glucose conversion/degradation, but without forming HMF. As NHCs are intimately connected with their precursors—imidazolium salts (ILs) that are typically used in the homogenous biomass conversion systems—the results of this study should be of considerable interest to the field.

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Appendix 1: X-ray crystallography data for $[(DDP)Cr(\mu\text{-}Cl)]_2$

Table A1. Crystal data and structure refinement for $[(DDP)Cr(\mu\text{-}Cl)]_2$.

Identification code	ec70r	
Empirical formula	C33 H49 Cl Cr N2 O	
Formula weight	577.19	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	P 42/m	
Unit cell dimensions	a = 12.9020(5) Å	α= 90∞.
	b = 12.9020(5) Å	β= 90∞.
	c = 20.0716(11) Å	γ = 90∞.
Volume	3341.2(3) $Å^3$	
Z	4	
Density (calculated)	1.147 Mg/m^3	
Absorption coefficient	0.448 mm^{-1}	
F(000)	1240	
Crystal size	0.55 x 0.47 x 0.33 mm^3	
Theta range for data collection	1.88 to 33.59°.	
Index ranges	-19<=h<=19, -19<=k<=19, -30<=l<=30	
Reflections collected	78413	
Independent reflections	6671 [R(int) = 0.0689]	
Completeness to theta = 33.59∞	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8652 and 0.7911	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6671 / 23 / 199	
Goodness-of-fit on F^2	1.043	
Final R indices [I>2sigma(I)]	R1 = 0.0541, wR2 = 0.1473	
R indices (all data)	R1 = 0.0624, wR2 = 0.1522	
Largest diff. peak and hole	3.573 and -3.184 e.$Å^{-3}$	

Table A2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (≈^{2}x 10^3) for [(DDP)Cr(μ-Cl)]$_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cr(1)	587(1)	6293(1)	10000	10(1)
N(1)	1211(1)	7227(1)	9263(1)	13(1)
Cl(1)	0	5000	10785(1)	15(1)
C(1)	1500(1)	8204(1)	9370(1)	15(1)
C(2)	1537(2)	8677(2)	10000	16(1)
C(3)	1882(1)	8882(1)	8804(1)	23(1)
C(4)	1366(1)	6838(1)	8596(1)	17(1)
C(5)	551(1)	6867(1)	8133(1)	21(1)
C(6)	744(2)	6529(2)	7483(1)	32(1)
C(7)	1708(2)	6159(2)	7299(1)	37(1)
C(8)	2490(2)	6100(2)	7763(1)	34(1)
C(9)	2338(2)	6431(1)	8420(1)	27(1)
C(10)	-517(1)	7264(1)	8320(1)	23(1)
C(11)	-1386(2)	6612(2)	8011(1)	34(1)
C(12)	-659(2)	8414(1)	8133(1)	31(1)
C(13)	3288(4)	6487(5)	8950(3)	22(1)
C(14)	4277(6)	6927(8)	8686(4)	40(2)
C(15)	3441(4)	5412(4)	9228(3)	39(2)
C(13A)	3124(5)	6157(6)	8906(3)	29(1)
C(14A)	4009(9)	6939(7)	8841(8)	93(5)
C(15A)	3567(4)	5069(3)	8849(3)	38(1)
O(1)	-1029(1)	7222(1)	10000	20(1)
C(16)	-1978(2)	6647(2)	10000	51(1)
C(17)	-2841(2)	7402(2)	10000	51(1)
C(18)	-2409(2)	8402(2)	10000	51(1)
C(19)	-1256(2)	8321(2)	10000	51(1)

Table A3. Bond lengths [Ĺ] and angles [°] for [(DDP)Cr(μ-Cl)]$_2$.

Cr(1)-N(1)#1	2.0702(12)
Cr(1)-N(1)	2.0702(12)
Cr(1)-O(1)	2.4048(16)
Cr(1)-Cl(1)	2.4169(4)
Cr(1)-Cl(1)#2	2.4170(4)
N(1)-C(1)	1.3330(18)
N(1)-C(4)	1.4441(19)
Cl(1)-Cr(1)#2	2.4169(4)
C(1)-C(2)	1.4047(17)
C(1)-C(3)	1.516(2)
C(2)-C(1)#1	1.4048(17)
C(4)-C(5)	1.404(2)
C(4)-C(9)	1.405(2)
C(5)-C(6)	1.398(2)
C(5)-C(10)	1.517(3)
C(6)-C(7)	1.384(3)
C(7)-C(8)	1.376(4)
C(8)-C(9)	1.399(3)
C(9)-C(13A)	1.451(7)
C(9)-C(13)	1.624(7)
C(10)-C(11)	1.533(2)
C(10)-C(12)	1.541(2)
C(13)-C(14)	1.493(9)
C(13)-C(15)	1.509(7)
C(13A)-C(15A)	1.520(8)
C(13A)-C(14A)	1.530(11)
O(1)-C(16)	1.431(3)
O(1)-C(19)	1.449(3)
C(16)-C(17)	1.479(4)
C(17)-C(18)	1.406(4)
C(18)-C(19)	1.491(4)
N(1)#1-Cr(1)-N(1)	91.17(7)
N(1)#1-Cr(1)-O(1)	92.72(4)
N(1)-Cr(1)-O(1)	92.72(4)

N(1)#1-Cr(1)-Cl(1)	93.31(4)
N(1)-Cr(1)-Cl(1)	171.63(4)
O(1)-Cr(1)-Cl(1)	94.13(3)
N(1)#1-Cr(1)-Cl(1)#2	171.63(4)
N(1)-Cr(1)-Cl(1)#2	93.31(4)
O(1)-Cr(1)-Cl(1)#2	94.13(3)
Cl(1)-Cr(1)-Cl(1)#2	81.408(19)
C(1)-N(1)-C(4)	116.04(12)
C(1)-N(1)-Cr(1)	123.01(10)
C(4)-N(1)-Cr(1)	120.95(9)
Cr(1)#2-Cl(1)-Cr(1)	98.59(2)
N(1)-C(1)-C(2)	124.40(14)
N(1)-C(1)-C(3)	121.10(14)
C(2)-C(1)-C(3)	114.41(13)
C(1)-C(2)-C(1)#1	128.37(18)
C(5)-C(4)-C(9)	120.80(15)
C(5)-C(4)-N(1)	120.09(14)
C(9)-C(4)-N(1)	119.11(15)
C(6)-C(5)-C(4)	118.43(18)
C(6)-C(5)-C(10)	119.85(17)
C(4)-C(5)-C(10)	121.72(14)
C(7)-C(6)-C(5)	121.2(2)
C(8)-C(7)-C(6)	119.82(18)
C(7)-C(8)-C(9)	121.25(19)
C(8)-C(9)-C(4)	118.45(19)
C(8)-C(9)-C(13A)	117.5(3)
C(4)-C(9)-C(13A)	123.0(3)
C(8)-C(9)-C(13)	121.7(3)
C(4)-C(9)-C(13)	119.5(3)
C(13A)-C(9)-C(13)	16.9(3)
C(5)-C(10)-C(11)	112.30(16)
C(5)-C(10)-C(12)	111.84(15)
C(11)-C(10)-C(12)	110.05(15)
C(14)-C(13)-C(15)	111.7(5)
C(14)-C(13)-C(9)	115.5(5)
C(15)-C(13)-C(9)	107.5(4)

C(9)-C(13A)-C(15A)	116.0(4)
C(9)-C(13A)-C(14A)	107.7(6)
C(15A)-C(13A)-C(14A)	108.7(6)
C(16)-O(1)-C(19)	109.52(19)
C(16)-O(1)-Cr(1)	118.92(14)
C(19)-O(1)-Cr(1)	131.55(15)
O(1)-C(16)-C(17)	107.6(2)
C(18)-C(17)-C(16)	107.8(2)
C(17)-C(18)-C(19)	109.3(2)
O(1)-C(19)-C(18)	105.7(2)

Symmetry transformations used to generate equivalent atoms:

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

Table A4. Anisotropic displacement parameters ($\approx^2$x 10^3) for [(DDP)Cr(μ-Cl)]$_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cr(1)	11(1)	8(1)	12(1)	0	0	0(1)
N(1)	14(1)	12(1)	14(1)	1(1)	0(1)	-1(1)
Cl(1)	23(1)	10(1)	12(1)	0	0	-4(1)
C(1)	15(1)	12(1)	18(1)	3(1)	1(1)	-1(1)
C(2)	18(1)	10(1)	20(1)	0	0	-2(1)
C(3)	33(1)	15(1)	22(1)	5(1)	5(1)	-6(1)
C(4)	24(1)	13(1)	14(1)	2(1)	4(1)	-1(1)
C(5)	33(1)	16(1)	15(1)	1(1)	-2(1)	-5(1)
C(6)	53(1)	27(1)	16(1)	-2(1)	-1(1)	-8(1)
C(7)	65(2)	26(1)	20(1)	-5(1)	15(1)	-7(1)
C(8)	48(1)	26(1)	29(1)	0(1)	20(1)	3(1)
C(9)	30(1)	27(1)	23(1)	4(1)	11(1)	6(1)
C(10)	28(1)	20(1)	21(1)	2(1)	-10(1)	-3(1)
C(11)	36(1)	28(1)	36(1)	4(1)	-18(1)	-6(1)
C(12)	40(1)	22(1)	31(1)	4(1)	-12(1)	1(1)
C(13)	16(2)	23(2)	28(2)	6(2)	7(2)	0(2)
C(14)	29(3)	47(3)	45(3)	20(2)	9(2)	-7(2)
C(15)	36(2)	30(2)	52(4)	15(2)	5(2)	-1(2)
C(13A)	16(2)	38(3)	32(2)	-12(2)	2(2)	0(2)
C(14A)	64(7)	29(3)	188(14)	0(6)	-72(7)	-7(4)
C(15A)	34(2)	27(2)	54(3)	1(2)	-7(2)	3(2)
O(1)	13(1)	14(1)	32(1)	0	0	1(1)
C(16)	17(1)	19(1)	118(2)	0	0	1(1)
C(17)	17(1)	19(1)	118(2)	0	0	1(1)
C(18)	17(1)	19(1)	118(2)	0	0	1(1)
C(19)	17(1)	19(1)	118(2)	0	0	1(1)

Table A5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (≈^{2}x 10 ^{3}) for [(DDP)Cr(μ-Cl)]$_2$.

	x	y	z	U(eq)
H(2)	1594	9411	10000	19
H(3A)	1831	8500	8383	35
H(3B)	2606	9075	8884	35
H(3C)	1456	9510	8779	35
H(6A)	203	6554	7163	38
H(7A)	1831	5947	6852	45
H(8A)	3145	5829	7636	41
H(10A)	-584	7208	8815	28
H(11A)	-1291	5883	8133	50
H(11B)	-1366	6681	7525	50
H(11C)	-2058	6855	8177	50
H(12A)	-101	8824	8333	46
H(12B)	-1329	8660	8300	46
H(12C)	-637	8488	7647	46
H(13A)	3059	6941	9326	26
H(14A)	4801	6928	9040	60
H(14B)	4159	7639	8534	60
H(14C)	4521	6503	8313	60
H(15A)	4009	5420	9552	59
H(15B)	3609	4933	8865	59
H(15C)	2802	5184	9449	59
H(13B)	2814	6233	9360	35
H(14D)	3733	7644	8880	140
H(14E)	4345	6856	8407	140
H(14F)	4518	6818	9196	140
H(15D)	3016	4560	8926	57
H(15E)	4115	4976	9181	57
H(15F)	3856	4970	8402	57
H(16A)	-2017	6200	10400	61
H(16B)	-2017	6200	9600	61

H(17A)	-3278	7303	9600	61
H(17B)	-3278	7303	10400	61
H(18A)	-2643	8786	10400	61
H(18B)	-2643	8786	9600	61
H(19A)	-962	8658	9599	61
H(19B)	-962	8658	10401	61

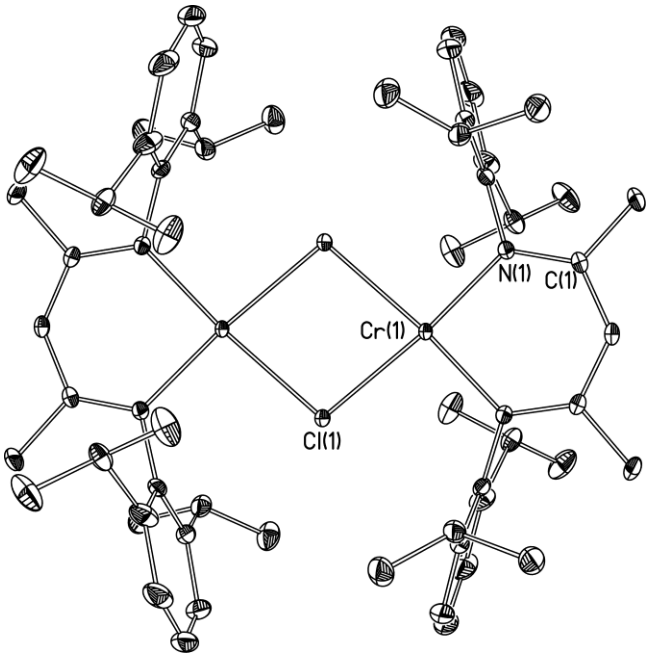

Figure A1. X-ray single crystal structure of the dinuclear chromium complex [(DDP)Cr(μ-Cl)]2. H atoms and the coordinated THF molecules were omitted for clarity.