Interactions of Lewis Acids and Carbonyls in the Presence of Ligands Or Additives: How Solution Behavior Differs and the Implication on Catalytic Systems

Sophi Rose Todtz
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INTERACTIONS OF LEWIS ACIDS AND CARBONYLS IN THE PRESENCE OF LIGANDS OR ADDITIVES: HOW SOLUTION BEHAVIOR DIFFERS AND THE IMPLICATION ON CATALYTIC SYSTEMS

A DISSERTATION SUBMITTED TO
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IN CANDIDACY FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

PROGRAM IN PHYSICAL ORGANIC CHEMISTRY

BY
SOPHI R. TODTZ
CHICAGO, IL
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<th>Description</th>
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<tbody>
<tr>
<td>BF$_3$</td>
<td>Boron trifluoride</td>
</tr>
<tr>
<td>BCl$_3$</td>
<td>Boron trichloride</td>
</tr>
<tr>
<td>EtOAc</td>
<td>Ethyl acetate</td>
</tr>
<tr>
<td>Et$_2$O</td>
<td>Diethyl ether</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>AlCl$_3$</td>
<td>Aluminum trichloride</td>
</tr>
<tr>
<td>TiCl$_4$</td>
<td>Titanium tetrachloride</td>
</tr>
<tr>
<td>SnCl$_4$</td>
<td>Tin tetrachloride</td>
</tr>
<tr>
<td>InCl$_3$</td>
<td>Indium trichloride</td>
</tr>
<tr>
<td>OTf</td>
<td>Trifluoromethanesulfonate</td>
</tr>
<tr>
<td>TMSCl</td>
<td>Trimethylsilyl chloride</td>
</tr>
<tr>
<td>GaCl$_3$</td>
<td>Gallium trichloride</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethylsulfoxide</td>
</tr>
<tr>
<td>Me</td>
<td>Methyl</td>
</tr>
<tr>
<td>AlBr$_3$</td>
<td>Aluminum tribromide</td>
</tr>
<tr>
<td>ATR-FTIR</td>
<td>Attenuated total reflection-Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>Et</td>
<td>Ethyl</td>
</tr>
<tr>
<td>tBu</td>
<td>tert-butyl</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Ph</td>
<td>Phenyl</td>
</tr>
<tr>
<td>Ar</td>
<td>Aryl</td>
</tr>
<tr>
<td>FeCl₃</td>
<td>Iron trichloride</td>
</tr>
<tr>
<td>EtOH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>SnBr₄</td>
<td>Tin tetrabromide</td>
</tr>
<tr>
<td>MeCN</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>iPr</td>
<td>Isopropyl</td>
</tr>
<tr>
<td>tBu</td>
<td>tert-Butyl</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>DCE</td>
<td>1,2 Dichloroethane</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>Equiv</td>
<td>Equivalent</td>
</tr>
<tr>
<td>Abs</td>
<td>Absorbance (cm⁻¹)</td>
</tr>
<tr>
<td>FTs</td>
<td>4-(trifluoromethyl)benzenesulfonyl protecting group</td>
</tr>
<tr>
<td>h</td>
<td>Hour</td>
</tr>
<tr>
<td>min</td>
<td>Minute</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>K₂CO₃</td>
<td>Potassium carbonate</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>Sodium sulfate</td>
</tr>
<tr>
<td>KMnO₄</td>
<td>Potassium permanganate</td>
</tr>
<tr>
<td>PBr₃</td>
<td>Phosphorous (III) bromide</td>
</tr>
<tr>
<td>NMM</td>
<td>N-methylmorpholine</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>DCC</td>
<td>N,N’-dicyclohexylcarbodiimide</td>
</tr>
<tr>
<td>WA</td>
<td>Weinreb amide intermediate</td>
</tr>
<tr>
<td>INT</td>
<td>Intermediate</td>
</tr>
<tr>
<td>TS</td>
<td>Transition state</td>
</tr>
<tr>
<td>TLC</td>
<td>Thin layer chromatography</td>
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</table>
CHAPTER 1
INTRODUCTION

Introduction

In the decades since the introduction of Gilbert Lewis’ definition of acids and bases, the field of Lewis acid catalysis has grown tremendously. These electron acceptors play a central role in organic chemistry and their commercial availability has only encouraged further development into their applicability.\(^1\) One crucial use of Lewis acids is in carbonyl chemistry. Carbonyls are incredibly powerful functional groups, capable of participating in a wide variety of transformations. Their importance to the field of organic synthesis is largely due to their unique reactivity. The electrophilic carbon is susceptible to nucleophilic attack and Lewis acids have been widely employed to enhance this property.\(^2\)–\(^4\) Perhaps the first pivotal event in Lewis acid-activation of a carbonyl was the development of the Grignard reaction by Victor Grignard around 1900.\(^5\) This development, which was awarded a Nobel prize in 1912, is possibly the most fundamental reaction in synthetic organic chemistry due to its facile availability and versatility.\(^6\)–\(^9\) The utility of the Mukaiyama-aldol reaction further advanced the field of Lewis acid catalyzed carbonyl transformations. Since then, synthetic chemists have continued utilizing Lewis acids to modify electron density of carbonyls and facilitate organic reactions.\(^10\)–\(^13\) Specifically, Lewis acids have been employed to catalyze Diels-Alder reactions,\(^14\) aldol reactions,\(^15\)–\(^17\) ene reactions,\(^18,19\) photochemical reactions,\(^20,21\) and more recently carbonyl-olefin metathesis.\(^22\)–\(^24\) This introductory chapter will explore the utility and catalytic behavior of a variety of Lewis acids.
acids with carbonyls. An overview of the synthetic use of B(III), Al(III), Ga(III), Fe(III), Ti(IV), Sn(IV), Zr(IV), and In(III) will be detailed.

**B(III) In Catalysis.**

Boron(III) Lewis acids are frequently utilized as catalysts in organic transformations due to their strongly electrophilic nature. The unique reactivity of these Lewis acids can be attributed to the empty p-orbital on the boron, which can accept electrons from Lewis bases.\(^1,25,26\) Boron(III) compounds of the nature BX\(_3\), RBX\(_2\), R\(_2\)BX (where X = Cl, Br, I, or F) and BF\(_3\)•OEt\(_2\) have become routine in synthesis as catalysts in Prins-Pinacol type reactions,\(^27\) Nazarov cyclizations,\(^28\) Diels-Alder reactions,\(^29\) and Mukaiyama condensations.\(^30\)

![Proposed mechanism:](image)

14 examples (up to 88%)

Figure 1. Tandem Prins-Pinacol reaction and proposed mechanism.

The Reddy group describes the BF\(_3\)•OEt\(_2\) catalyzed Prins/Pinacol cascade reaction towards the synthesis of oxaspirocycles from homoallylic diol, 1, and aldehydes, 2 (Figure 1).\(^27\) The group is able to achieve good yields and excellent stereoselectivity of 14 different substituted oxaspirocycles. The group proposes a mechanism for this transformation but does not detail the activity of the Lewis acid. It is plausible that the mechanism begins with the
coordination of BF$_3$•OEt$_2$ to the oxygen of the aldehyde,activating the carbon atom towards reaction with the homoallylic diol 1 (Figure 1). Through Prins-type reactivity, an oxocarbenium ion, 6, is generated in-situ. This ion then undergoes an attack by the internal olefin, yielding carbocation 7. The desired oxaspirocycle 3 is formed through a final Pinacol 1,2-shift (Figure 1). Despite the presence of multiple Lewis basic moieties in both the products and reactants which may sequester the B(III) catalyst, the group achieves formation of a single diastereomer in high yields.

![Figure 2](image)

Figure 2. BF$_3$•OEt$_2$-catalyzed Nazarov cyclization (A) and BF$_3$•OEt$_2$-catalyzed Diels-Alder reaction (B).

Similarly, Nazarov cyclizations and Diels-Alder reaction in which more than one Lewis base is present in the system have proven successful with the use of BF$_3$•OEt$_2$. In their stereoselective convergent synthesis of trichodiene, Harding & Clement employ a BF$_3$•OEt$_2$ catalyzed Nazarov cyclization to establish the desired stereocenters (Figure 2, A). Starting with dienone 8, the group was able to achieve yields of 75-80% of product 9. The Danishefsky group details an intramolecular Diels-Alder reaction between cycloalkenones like 10 (Figure 2, B). Moderate to quantitative yields of cycloaddition products 11 were achieved using BF$_3$•OEt$_2$ as a Lewis acid catalyst. Additionally, the group reports obtaining high endo selectivity.

Diarylborinic acids have proven to be effective Lewis acid catalysts in organic transformations like the Mukaiyama aldol condensation described by Yamamoto and coworkers (Figure 3). They obtain a quantitative yield of condensation product 17 when a diarylborinic
acid catalyst is employed, while no reaction is observed when an arylboronic acid is used. Additionally, it is noted that $\alpha,\beta$-enones like 17 are formed exclusively from anti-aldol products whereas the syn-aldol products are unreactive towards condensation. The group proposes that the mechanism of the condensation reaction proceeds through a cyclic intermediate, 15, that is susceptible to dehydration. Enolate intermediate, 16, is formed after the removal of the pseudo-axial $\alpha$-proton. Yamamoto and coworkers explain that the selective reactivity of anti-aldol products towards condensation is due to the thermodynamic stability of cyclic intermediate 15.

![Chemical diagram](image)

**Figure 3. Selective condensation of anti-aldol products employing B(III) catalyst.**

**In(III) in Catalysis.**

In(III) salts have gained considerable attention as Lewis acid catalysts for C-C bond forming reactions and other organic transformations. The surge of interest into In(III) catalysis began in the 1990s as chemists searched for air and moisture stable compounds to facilitate organic processes.\(^{33,34}\) Particularly, a review by Cintas in 1995 highlighted the utility of In(III) as a milder Lewis acid, making it an attractive alternative to other commonly employed salts like $\text{AlCl}_3$, $\text{TiCl}_4$, and $\text{SnCl}_4$.\(^{35}\) Additionally, In(III) compounds are air and moisture stable, even tolerating aqueous media, which broadens their applicability to the field of catalysis.\(^{36,37}\) In the years since Cintas’ review, In(III) catalysts have been employed in many organic
transformations, including Michael reactions, Mannich type reactions, alkynylations, annulations, and Barbier type allylations.

Figure 4. Michael addition of silyl enol ethers to $\alpha,\beta$-unsaturated ketones (A). Mannich-type reaction of aldehydes, amines, and silyl enol ethers (B).

Wei and Loh describe the Michael addition of silyl enol ethers, $20$, to $\alpha,\beta$-unsaturated ketones, $19$, facilitated by $\text{InCl}_3$ (Figure 4). The group was able to expand the scope of the Michael reaction to tolerate neutral conditions by employing a moisture stable $\text{In}(\text{III})$ catalyst. Under these mild conditions, moderate to good yields of Michael adducts, $21$, were obtained. Additionally, the Loh group reports the Mannich-type reaction of aldehydes, $22$, amines, $23$, and silyl enol ethers, $24$, to yield up to 82% of $\beta$-amino ketones, $25$. Notably, formation of the corresponding Aldol product $26$ is not observed with the use of $\text{InCl}_3$. When $\text{InCl}_3$ is removed from the system, the group reports a yield of 42% of $26$ and no Mannich-type product $25$. This suggests that $\text{InCl}_3$ exhibits a unique selectivity towards Mannich-type reactivity over the Aldol reaction. This system includes multiple Lewis bases that may interact with the acid catalyst and yield different reactivity. However, $\text{InCl}_3$ can selectively react to yield one desired product in an 82% yield.
The utility of In(III) as a Lewis acid catalyst is further demonstrated in a report on the alkynylation of carbonyl compounds by the Shibasaki group (Figure 5).\textsuperscript{40} \textit{In situ} IR and NMR spectroscopic analysis reveal that the dual activation of the soft nucleophile, 27, and hard electrophile, 22, by the InBr\textsubscript{3} catalyst is key to the reactivity of this system. Beginning with \textit{in situ} IR analysis, the group examined the interactions of the InBr\textsubscript{3} catalyst with phenylacetylene. Reaction conditions were simulated and a background spectrum of InBr\textsubscript{3} and \textit{iPr\textsubscript{2}NEt} in DME was measured. Next, 1 equiv of phenylacetylene was added and changes in spectra were observed. Initially, a signal at 3246 cm\textsuperscript{-1}, which is associated with the C-H stretch of the alkyne, was visible. This signal was consumed in under a minute.

![Mechanistic proposal:](image)

**Figure 5.** Alkynylation of aldehydes via dual activation proposed by Shibasaki and coworkers.

When beyond 1 equiv phenylacetylene was added to the solution in steps, the stretch at 3246 cm\textsuperscript{-1} increased with each addition. Without the presence of InBr\textsubscript{3}, the signal at 3246 cm\textsuperscript{-1} is not consumed. The results of the in-situ IR experiments suggest that InBr\textsubscript{3} reacts with the alkyne, likely forming an activated species like 29 (Figure 5). Next, NMR spectroscopic analysis was conducted to investigate the activation of carbonyl’s like 22. The group observed a shift in the peak associated with the aldehyde proton on \textsuperscript{1}H NMR and a shift in the carbonyl carbon on \textsuperscript{13}C.
NMR once InBr$_3$ was added to the aldehyde. The presence or absence of $i$Pr$_2$NEt and phenylacetylene does not appear to change this observation. These results led the Shibasaki group to conclude that the InBr$_3$ forms activated carbonyl species 31 when combined with aldehydes.

Figure 6. Domino reaction towards the synthesis of 2H-chromene-2-ones through am InCl$_3$-catalyzed [4+2] annulation.

The Singh group reports an InCl$_3$-catalyzed [4+2] annulation reaction of $\alpha$-oxoketene dithioacetals, 33, and 2-hydroxyarylaldehydes, 34, that affords a variety of substituted chromen-2-ones, 35 (Figure 6).$^{41}$ This transformation efficiently employs both 33 and 34 to construct a new pyran ring under neat conditions through In(III) catalysis. The 35 product is obtained in high yields and the reaction is tolerant of a variety of different functional groups in the starting materials. Singh and coworkers report yields up to 94% across 43 examples. Notably, multiple Lewis basic moieties are present in the described reaction system. A ketone in each starting material, as well as two in the product could present a challenge. To avoid termination of
reactivity or formation of side products, the InCl₃ catalyst will need to differentiate between all Lewis bases present in the system, selectively interacting with one over the other. The Singh group proposes a mechanism in which InCl₃ initially coordinates to the carbonyl oxygen of 33 selectively over the ketone present in 34. Next, 34 and the activated substrate 36 will undergo an oxa-Michael type reaction, yielding enolate intermediate 37. Here, the group suggests that the InCl₃ catalyst is no longer coordinated to the oxygen of 33 but instead is coordinated to the oxygen of 34. In this position, the catalyst activates the aldehyde towards an Aldol-type cyclization to produce intermediate 38. Dehydration of 38 gives intermediate 39 which undergoes consecutive hydrolysis of both methylthiol groups and yields product 35. The final processes in this domino reaction are described to occur without mediation by InCl₃. Singh and coworkers obtain high yields of a single desired product, lending support to their mechanistic proposal detailing the selectivity of InCl₃.

Figure 7. Barbier type regioselective allylation of 1,5-dicarbonyls.

In another system that demonstrates good selectivity of an In(III) catalyst, Kim and coworkers reported an InCl₃-mediated Barbier type regioselective allylation of 1,5-dicarbonyl compounds, 41, and subsequent dehydrative cyclization of 42 to generate dihydro-pyranones,
43, and oxazines (Figure 7). The group proposes the selective mono-allylation at C₁ occurs due to the formation of intermediate 43 which is stabilized by chelation of In(III) center with the C₃ carbonyl and an additional intramolecular hydrogen bond. Importantly, they do not observe 46, which would proceed via less favorable intermediate 45. The group obtains yields of 43 up to 91%.

**Al(III) in Catalysis.**

Al(III) halides have proven to be extremely valuable in modern organic synthesis. Known for their strong Lewis acidity, Al(III) halides are some of the most commonly employed and commercially available catalysts. AlCl₃ is utilized as a Lewis acid catalyst in the Friedel-Crafts reaction, a transformation that has formed the basis of many industrial processes. AlCl₃ has demonstrated a wide nature of reactivity aside from the Friedel-Crafts reaction, and this section will be focused primarily on carbonyl-based synthetic transformations.

![Proposed Mechanism](image)

**Figure 8.** AlCl₃ catalyzed [3+2] annulation of cis-disubstituted cyclopropane diesters and proposed mechanism.
Chai and coworkers report the AlCl₃-catalyzed [3+2] annulations of cis-disubstituted cyclopropane diesters, 47, with cyclic ketones, 48, in the diastereoselective synthesis of spirotetrahydrofurans, 49 (Figure 8).⁴⁵ The group proposes that the C₁-C₃ bond of cyclopropane 47 is activated by AlCl₃ chelation to undergo nucleophilic attack from 48, forming zwitterion 51. 51 undergoes a bond rotation to facilitate the subsequent nucleophilic attack of the carbanion to complete the [3+2] annulation and yield final product 49. Notably, the proposed mechanism involves the selective coordination of the AlCl₃ catalyst to the diester over other Lewis basic moieties present in solution. Using a substoichiometric amount of AlCl₃, the group achieves moderate to excellent yields of spirotetrahydrofuran products.

![Figure 9. AlCl₃-catalyzed selective Prins reaction of homoallylic alcohols.](image)

Li and coworkers report the AlCl₃-catalyzed Prins reaction in the synthesis of trans-substituted halopiperidines and cis-substituted halotetrahydropyrans, 54, in high yields, employing the additive TMSCl as a chloride source (Figure 9).⁴⁶ Importantly, they observe the products in high diastereomeric ratios (90:10 cis:trans). The group concludes that the selectivity towards the cis product is a result of the more favorable equatorial attack of the chloride anion.

The Singh group reports the synthesis of chromene-thiones, 57, via an AlCl₃-catalyzed Pechmann condensation (Figure 10).⁴⁷ The group proposes that the reaction initiates with the nucleophilic addition of the OH group of 56 to the dithioester 58 with the elimination of methanethiol to generate Lewis pair 58. Subsequent ring closure through electrophilic attack of
the π-electrons at the carbonyl carbon form intermediate 59, which, upon elimination of water, yields product 57. Again, the proposed reaction mechanism describes AlCl₃ selectively coordinating to one Lewis basic moiety over multiple others present under reaction conditions.

![Proposed Mechanism](image1)

Figure 10. AlCl₃ catalyzed Pechmann condensation and proposed mechanism.

![Proposed Mechanism](image2)

Figure 11. AlCl₃ mediated one-pot cyclization yielding multisubstituted 1,3-dicyclochexadienes and proposed mechanism.
The Li group developed a protocol for the synthesis of multisubstituted 1,3-dicylclohexadienes, 62, via a one-pot direct cyclization between chalcones, 60, and β-enamines, 61, mediated by AlCl₃ (Figure 11). They propose AlCl₃ activates chalcone 60 through coordination to the C=O group, forming Lewis pair 63. A subsequent Michael addition of enamine 65 yields intermediate 66. Upon elimination of AlCl₃, intermediate 67 tautomerizes to 68, which then cyclizes to form key intermediate 69. Subsequent dehydration and tautomerization forms product 62 in up to excellent yields.

**Ga(III) in Catalysis.**

Ga(III) and Al(III) display divergent reactivity, though they are both group 13 elements. Al(III)-based Lewis acids have been a popular choice in organic synthesis, though the utility of Ga(III) compounds in catalysis has grown in recent years. Ga(III) Lewis acids exhibit different reactivity from other metal halides due to its soft nature. The soft acidity of Ga(III) has proven to be beneficial in activating soft functional groups like alkynes, which makes it a valuable catalyst for reactions like the Friedel-Crafts Alkylation. Additionally, Ga(III) Lewis acids have become a desirable choice due to their increased solubility in a variety of organic solvents as opposed to other Lewis acids like Fe(III). Though Ga(III) has been employed in many different types of reactions, this section will focus on systems in which GaCl₃ interacts with carbonyls.

The Sakai group developed a GaCl₃-mediated reductive lactonization of γ-keto acids, 71, utilizing a hydrosilane (Figure 12). They propose the reaction is initiated via the activation of C=O group of the carboxylic acid upon the coordination of GaCl₃, facilitating the subsequent silylation upon the addition of PhSiH₃. A di-silyl ether is then generated upon further addition of PhSiH₃ and subsequent intramolecular cyclization leads to the generation of γ-lactone 72. Notably, 71 contains two carbonyls in which the GaCl₃ catalyst could potentially coordinate.
Selective coordination of GaCl₃ catalyst to the C=O group of the carboxylic acid is required for success of the reaction and mitigation of potential side product formation.

Figure 12. GaCl₃-mediated reductive lactonization utilizing hydrosilanes.

Bour and Gandon describe a GaCl₃-catalyzed Scriabine reaction in the synthesis of γ-aryl enol acetates, 75, in moderate to good yields (Figure 13). In order to examine the role of GaCl₃ in the mechanism of this Scriabine reaction, the groups performed DFT calculations. The group proposes a mechanism in which two molecules of GaCl₃ coordinate to one of each carbonyl group in 73. Anisole, 74, then approaches the terminal carbon of 76, causing the elimination of GaCl₃(OAc)− which subsequently deprotonates the Wheland-type intermediate 77. This results in the generation of the product 78, still complexed to a molecule of GaCl₃. Notably, they calculated the addition of 74 to be strongly endergonic when only one molecule of GaCl₃ was complexed to the substrate.

Figure 13. GaCl₃-catalyzed Scriabine reaction yielding γ-aryl enol acetates.
Sakai and coworkers reported the direct chlorination of carboxylic acids, 80, via a GaCl₃-mediated reduction in the presence of hydrosiloxane (TMDS) using CuCl₂ as a chloride source (Figure 14). They propose the reaction is initiated with the activation of the C=O group of 80 by GaCl₃, allowing for subsequent silylation upon addition of TMDS, generating species 82. Further addition of TMDS results in the formation of silyl ether 83. The group proposes that the following transformation to the alkyl chloride occurs via the intermediate of the chlorocopper species coordinated Ga(III) complex 84, generating alkyl chloride 80.

Figure 14. Direct chlorination of carboxylic acids via a GaCl₃-mediated reduction with TMDS.

The Schindler lab developed a GaCl₃-catalyzed ring-opening carbonyl-olefin metathesis reaction, of particular interest to our lab. The group obtains acyclic ring-opening carbonyl-olefin metathesis product, 87 from methyl cyclopentene, 85, and 12 in yields up to 47% (Figure 15). In the metathesis reaction of 85 and 12, two possible oxetane intermediates may form.
Oxetane 86 results in the formation of metathesis product 87 while oxetane 88 results in an aldehyde side product, 89, which the group does not observe. Through NMR studies tracking the reactions of oxetanes 86 and 88, the group discovered that oxetane 88 and its corresponding product, 89, are not stable towards isolation, leading to the conclusion this GaCl₃-mediated metathesis reaction regioselectively forms 86 as the predominant intermediate.

Though this system can achieve some regioselectivity for one oxetane intermediate over another, the reaction experiences side reactions also catalyzed by the GaCl₃ Lewis acid. The competing carbonyl-ene reaction pathway yields product 91 in a 20% yield and pyran 92 in a 10% yield through diene intermediate 90. The poor selectivity of the Lewis acid catalyst towards one reactive pathway over another is a limitation to this system.

Figure 15. GaCl₃-mediated ring-opening carbonyl-olefin metathesis and side product formation.
Ti(IV) compounds, in particular TiCl$_4$, are commonly employed as Lewis acid catalysts in synthetic methods due to titanium’s high abundance, low cost, and low toxicity.$^{56}$ Though Ti(IV) Lewis acids are widely utilized in a broad range of organic transformations,$^1$ this section will primarily focus on carbonyl-based reactions.

Figure 16. TiCl$_4$-promoted cyclization of aminoacetals and ethenetricarboxylates, yielding piperidines.

Yamazaki and Takebayashi report the TiCl$_4$-promoted cyclization of aminoacetals, 94, and ethenetricarboxylates, 93, to yield piperidines, 95, (Figure 16).$^{57}$ The group proposes that the mechanism begins with the conjugate addition of 94 to Lewis pair 96, which is followed by chelation of the TiCl$_4$ catalyst to an ester carbonyl and one oxygen of the ethyl ether group, forming intermediate 97. Oxonium intermediate 98 is produced after TiCl$_4$-promoted ethoxide abstraction. A nucleophilic attack yields piperidine, 95. In this reaction system, the TiCl$_4$ catalyst must selectively chelate with some Lewis basic moieties over others to yield the product; for
example, Multiple esters are present, but the group describes how TiCl₄ only coordinates with the axial ester group. The group observes up to quantitative yields of nitrogen heterocycles, indicating that the catalyst may not be inhibited by the presence of extra Lewis bases in solution.

Ishibashi and coworkers report the ring cleavage and successive Aldol reaction of trialkylsilyl cyclobutanones, 99, with aldehydes, 22, to selectively yield β,γ-unsaturated ketones, 100, over α,β-unsaturated ketones, 101, (Figure 17).¹⁵⁸ The selectivity for 100 over 101 was not observed with other Lewis acids like TiBr₄ or SnCl₄. The group describes a mechanism for the transformation that begins with the activation of cyclobutanone 99 by TiCl₄ to yield bicyclobutonium ion, 102. An attack on the trialkylsilyl group by a chloride anion forms titanium enolate, 103. The regioselectivity for 100 over 101 is a product of the formation of bicyclobutonium ion 102. When the more substituted bicyclobutonium ion forms, the β,γ-unsaturated titanium enolate, 103, will be the result. The Ishibashi group observes that this regioselectivity is maintained through the following Aldol reaction to yield 105.

Proposed mechanism:

Figure 17. Ring cleavage and subsequent Aldol reaction of trialkylsilyl cyclobutanones and aldehydes.
The Langer group investigated the TiCl$_4$ catalyzed formal [3+3] cyclization of 1,3-bis(silyl enol ethers), 107, with 1,3-dielectrophiles, 106, to yield substituted phenols, 108 (Figure 18).$^{59}$ The transformation begins with the formation of Lewis pair 109. The coordination of TiCl$_4$ to the carbonyl of 106 activates it towards attack by the pendant CH$_2$ of 107, which yields intermediate 110. When 110 loses the trimethylsiloxide group, 111 forms. The cyclization of 111 delivers 112. After aromatization resulting from the loss of trichlorotitatium hydroxide, substituted phenol 108 is formed. The Langer group notes that this mechanism contains a 1,4-addition of 107 to 106 and the competing 1,2-addition product is not observed. Once again, TiCl$_4$ is able to deliver regioselectivity over a reaction system with multiple Lewis bases present.

Figure 18. TiCl$_4$ catalyzed formal [3+3] cyclization of 1,3-bis(silyl enol ethers) with 1,3-dielectrophiles, to yield substituted phenols.

Zr(IV) in Catalysis.
Though zirconium and titanium belong to the same group, Zr(IV) Lewis acids are much less explored than Ti(IV) Lewis acids. Zr(IV) compounds tend to be milder than other Lewis acids. This property may allow for reactivity with moderate or good selectivity.\(^1\) Zr(IV) may have a less established role in organic synthesis than other Lewis acids, but interest in the compound has been rising in recent decades. Several reactions employing ZrCl\(_4\) as a catalyst have been reported.

![Figure 19. Various ZrCl\(_4\) catalyzed reactions.](image)

The Shabani group details the ZrCl\(_4\) catalyzed synthesis of 2,3-dihydroquinazolin-4(1H)-ones, 115, through the condensation of 2-aminobenzamides, 113, and carbonyls, 114 (Figure 19, A).\(^{60}\) Under mild reaction conditions, the group is able to obtain high to excellent yields of 115. The Kobayashi group investigated the aza-michael reaction of enones, 116, and carbamates, 117, to yield β-aminocarbonyls, 118, (Figure 19, B).\(^{61}\) Catalytic activity of a variety of metal salts was explored; ZrCl\(_4\) was found to perform better than many other traditional Lewis acids like AlCl\(_3\).
or TiCl₄. Up to quantitative yields of desired β-aminocarbonyls were obtained when ZrCl₄ was employed. Similarly, the Kumar group described the Michael reactions of heterocyclic enamines, 119, and α,β-unsaturated ketones, 120 (Figure 19, C).⁶² The Michael addition employs ZrCl₄ as a catalyst and the group reports obtaining excellent yields with high selectivity.

Li and coworkers have developed the synthesis of (E)-β-iodo aza Morita–Baylis–Hillman (MBH) adducts, 125, through a three component Mannich-type reaction (Figure 19, D).⁶³ High to excellent yields are obtained under mild conditions when ZrCl₄ is utilized as a catalyst. The Yin group detail the synthesis of isoindigo derivatives, 128, from isatins, 127, and indolin-2-ones, 126, (Figure 19, E).⁶⁴ Using ZrCl₄, the group obtained yields of isoindigo derivatives up to 95%.

![Proposed mechanism for the stereoselective ZrCl₄-catalyzed Mannich-type reaction of β-keto-esters with chiral trifluoromethyl aldimines.](image)

Figure 20. Proposed mechanism for the stereoselective ZrCl₄-catalyzed Mannich-type reaction of β-keto-esters with chiral trifluoromethyl aldimines.

Fioravanti and coworkers investigated the diastereoselective ZrCl₄-catalyzed Mannich-type reaction of β-keto-esters, 129, with chiral trifluoromethyl aldimines, 130, (Figure 20).⁶⁵ This asymmetric reaction yields fluorinated β'-amino β-dicarbonyl compounds, 131, with a quaternary chiral center. The group explains that the stereoselective control in this system is dependent upon the steric hindrance of the double bond in ZrCl₄ complex, 132: Bulkier ester groups led to higher diastereomeric ratios.
The Tummatorn group examined the ZrCl₄ catalyzed synthesis of indole derivatives, 134,

via nitrogen extrusion of aryl azidoacrylates, 133, and consecutive annulation process (Figure 21). The described transformation begins with the coordination of ZrCl₄ to the nitrogen and carbonyl groups of 133. The hexacoordinate zirconium complex, 136, then undergoes a rearrangement followed by nitrogen extrusion to yield 137. At this point in the mechanism, 137 may participate in two competing reaction pathways: Pathway A results in the desired indole product 134 while pathway B yields chlorinated side product 135. Pathway A occurs when 137 undergoes an intramolecular nucleophilic aromatic substitution type reaction, producing intermediate 138. Next, complex 138 rearomatizes, yielding 139, which becomes desired product 135 after hydrolyzation. Pathway B occurs when 137 participates in an intramolecular chlorine
atom transfer, producing 140. Similar to pathway A, hydrolyzation yields side product 135. Using DFT calculations, the group determined that pathway A is more thermodynamically favorable which is supported by the observation of exclusive formation of 134 in most systems.

**SnCl(IV) in Catalysis.**

Tin has become an important reagent in organic synthesis. Its utility as a Lewis acid for selective transformation has led to its increasing popularity.\(^1\) Sn(IV) reagents, like many other Lewis acids, have proven to be effective catalysts for the Diels-Alder reaction. Naimoli and coworkers reported a SnCl\(_4\)-mediated Diels-Alder reaction of \(\beta\)-acylacrylic acids, 141, with cyclic dienes, 142 (Figure 22).\(^6\) They propose the success of employing a SnCl\(_4\)/DIPEA system is due to the complexation of the acyl group over the carboxylate. They suggest the first equiv SnCl\(_4\) reacts with the carboxylate ion to form the Lewis pair 144 and the second equiv of SnCl\(_4\) coordinates to the acyl group forming complex 145. Importantly, Naimoli and coworkers do not observe this behavior when other Lewis acids, such as BF\(_3\)·OEt\(_2\), were employed. The success of this reaction may be attributed to the ability of SnCl\(_4\) to coordinate selectively to one Lewis basic moiety over another.

![Proposed Intermediates:](image)

**Figure 22.** SnCl\(_4\)-mediated Diels-Alder reaction of \(\beta\)-acylacrylic acids.
Additionally, the Bredenbeck group proposes an enantioselective Diels-Alder reaction of crotonyloxazolidinone, 146, and cyclopentadiene, 147, catalyzed by SnCl₄ (Figure 23). The group employs IR spectroscopy to analyze reaction progress by dissolving 146 in DCM and adding the SnCl₄ catalyst. When SnCl₄ is combined with 146, the group observes a downfield shift in the peaks associated with the carbonyls of 146. Taking these observations into consideration, Bredenbeck and coworkers propose the Diels-Alder reaction occurs through intermediate 149 in which SnCl₄ coordinates with both carbonyls.

![Figure 23. SnCl₄-promoted Diels-Alder reaction of crotonyloxazolidinone.](image)

Besides Diels-Alder reactions, SnCl₄ has been shown to effectively catalyze many other organic transformations; The Sierra group developed a SnCl₄-catalyzed [8+3] cycloaddition between tropone derivatives, 150, and aminocyclopropanes, 151, (Figure 24). Based on their DFT calculations, the group proposes the reaction initiates through the coordination of the diester moiety of 151 to SnCl₄, generating the chelated complex 153. Complex 153 is in equilibrium with zwitterion 154, which then undergoes nucleophilic attack by 150. This process yields intermediate 155, which is in resonance with 156. A subsequent ring closure reaction occurs to produce the [8+3]-cycloadduct 152 and regenerate the catalyst. Moreover, they observe a larger
activation barrier for the anti-process compared to the syn-process ($\Delta \Delta G_a$(syn-anti) = 3.4 kcal mol$^{-1}$). Again, this reaction system contains multiple different Lewis basic moieties in solution which will require the SnCl$_4$ to differentiate between them for success.

Figure 24. SnCl$_4$-catalyzed [8+3] cycloaddition of tropone derivatives and donor-acceptor cyclopropanes.

Shirinian and coworkers reported the synthesis of new photochromic diarylethenes, 158, via a SnCl$_4$-mediated Nazarov reaction of divinyl ketones, 157, as the key step (Figure 25).$^{69}$ The group proposes the reaction involves pre-coordination of SnCl$_4$ at the keto group of divinyl ketone 157, which forms Lewis pair 158. Subsequent 4\pi-electron cyclization of 159 generates 160. Importantly, the positive charge of the cation was preferentially located on the carbon atom of Ar$^1$ (160) and not at the C$_2$ position (161). Subsequent deprotonation of 160 concurrent with the elimination of SnCl$_4$ yielded cyclopentanone 158.
Figure 25. SnCl₄-mediated Nazarov cyclization in the synthesis of cyclopentanones.

Figure 26. SnCl₄-promoted tandem C-O bond cleavage/Nazarov cyclization/nucleophilic addition reaction to generate multisubstituted indenes.
Interestingly, the Wang group developed a SnCl₄-promoted tandem Nazarov cyclization/nucleophilic addition reaction in the synthesis of multisubstituted indenes, 166, with an all-carbon quaternary center (Figure 26).⁷⁰ The group proposes the reaction initiates with a SnCl₄-mediated C-O bond cleavage to generate cation 167. Intermediate 167 then undergoes a Nazarov cyclization to form cyclic carbocation 168, which undergoes a subsequent deprotonation to rearomatize, 169. The SnCl₄-promoted nucleophilic addition of 170 with 169 affords intermediate 171, which undergoes a subsequent proton shift to yield desired product 166.

**Fe(III) in Catalysis.**

The natural abundance, commercial availability and low cost of Fe(III) compounds have made them desirable targets in the field of Lewis acid catalysis. Much investigation into Fe(III) halides as catalysts has been conducted, and compounds like FeCl₃ are ubiquitous in organic synthesis today.¹ This section will focus on FeCl₃-catalyzed carbonyl transformations.

Khan and Sreenivas report an FeCl₃-mediated 1,6-conjugate addition of phenol nucleophiles, 56, in the synthesis of diarylmethanes, 173, which they observed in high yields (Figure 27).⁷¹ Interestingly, they observed bis-addition of cyclohexadienone, 172 to 56 when 172 was employed in excess (2 equiv); however, if 172 was employed stoichiometrically, they observed mono-addition product 173. They propose FeCl₃ activates 172 by coordinating to the carbonyl group, resulting in Lewis pair 174. Subsequent 1,6-conjugate addition of 175 generates dienolate 176. Methoxy assisted elimination of chlorine forms intermediate 177, which is subsequently deprotonated to yield product 173.
Figure 27. FeCl₃-catalyzed 1,6-conjugate addition of phenol nucleophiles.

The Yang group reported the FeCl₃-promoted [3+2] annulation of γ-butyrolactone-fused cyclopropanes, 179, with heterocumulenes (Figure 28). They posit that FeCl₃ coordinates to the diester group to activated cyclopropane 179, yielding chelated complex 182. Complex 182 then undergoes ring opening via nucleophilic attack of 181, forming intermediate 183. Importantly, a bond rotation is required to generate the desired cyclic product 185.

Figure 28. FeCl₃-promoted [3+2] annulation of cyclopropane derivatives with heterocumulenes.
Importantly, our lab probed the catalyst behavior of an FeCl₃-catalyzed carbonyl-olefin metathesis (Figure 29, A) originally developed by Schindler and coworkers. Utilizing titration coupled with in situ IR spectroscopy, we proposed that, at the start of the mechanism, the reaction proceeds through the primary cycle we previously described. However, as byproduct carbonyl, 187, begins to build up in solution throughout the course of the reaction, highly ligated complex 191 is formed. This complex either sequesters FeCl₃, preventing the catalyst from participating in carbonyl-olefin metathesis and terminating reactivity, or it remains catalytically active operating via the secondary cycle. In the secondary cycle, substrate 185 can displace a molecule of 187 from 191 to access the Fe center, generating complex 192. Subsequent [2+2] cycloaddition would produce key oxetane intermediate 193 and a further retro-[2+2] cycloaddition would yield cyclopentene 186 and regenerate highly ligated catalytic complex 191 (Figure 29, A). Depending on the identity of the carbonyl byproduct, catalytic activity may be terminated when the highly-ligated complex forms. When carbonyl-olefin metathesis reactions are carried out on substrates with styrenyl pendant olefins like 195 (Figure 29, C), the carbonyl byproduct formed is benzaldehyde, 12. When 12 builds up in solution, highly ligated complex 194 is formed (Figure 29, B). Likely due to the steric bulk of 194, carbonyl-olefin metathesis reactions in which 12 is the byproduct are often plagued with slow rates, low consumption of starting material, and complete termination of reactivity.

Both the Schindler and Li groups have investigated the utility of additive allyltrimethyl silane in mitigating byproduct inhibition caused by 194 (Figure 29, C). Without the allyltrimethyl silane additive, both groups report low consumption of 195. A high yield of 83% is obtained in the presence of 5 equiv additive. Schindler, Li and coworkers propose that allyltrimethyl silane removes 12 from the system through two consecutive Hosomi-Sakurai
Figure 29. FeCl₃ catalyzed carbonyl-olefin metathesis and proposed mechanism (A). Highly ligated benzaldehyde species (B). Additive inclusion to mitigate byproduct inhibition (C). Carbonyl-olefin metathesis of aliphatic ketones catalyzed by FeCl₃ heterodimer species (D).
mechanisms, yielding byproduct 197 which no longer interacts with the FeCl₃ catalyst. Carbonyl-olefin metathesis systems benefit from preventing the formation of 194.

In the Schindler lab’s exploration of aliphatic ketones like 198 as starting materials in carbonyl-olefin metathesis reactions, another system resulting in increased yields of recalcitrant substrates is presented (Figure 29, D). The group proposes an analogous mechanism in which an Fe₂Cl₆ heterodimer is the active catalyst species. When considering aliphatic ketone substrates like 198, the group proposes that a monomeric FeCl₃ coordinated to the carbonyl does not sufficiently activate the substrate towards carbonyl-olefin metathesis reactivity. Because aliphatic ketones do not have an aryl ring, which is capable of stabilizing transition states with delocalized electron density, the catalyst would likely remain in its resting state, 200, until another molecule of FeCl₃ binds to the first. Through a bridging chlorine atom, homodimer species 201 is formed. The association of a second equivalent of FeCl₃ creates a much stronger Lewis acid and the homodimer’s super-electrophilic nature provides the extra activation required by the aliphatic substrate to form oxetane intermediate 202. The retro process yields product 199 and carbonyl 187.
CHAPTER 2
SYNTHESIS AND CHARACTERIZATION OF TRIGONAL BIPYRAMIDAL Fe(III) COMPLEXES AND THEIR SOLUTION BEHAVIOR.

Introduction

This chapter is adapted from a previously published manuscript in Polyhedron. Iron is the most abundant transition metal in the earth’s crust, making it a highly attractive element from which reagents and catalysts can be readily developed. In particular, a great deal of effort has been focused on the development of FeCl$_3$ as both a stoichiometric reagent and a catalyst. Often, reactions with FeCl$_3$ are performed in chlorinated solvents (i.e. CHCl$_3$, CH$_2$Cl$_2$, 1,2-dichloroethane (DCE), etc.). Under anhydrous conditions, FeCl$_3$ is largely insoluble in these solvents, and systems can require the addition of silica gel as a solid support, Lewis basic additives like nitromethane, or ligand systems. Previous studies from our lab have shown that in the absence of these additives, the substrate must interact directly with heterogeneous FeCl$_3$, resulting in the substrate increasing the solubility of the Lewis acid via the formation of a Lewis pair. However, this interaction changes dramatically when FeCl$_3$ is employed as a catalyst, allowing for the formation of complex Fe$^{III}$-centered aggregates. We report herein the characterization of complexes derived from FeCl$_3$ and NNN pincer ligands. Full ground state characterization data are provided to analyze the impact of the ligand system via electrochemical and spectroscopic analysis, as well as how the ligand perturbs the behavior of these systems in the presence of acetone in solution.
Previous efforts from our lab have focused on the examination of the impact of NNN pincer ligands on the behavior of first-row transition metals. We have examined, in depth, complexes generated with Ni$^{II}$,$^{92,93}$ V$^{III/IV}$,$^{94}$ as well as an Fe$^{II}$ complex that was able to undergo C–H activation to yield an unusual pyrazolide-bridged iron(II) complex at elevated temperatures.$^{95}$ We sought to examine the impact of our ligand system on Fe$^{III}$ because of a report by Nishiyama and coworkers, who employed a structurally analogous NNN pincer ligand to facilitate the asymmetric hydrosilylation of ketones to alcohols in THF.$^{96}$ What further intrigued us about their results was that the starting material, product, and solvent are all competent Lewis bases that can compete for access to the Lewis acid. With these observations in mind, we sought to study how our NNN pincer system impacts the solubility of Fe$^{III}$ chloride complexes and how it may facilitate similar intermolecular interactions.

**Results and Discussion**

**Synthesis and Characterization of Complexes 1–3.**

Figure 30. Preparation of Fe(III) pincer complexes.

Dark green complexes 1–3 can be prepared in high yield (>90%) by deprotonation of HCz$^t$Bu(Pyr$^R$)$_2$ (R = iPr (1), Me (2), H (3)) using LDA followed by transmetallation with FeCl$_3$ at ambient temperature in a N$_2$ atmosphere (Figure 30).

Unlike 1 and 2, formation of 3 is dependent upon concentration during synthesis based on $^1$H NMR spectroscopy; since the coordination site of 3 is more exposed than in 1 or 2, the use of
dilute concentrations prevents the formation of undesired byproducts, e.g. \([\text{CZ}^{\text{Bu}}(\text{Pyr}^{\text{H}})_{2}]_2\text{Fe}\text{Cl}\).

$^1$H NMR spectroscopy of 1–3 shows broad, paramagnetically shifted resonances ranging from 5.53 to 90.81 ppm in various deuterated solvents. Note that one resonance is missing for each complex, which could be due to the fast relaxation of protons that are close to the Fe$^{\text{III}}$ center.

Solution magnetic measurements in CDCl$_3$ (for 1 and 2) and CD$_2$Cl$_2$ (for 3) at room temperature (298 K) using Evans method gave $\mu_{\text{eff}} = 5.3(2), 5.4(2),$ and $5.5(3)$ $\mu$B for 1–3, respectively, all of which are consistent with spin-admixed $S = 5/2, 3/2$ Fe$^{\text{III}}$ systems.$^{97,98}$ Complexes 1–3 are highly soluble in various organic solvents and 1 is even soluble in $n$-pentane. In the solid state, 1–3 are all dark green powders. Interestingly, 1 and 2 exhibit the same color when dissolved in both coordinating (acetone) and non-coordinating solvents (CH$_2$Cl$_2$); whereas we observed dark green and teal solutions when dissolving 3 in CH$_2$Cl$_2$ and acetone, respectively (*vide infra*). Finally, complexes 1–3 are air-stable indefinitely and resistant to decomposition upon heating up to 80 $^\circ$C.

**Crystal Structures of 1 and 3.**

We obtained single crystals suitable for X-ray structure determination for complexes 1 (Figure 31) and 3 (Figure 32).$^1$ The solid-state structures confirm complexes 1 and 3 as mononuclear iron complexes with one NNN pincer ligand in association with two Cl atoms. Both 1 and 3 have a slightly distorted trigonal bipyramidal geometry ($\tau_5$ values are 0.86 and 0.83, respectively) with two neutral pyrazole-nitrogen atoms ($\text{N}_{\text{pyr}}$) in the axial positions and three anionic atoms in the equatorial plane.$^{99}$

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$^1$ See appendix A for more information.
Figure 31. Molecular structure of 1 with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Color key: orange = Fe, blue = N, gray = C, green = Cl.

The structural parameters of 1 and 3 agree well with those of closely related carbazolide-based pincer-supported Fe$^{III}$ chloride complexes, except for slightly shorter iron to carbazolide nitrogen ($N_{c2}$) distances.\textsuperscript{100,101} This could be attributed to the stronger electron-donating tert-butyl groups, compared to previously reported methyl and phenyl groups on the carbazolide backbone. Different from complex 3, the carbazolide and two flanking pyrazole rings in 1 are not coplanar due to steric hindrance resulting from the bulkier iso-propyl substituents.

Figure 32. Overlaid structure of complexes 1 (blue) and 3 (red). Spheres represent Fe atoms. Hydrogen atoms and tert-butyl groups are omitted for clarity.

The dihedral angles between the pyrazole groups and the carbazolide ring are $28.7(9)$ ° and $0$ ° for 1 (Figure 31) and 3, respectively (Figure 32). Surprisingly, we observed a lesser
distortion (17.7(2)°) for the V\textsuperscript{III} congener, Cz\textsuperscript{Bu}(Pyr\textsuperscript{dPr})\textsubscript{2}VCl\textsubscript{2},\textsuperscript{8} despite comparable ionic radii for both Fe\textsuperscript{III} and V\textsuperscript{III}.\textsuperscript{102}

**Electrochemical studies.**

Cyclic voltammetry analysis of the Fe\textsuperscript{III} complexes carried out in CH\textsubscript{2}Cl\textsubscript{2} and acetone solutions using 0.1 M n-Bu\textsubscript{4}NPF\textsubscript{6}, a platinum wire auxiliary electrode, glassy carbon working electrode, and Ag wire reference electrode gave insight into the electrochemical behavior. We varied scan rates from 100 mV s\textsuperscript{−1} to 500 mV s\textsuperscript{−1} and referenced to [FeCp\textsubscript{2}]/[FeCp\textsubscript{2}]\textsuperscript{+}. In CH\textsubscript{2}Cl\textsubscript{2}, two distinct quasi-reversible events represent a diffusion-controlled process for complexes 1–3 (Figure 33), whose Δ\textit{E}_p values do not differ significantly in different scan rates (Figure 34).\textsuperscript{1}

![Cyclic voltammograms](image)

Figure 33. Cyclic voltammograms of 0.1 mM of 1 (blue), 2 (green), and 3 (red) in CH\textsubscript{2}Cl\textsubscript{2} (0.1 M n-Bu\textsubscript{4}PF\textsubscript{6}) at scan rates of 100 mV s\textsuperscript{−1}.\textsuperscript{1}

Complex 3 exhibited \textit{E}_{1/2} values of −0.41 and 0.72 V, consistent with metal-centered (Fe\textsuperscript{III/II}) and ligand-centered Cz\textsuperscript{Bu}(Pyr\textsuperscript{H})\textsubscript{2}/Cz\textsuperscript{Bu}(Pyr\textsuperscript{H})\textsubscript{2}\textsuperscript{+} redox couples, respectively. The plots of

\textsuperscript{1} See appendix A for more information.
$v^{1/2}$ vs. the $I_{pa}$ and $I_{pc}$ for both events suggest these electron transfer processes are governed by diffusion control.

Voltammograms similar to those for 3 obtained for 1 and 2 yielded lower potentials ($-0.38$ V for 1 and $-0.39$ V for 2) for the metal-centered redox step, which are conversely related to the increasing electron donation from the pyrazole substituents to the Fe center. The same unusual trend shared by 1 and 2 is present for the ligand-centered oxidation, where 1 (0.70 V) $\approx$ 2 (0.69 V). This contradiction could be attributed to the poor overlap between the $p$-orbital of $N_{cz}$ and $d$ orbital of Fe, resulting from the increased out-of-plane distortion of the Fe from the carbazolide plane in 1. This out-of-plane movement can also be observed in the electrochemical reversibility of the metal-centered process as 3 being the most reversible, while 1 is the least. In acetone, complexes 1–3 exhibit more complicated redox events, which could be due to multiple species in solution, owing to the solvent-specific coordination of acetone to the Fe center.

Figure 34. Cyclic voltammograms of 0.1 mM 3 in CH$_2$Cl$_2$ (0.1 M n-Bu$_4$PF$_6$) at scan rates of 100, 200, 300, 400, and 500 mV s$^{-1}$. Inset: Plot of anodic, $I_{pa}$, and cathodic, $I_{pc}$, peak current, versus square root of scan rate for the first (*, blue; $R^2 = 0.9992$) and second oxidation (•, red; $R^2 = 0.9650$).
Electron paramagnetic resonance studies.

EPR spectroscopy of 1–3 was conducted in both the powder and solution state at room temperature and 77 K. At room temperature, the solid-state spectra of complexes 2 and 3 exhibit a broad spectrum with \( g = 2.05003 \) and 2.10422, respectively. The broadness may be attributed to multiple transitions coinciding at the same time, presenting as an imperfect rhombic signal.

When solids of 2 and 3 are measured at 77 K, the broad spectrum is accompanied by a small shoulder with \( g \approx 4 \), which may be due to mixing of another spin state, e.g. a purely high-spin species.\(^{103}\) EPR spectra of solid 1 at room temperature yields a broad signal with \( g = 4.2163 \) and a defined asymmetric signal at \( g = 2.02017 \).\(^1\) At 77 K, solid 1 gives rise to an asymmetric rhombic signal at \( g = 4.3329 \) and an intense asymmetric signal at \( g = 2.01789 \).\(^1\) In both the room temperature and 77 K spectra of 1, the resonance at \( g \approx 2 \) mostly likely arises from the presence of an iron complex with a different spin state.

At room temperature, the EPR spectra of 1–3 in CH\(_2\)Cl\(_2\) all display strong rhombic signals with \( g = 2.01499 \) (Figure 5), 2.01799, and 2.01801, respectively. Additionally, 1 has a diffuse wing stretching resonance at \( g \approx 4.3 \). There is an increase in linewidth of the \( g \approx 2 \) signal from 3 to 1, likely due to 3 having the best rotation and therefore a better zero-field splitting average. Frozen CH\(_2\)Cl\(_2\) solutions of 2 and 3 show broad signals (\( g = 2.01698 \) and 2.04200, respectively) in combination with a more well-defined shoulder at \( g \approx 4.3 \), compared to the solid-state spectra. The EPR spectrum of 1 in frozen CH\(_2\)Cl\(_2\) shows a rhombic feature at \( g = 4.30074 \) with a weak but distinct feature at \( g = 2.00311 \) (Figure 35). Indeed, the intensity of the signals at \( g \approx 4.3 \) and 2 for 1, changes with respect to temperature. At low temperatures, the \( g \approx 4.3 \) resonance dominates the spectrum, while at room temperature the \( g \approx 2 \) signal is the most noticeable.\(^{92,93}\)
Figure 35. EPR spectra of 1 in CH$_2$Cl$_2$ at room temperature (left) and 77 K (right).

Overall, the diminished intensity of the EPR signals of solid 1–3 at room temperature compared to the signals at 77 K can be attributed to averaging of the spin and orbital momentums.$^{104}$ The broad spectra obtained for solids of 2 and 3 could arise from the random orientation of spins within the sample, causing a more derivative shaped curve. To the best of our knowledge, these are the first reported trigonal bipyramidal Fe$^{III}$ complexes supported by an NNN pincer ligand system, making assessment of the spin-state difficult. Complexes 1–3 exhibit similar features to admixed-spin ($S = 5/2, 3/2$) Fe$^{III}$ heme systems with nitrogen-donor porphyrins, where EPR spectra show two resonances at $g$-values between 4 to 6 and around 2.$^{90,103,105-109}$ Although assignment of a bona-fide spin-admixed species requires careful consideration of geometry effects, ligand field strength, and external environments,$^{90}$ we plan to investigate further these properties using Mössbauer spectroscopy and SQUID magnetometry in the near future. In conjunction with the results of solution magnetic measurements, we hypothesize 1–3 are the first examples of a $S = 5/2, 3/2$ spin-admixed Fe$^{III}$ species supported by an NNN pincer ligand in a trigonal bipyramidal molecular geometry.

Electronic absorption spectra.
Figure 36. Electronic spectra of $6.66 \times 10^{-5}$ mM of 1 (blue), 2 (green), and 3 (red) in CH$_2$Cl$_2$ (left) and acetone (right).\textsuperscript{1}

The UV-Vis spectra of complexes 1–3 in CH$_2$Cl$_2$ and acetone have been recorded and are shown in Figure 6. “Cz$^{\text{Bu}}$(Pyr$^{\text{Pr}}$)$_2$” pincer complexes typically have $\pi \rightarrow \pi^*$ transitions below the 400 nm region, and the lowest absorption bands are best described as ligand-to-metal charge transfer bands (LMCT).\textsuperscript{92-93} The position of the LMCT bands shifts toward shorter wavelengths (3 (680 nm) $<$ 2 (739 nm) $<$ 1 (743 nm)), when there are less electron donating substituents on the pyrazole groups. Although it is well understood that the ligand field is enhanced with electron donating substituents, the same kind of reverse trend has been observed in the cyclic voltammograms that led to conclude that the extent of out-of-plane movement of Fe dictates the degree of metal-ligand orbital overlap. In acetone, complexes 1 and 2 exhibit a slight blue shift in the visible range, e.g. 743 $\rightarrow$ 725 nm and 739 $\rightarrow$ 712 nm for 1 and 2, respectively; whereas, the spectrum of 3 shows a drastic red-shift from the visible to the near infrared region 680 $\rightarrow$ 939 nm (Figure 36). We believe that the drastic red-shift is not simply due to the polarity of solvents, but rather the effect of acetone coordination to the Fe center in 3, under forcing conditions.

\textsuperscript{1} See appendix A for more information.
However, when 3 is exposed to 10 equiv acetone in CH₂Cl₂ solution, this spectral feature is not observed, consistent with a lack of acetone binding.

**Solution behavior.**

To examine the intermolecular interactions further, we turned to spectroscopic investigation under synthetically relevant conditions. A variety of methods have been developed to measure the binding ability of Lewis acid catalysts such as NMR spectroscopy,¹¹⁰⁻¹¹⁷ UV-Vis spectroscopy,¹¹⁸ selectivity,⁷⁴,¹¹⁹ and mass spectrometry.¹²⁰,¹²¹ More specifically, chemists have employed infrared (IR) spectroscopy when examining the interactions of paramagnetic Lewis acids and carbonyl-containing compounds, allowing for the determination of Lewis acidity.¹²²⁻¹²⁸ To probe the solution interactions of Lewis acids and carbonyls, we have developed a titration-based method, utilizing *in situ* IR as a detector.⁷⁵ With this method, we benchmarked a range of Lewis acid/carbonyl interactions in solution³¹ and were able to employ these benchmarks to gain insight into the mechanism of Fe³⁺-catalyzed carbonyl-olefin metathesis.⁷³ Because of these benchmarks, we chose to examine the ability of our Fe complexes to be Lewis acids via their interactions with acetone in DCE.

Complexes 1, 2, and 3 are highly soluble in DCE, and we performed titrations into homogeneous mixtures. When acetone is added to a solution of 1 from 0–4 equiv, we observe a vibration at 1714 cm⁻¹ consistent with acetone, as well as a shoulder to this peak (Figure 7, left).

When analogous titrations were carried out with 2 and 3, only unbound acetone was observed in the IR spectrum.¹ We have previously demonstrated that when ≤1 equiv acetone is added to FeCl₃, this mixture forms a Lewis pair with a characteristic vibration at 1633 cm⁻¹.⁷³

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¹ See appendix A for more information.
Figure 37. Solution IR data for titration of 1 (1 mmol in 6 mL DCE) with 0–4.2 equiv acetone (left). Titration proceeds from black to violet with increasing amounts of acetone ([acetone] = 0 M, 0.089 M, 0.178 M, 0.243 M, 0.330 M, 0.499 M, 0.664 M). Spectral deconvolution of solution with 1 and 0.664 M acetone (right). Observed spectrum (solid black), simulated total (dashed black), simulated acetone (red), simulated complex (blue).\textsuperscript{15} Acetone, suggest that the Cz\textsuperscript{Bu}(Pyr\textsuperscript{Pr})\textsuperscript{2+} ligand produces the same coordinative saturation that results in a less pronounced shift in the vibration of the C=O of acetone. Deconvolution of the spectrum shows a vibration with \( \lambda_{\text{max}} \) at 1696 cm\textsuperscript{-1}, which is consistent with a low affinity interaction, resulting in a slight decrease in the \( \pi \)-character of the C=O of acetone (Figure 7, right).

When the titration proceeds beyond 1 equiv, this initial complex is consumed, and high wavenumber vibrations are observed. This change in IR is consistent with the formation of a highly ligated complex, with multiple Lewis basic carbonyls coordinating to Fe. Our previous data, combined with our observations for 1 and acetone, suggest that the Cz\textsuperscript{Bu}(Pyr\textsuperscript{Pr})\textsuperscript{2+} ligand produces the same coordinative saturation that results in a less pronounced shift in the vibration of the C=O of acetone. Deconvolution of the spectrum shows a vibration with \( \lambda_{\text{max}} \) at 1696 cm\textsuperscript{-1}, which is consistent with a low affinity interaction, resulting in a slight decrease in the \( \pi \)-character of the C=O of acetone (Figure 37, right).

We also examined the solution conductivity (\( \kappa \)) of our Fe complexes as compared to FeCl\textsubscript{3}.\textsuperscript{31,73} When each of the respective complexes are dissolved in DCE, we measured the \( \kappa \) for
the resulting solution. When FeCl₃, 1, 2, and 3 are added to DCE, we observe values of κ equal to 1.5, 84.4, 27.4, and 827.3 μS cm⁻¹, respectively. A value of 827.3 μS cm⁻¹ for complex 3 suggests that this structure is spontaneously forming a solvent-separated ion pair, likely via chloride ion dissociation. Interestingly, we do not observe this behavior for the other two complexes. This unique behavior of 3 in DCE is consistent with the unique behavior we observed via our UV-Vis analysis (vide supra), suggesting that the origin of the spectral features we see in the UV-Vis may arise from the change in the solvation sphere of 3.

We next examined the combination of 1 and acetone via conductivity, using concentrations identical to our IR investigation. We, previously, demonstrated that when acetone is added to FeCl₃, a negligible conductivity results between 0–1 equiv, with a conductivity of 96 μS cm⁻¹ at the equivalence point (red, Figure 8).

![Figure 38](image)

Figure 38. Conductivity of FeCl₃ (red, 2 mmol in 12 mL DCE) and 1 (blue, 2 mmol in 12 mL DCE) with increasing equivalents of acetone. Solution conductivity of each Fe complex in DCE (inset).

1 See appendix A for more information.
However, at 2 equiv acetone, increases to 733 µS cm\(^{-1}\), which continues up to 1244 µS cm\(^{-1}\) at 5 equiv acetone. Over the course of titration of 1 with acetone, \(k\) doubles from 84.4 µS cm\(^{-1}\) to 163.8 µS cm\(^{-1}\). When compared with the three order of magnitude increase in \(k\) for the addition of acetone to FeCl\(_3\), our titration of 1 with acetone is inconsistent with acetone-facilitated displacement of one of the chloride ligands.\(^7\)

**Conclusion**

Three Fe\(^{III}\) complexes bearing a Cz\(^{Bu}\)(Pyr\(^R\))\(_2\)\(^{++}\) (\(R = i\)Pr (1), Me (2), or H (3)) ligand are reported as the first examples of trigonal bipyramidal NNN pincer complexes with a quantum mechanically admixed-spin state (\(S = 3/2, 5/2\)), as assigned by solution magnetic susceptibility and EPR spectroscopy. We are currently pursuing Mössbauer spectroscopy and SQUID magnetometry to further investigate the unique admixed-spin state. Complexes 1-3 exhibit quasi-reversible redox activity at both the metal center and organic ligand scaffold. We propose that the degree of metal \(d\) orbital and N\(_{cz}\) \(p\) orbital overlap is directly influenced by the degree of out-of-plane movement of the Fe atom and plays a major role in the redox activity. This behavior is well illustrated by the difference in metal-center reduction potentials of 1 and 3, where the reduced metal-ligand orbital overlap of 1 may inhibit electron-donation from the ligand, therefore reducing the overall effect that the electronic environment of the ligand has on reduction potential. Solvation of 1-3 in non-coordinating (CH\(_2\)Cl\(_2\)) and coordinating (acetone) solvents produces noticeable changes within the UV-Vis spectra, corresponding to interactions between the coordinating carbonyl of acetone and the Lewis-acidic Fe atom of Cz\(^{Bu}\)(Pyr\(^R\))\(_2\)FeCl\(_2\). Indeed, *in situ* IR spectroscopy revealed that 1 (in DCE) possesses a low affinity interaction, rather than traditional coordination, with added acetone as suggested by the presence of an additional less-intense stretch near \(~1700\) cm\(^{-1}\). As a result of these studies, we
propose that complexes 1-3 can serve as geometrically constrained models for further investigation of the complex interactions between Lewis-acids, such as Fe, and various carbonyl substrates.
CHAPTER 3

CONTROLLING CATALYST BEHAVIOR IN LEWIS ACID-CATALYZED CARBONYL-OLEFIN METATHESIS

Introduction

In the almost 100 years since Prof. Lewis published his textbook definition of the acid,\textsuperscript{129} electron acceptors have played a crucial role in organic synthesis. In particular, their interactions with carbonyl compounds have been of critical importance in the construction of high-value molecules.\textsuperscript{1,11,13,122,130} This interaction typically involves the pairwise behavior succinctly described by Lewis: one donor and one acceptor.\textsuperscript{129} However, chemists continue to observe increasingly complex behavior when proceeding from the stoichiometric regime into catalysis, gaining evidence of 2:1,\textsuperscript{132,133} 3:1,\textsuperscript{31} and even 4:1 solution structures.\textsuperscript{31,73,134} These \textit{in situ} interactions need to be considered when exploring the mechanistic behavior of Lewis acid-catalyzed processes such as Diels–Alder reactions,\textsuperscript{135} aldol reactions,\textsuperscript{15-17} ene reactions,\textsuperscript{136,137} photochemical reactions,\textsuperscript{138-139} and more recently, carbonyl-olefin metathesis.\textsuperscript{79}

Lewis acid-catalyzed, ring-closing carbonyl-olefin metathesis efficiently assembles cyclic systems, \textit{5}, from accessible linear motifs, \textit{1}.\textsuperscript{74} Di- and trisubstituted cyclopentenes and cyclohexenes, polycyclic aromatic hydrocarbons,\textsuperscript{140} and 2,5-dihydropyrrole\textsuperscript{78,141} are formed as a result of this transformation, which is most often facilitated by Fe(III).\textsuperscript{78,79,140-144} Additionally, reactions employing Ga(III),\textsuperscript{23,145} Al(III),\textsuperscript{146} AuCl\textsubscript{3},\textsuperscript{147} BF\textsubscript{3}·OEt\textsubscript{2},\textsuperscript{148} I\textsubscript{2},\textsuperscript{149} HCl,\textsuperscript{150,151} trityl cation,\textsuperscript{152,153} TsOH,\textsuperscript{154} and clays\textsuperscript{148,155} have also been reported. What makes Fe(III) stands out among these systems
due to the multiple solution interactions that are accessible. In metathesis of aryl ketones, Fe(III) activates the substrate carbonyl via the 1:1 interaction in the resting state.\textsuperscript{76} Schindler and coworkers demonstrated that when aliphatic ketones react, Fe(III) increases its acidity via a dimeric interaction.\textsuperscript{79} Importantly, the success of these carbonyl-activation pathways depends on efficient access to the Lewis acid by the substrate.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{catalyst_behavior}
\caption{Catalyst behavior in FeCl\textsubscript{3}-catalyzed carbonyl-olefin metathesis.}
\end{figure}

We have previously demonstrated that FeCl\textsubscript{3} forms highly-ligated complexes, 6, in the presence of superstoichiometric amounts of acetone and benzaldehyde, 2: typical byproducts of carbonyl-olefin metathesis (Figure 39).\textsuperscript{31,73,134} These byproducts decrease reaction rates and conversions via competitive interaction with the metal center or via production of a more sterically encumbered Lewis acid, decreasing the efficiency of the turnover-limiting oxetane formation.\textsuperscript{76} Further, work alongside Schindler and coworkers has shown that other Lewis bases present in the reaction mixture can inhibit reactivity,\textsuperscript{76} including those in the substrate.\textsuperscript{78} To overcome the issue of byproduct inhibition, allyltrimehtylsilane is employed to chemically remove
the 2 byproduct from the reaction mixture (Figure 40). The inclusion of this additive deters reaction byproducts from inter-acting with the Lewis acid catalyst. While beneficial, superstoichiometric amounts of allyltrimethylsilane are re-quired to observe this effect.

![Figure 40. Additive improved yields in carbonyl-olefin metathesis systems.](image)

In 2012, Feng and coworkers reported a Prins cyclization catalyzed by FeCl$_3$ (Figure 41). They observed an increase in yield as well as a pronounced decrease in reaction time when 1 equiv of the chlorosilane TBSCl, relative to the FeCl$_3$ catalyst, was added to the reaction mixture. They examined the benefit of this additive because they observed overreaction of their product; in other words, they included this additive to deter a reaction product from interacting with the Lewis acid catalyst. Importantly, the reaction product contains a carbonyl and two additional Lewis basic oxygens. In their computational analysis of this transformation, they proposed the formation of Lewis pair 14. The added TBSCl displaces the reaction product from the FeCl$_3$ catalyst, preventing further reactivity with the product. This catalyst surrogate behavior directs the catalyst to favor the formation of product 13 over other interactions.

It is our hypothesis that the primary carbonyl-olefin metathesis mechanism relies on the equilibrium exchange of FeCl$_3$ between free salt, substrate Lewis pair 15, and by-product Lewis pair 17 (Figure 42). As the concentration of byproduct 18 increases, Lewis pair 17 is converted to coordinatively saturated complex 19. Moreover, we observed that substrate can displace...
byproduct 18 effectively under conditions that favor the formation of Lewis pair 17. However, under conditions that yield aggregate 19, the substrate is less successful at accessing the Lewis acid. When you combine our observations with those of the Feng lab, they collectively suggest a process exists to improve free access to the FeCl₃ catalyst in the presence of Lewis basic products.

Figure 41. Effect of TBSCI additive on Prins cyclization reported by Feng and coworkers.

The inclusion of a chlorosilane will add an additional species to the equilibria, 16. By adding this placeholder to the mass balance, the system could favor FeCl₃ attached to individual Lewis bases over the formation of aggregate 19.

Figure 42. Proposed equilibria between Lewis pair species and chlorosilane placeholder complex.

Olah and coworkers previously examined the interaction of chlorosilanes and Lewis acids, observing behavior similar to that required by Friedel-Crafts C–X bond activation. Gansäuer and Flowers previously used Ti–X solution inter-actions between collidine•HCl and
Cp$_2$TiCl to prevent catalyst deactivation. This placeholder may yield a decrease in the initial rate of reaction through creation of an additional species which is not product-generating. Nonetheless, the preference for Lewis pair species could the observed product inhibition process by delaying the formation of 19 until higher turnovers.

Results and Discussion

Kinetic Investigation.

We set out to investigate the impact of chlorosilanes on the rate of carbonyl-olefin metathesis using the inhibition model we previously developed. Through the ring-closing carbonyl-olefin metathesis of 20 (Figure 43), we are able to compare the rate of the baseline metathesis reaction to a reaction in the presence of added 2. We monitored the [20] via reverse-phased ultra-performance liquid chromatography coupled with a transmission UV-vis detector. Reaction preparation required the mixing of FeCl$_3$ in DCE to form a slurry. While maintained at 0 °C, the addition of 20 initiated catalysis. The baseline reaction was catalyzed by a loading of 50 mol% FeCl$_3$ (Figure 43B, gold ■). Next, we initiated the same reaction in the presence of 50 mol% 2 (Figure 43B, maroon ○), which was mixed with the FeCl$_3$/DCE slurry before addition of substrate 20. We observe a significantly slower reaction due to byproduct inhibition. Previous work in our lab suggests that a bulkier environment results in a significant decrease in reaction rate; therefore, we chose to begin our examination with TMSCl because it is smaller than TBSCl. Using TMSCl, we initiated the reaction in the presence of both 50 mol% 2 as well as 100 mol% TMSCl (Figure 43B, maroon ●). We do not simply observe recovery of the reaction rate, but rather a reaction that is significantly faster than baseline. Indeed, direct comparison of the [20] at 120 s displays 8.6 mM in the absence of TMSCl and 3.0 mM in its presence.

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1 See Appendix B for more information.
Decreasing the amount of FeCl₃ to 8 mol% and TMSCl to 20 mol% yielded a reaction with approximately the same rate as 50 mol% FeCl₃ alone (Figure 43C). The addition of TMSCl yields more than a factor of five increase in rate with respect to FeCl₃. Examination of the chlorosilane identity allowed us to determine that TMSCl provided the largest improvement in reaction rate.¹ These observations suggest that the goal of our hypothesis is achievable. However, these data suggest that our proposed interaction for TMSCl is incorrect, requiring more observations to answer the following question: How has the turnover-limiting step of the carbonyl-olefin metathesis reaction changed with the addition of TMSCl?

A: Model Reaction Scheme

B: Inhibition Model Rates

C: FeCl₃ and TMSCl Loading screen

Figure 43. FeCl₃-catalyzed carbonyl-olefin metathesis of 20 (A), 50 mol% FeCl₃ catalyzed system (gold ■), 50 mol% FeCl₃ catalyzed system with 50 mol% 2 (maroon ○), and FeCl₃-mediated system with 50 mol% 2 and 100 mol% TMSCl (maroon ●) (B). Comparison of 50 mol% FeCl₃ (gold ■) to 8 mol% FeCl₃/20 mol% TMSCl (maroon ●) (C).¹

Spectroscopic Investigation.

¹ See Appendix B for more information.
The larger than anticipated rate increase when TMSCl is included as an additive in the reaction of 20 suggests that TMSCl is acting as more than just a placeholder ligand. To gain more insight into the solution behavior of TMSCl, we turned to in-situ IR titrations.\textsuperscript{75} Our group has previously utilized this technique to characterize the interactions of Lewis basic carbonyls with Lewis acids.\textsuperscript{31,73,134,159} To establish the baseline interaction between FeCl\textsubscript{3} and carbonyls in DCE, we began by titrating a slurry of FeCl\textsubscript{3} in anhydrous DCE with acetone (22), 2, and crotonaldehyde (23).\textsuperscript{1} As observed previously, before carbonyl is added, FeCl\textsubscript{3} is insoluble in anhydrous DCE.\textsuperscript{31,73} The introduction of carbonyl into the slurry induces FeCl\textsubscript{3} to dissolve. Between 0-1 equiv 22 with respect to FeCl\textsubscript{3}, we observe exclusive formation of a vibration at 1633 cm\textsuperscript{-1} (Figure 44A). An analogous titration with 2 yields vibrations at 1610, 1592, and 1569 cm\textsuperscript{-1} (Figure 44B), and titration with 23 yields 1625 and 1593 cm\textsuperscript{-1} (Figure 44C). In all cases, FeCl\textsubscript{3} is dissolved upon the addition of 1 equiv carbonyl, consistent with the formation of Lewis pair complexes containing one FeCl\textsubscript{3} and one carbonyl molecule in all three systems. Lastly, we do not observe vibrations consistent with free carbonyl in any of the systems.

With baseline observations in hand, we, next, repeated these titrations in the presence of 1 equiv TMSCl with respect to FeCl\textsubscript{3}. We again observed that the mixture of FeCl\textsubscript{3}, TMSCl, and anhydrous DCE is heterogeneous. In fact, the amount of insoluble FeCl\textsubscript{3} does not appear to decrease when TMSCl is introduced, suggesting that TMSCl is not a competent agent for improving the solubility of FeCl\textsubscript{3} in DCE. When 0-1 equiv 22 is introduced into the heterogeneous mixture, we observe a conversion to homogeneity, as well as formation of the 1633 cm\textsuperscript{-1} vibration (Figure 44D), yielding no significant change from baseline. Interestingly, we observe a departure from the baseline titration when 2 and 23 are introduced into the slurry. In

\textsuperscript{1} See Appendix B for more information.
the 2 system, we observe the original vibrations that appear in the absence of TMSCl, and we also observe a new vibration at 1555 cm\(^{-1}\) (Figure 44E). Similarly, when 23 is added to the mixture, the two baseline vibrations appear, and we also observe an additional vibration at 1566 cm\(^{-1}\) (Figure 44F). Again, we do not observe vibrations consistent with free carbonyl in any of the systems.

Intrigued by these observations with TMSCl, we repeated these experiments with 2 equiv TMSCl to determine if the observations are concentration dependent. Again, addition of 22 to the FeCl\(_3\)/TMSCl slurry yielded no significant change from baseline beyond what appears to be a change in peak shape (Figure 44G). For the system with 2, we observe the same four vibrations that are present at 1 equiv TMSCl (Figure 44H); however, there are differences in the appearance of the spectrum. First, there is a noticeable broadening of the peak at 1610 cm\(^{-1}\), suggesting at least one additional vibration is forming in the region >1610 cm\(^{-1}\). Second, the absorbances of the three baseline vibrations from Figure 3B are lower in both intensity and with respect to the new vibration at 1555 cm\(^{-1}\). Similarly, the system titrated with 23 (Figure 44I) yielded a decrease in the absorbance of the two baseline vibrations observed in Figure 44C as well as an increase in the new vibration at 1566 cm\(^{-1}\). Collectively, the titrations of systems with 1 equiv and 2 equiv TMSCl with 2 and 23 suggest that the spectral changes are related to the amount of TMSCl present. Finally, no free carbonyl is observed.

To examine the impact of [TMSCl] further, we performed two experiments in parallel. The first involved repeating the titrations with 2 at loadings of 3 and 4 equiv TMSCl with respect to FeCl\(_3\). We then sought to compare the IR spectra at equivalent concentrations of 2, which is shown in the stacked plot in Figure 45A, showing 0 equiv TMSCl (black) through 4 equiv
TMSCl (green). All five spectra in the plot are at approximately the same [2] with the key difference being the amount of TMSCl present in solution.

**Figure 44.** Solution IR data for titrations of FeCl$_3$ (1 mmol in 6 mL DCE) with 0-1 equiv 22 (A), 2 (B), or 23 (C). Solution IR data for the titrations of FeCl$_3$ (1 mmol in 6 mL DCE) in the presence of 1 mmol TMSCl with 22 (D), 2 (E), or 23 (F). Solution IR data for the titrations of FeCl$_3$ (1 mmol in 6 mL DCE) in the presence of 2 mmol TMSCl with 2 (G), 2 (H), or 23 (I). Titrations proceed from red to violet with increasing amounts of titrant, with black representing the solution baseline in the absence of titrant.

As is evident from this comparative analysis, the new vibration at 1555 cm$^{-1}$ appears to increase with increasing TMSCl. Further, the increase in this vibration is concomitant with the decrease in absorbance of the baseline vibrations of the FeCl$_3$-2 Lewis pair, suggesting that the
new vibration is formed at the expense of the Lewis pair. The second experiment we implemented began by preforming the FeCl$_3$-2 Lewis pair, which we then titrated with TMSCl (Figure 45B). In this system, the new vibration at 1555 cm$^{-1}$ grows with increasing amounts of TMSCl concomitant with the decrease in absorbance of the vibrations at 1610, 1592, and 1569 cm$^{-1}$. The system displays an isosbestic point at 1612 cm$^{-1}$. Interestingly, when more sterically demanding chlorosilanes are examined (TBSCl and Ph$_3$SiCl), we observe dramatically suppressed interaction relative to TMSCl (Figure 45C). This observation is consistent with our previous observation that steric encumbrance inhibits access to the carbonyl-reactive Lewis acid.$^{73}$

Taken together, the titration-IR experiments show the following: 1) TMSCl does not improve the solubility of FeCl$_3$, consistent with a weak interaction. 2) Carbonyl 18 is capable of bringing FeCl$_3$ into solution, forming Lewis pair 17. 3) In the presence of increasing amounts of TMSCl, 17 can be converted into a new species. 4) In no system do we observe carbonyl that is not bound to a Lewis acid when 0-1 equiv 18 is present with respect to FeCl$_3$. These observations are consistent with 24 being present in solution, representing a heterodimer variant of the superelectrophilic homodimers proposed by Schindler and coworkers (Figure 4D).$^{79}$ In their examination of the properties of the 2:1 FeCl$_3$/carbonyl complexes, they probed whether or not the solution species existed as a contact complex or a solvent-separated ion pair. In their system, they did not detect ionization in the ground state. Given that our system is compositionally different, we believed it necessary to make a similar examination of the ground state of this interaction.
Figure 45. Analysis of concentration dependence on relative intensity of peak at 1555 cm\(^{-1}\) in titrations of FeCl\(_3\) (1 mmol in 6 mL DCE) with 2 (1 mmol) (A). Data proceeds from black to green with increasing amounts of TMSCl (0 mmol, 1 mmol, 2 mmol, 3 mmol, 4 mmol) (A). Solution IR data for the titration of FeCl\(_3\) (1 mmol in 6 mL DCE) and 2 (1 mmol) with TMSCl (B). Titration proceeds from red to violet with increasing amounts of titrant. Analysis of identity of chlorosilane on relative intensity of peak at 1555 cm\(^{-1}\) in titrations of FeCl\(_3\) (1 mmol in 6 mL DCE) with 2 (1 mmol) and chlorosilane (1 mmol) (C). Proposed equilibria including TMSCl (D). (Ano chlorosilane = black. TMSCl = red, TBSCl = blue, Ph\(_3\)SiCl = green).

**Colligative Measurements.**

We previously examined the existence of solvent-separated ion pairs when carbonyls are added to the FeCl\(_3\) slurry in anhydrous DCE using solution conductivity (\(\kappa\)).\(^{31,73}\) We performed this analysis for titrations with 22, 2, and 23. Consistent with our previous results, between 0-1 equiv added carbonyl, we observed negligible values of \(\kappa\) when TMSCl is absent (Figure 46A-C, black ▲). Interestingly, we observe an increase in \(\kappa\) for all three carbonyls when TMSCl is present. For the titration of 22, we see a slight increase in conductivity when 1 equiv TMSCl is present, and then a further increase for 2 equiv TMSCl (Figure 46A). For example, when 0.6 equiv 2 is present, the solution displays a \(\kappa\) of 0 \(\mu\)S cm\(^{-1}\) for 0 equiv TMSCl, 78 \(\mu\)S cm\(^{-1}\) for 1 equiv TMSCl, and 124 \(\mu\)S cm\(^{-1}\) at 2 equiv TMSCl. Titration with 2 displays a dramatic increase in \(\kappa\) for 1 equiv TMSCl and a further increase with 2 equiv TMSCl (Figure 46B). When 0.6
equiv 2 is present, we observe a $\kappa$ of 0 $\mu$S cm$^{-1}$ for 0 equiv TMSCl, 229 $\mu$S cm$^{-1}$ for 1 equiv TMSCl, and 648 $\mu$S cm$^{-1}$ at 2 equiv TMSCl. Titration with 23 similarly displays a dramatic increase in $\kappa$ for 1 equiv TMSCl, but then negligible increase with 2 equiv TMSCl (Figure 46C). When 0.6 equiv 23 is present, we observe a $\kappa$ of 35$\mu$S cm$^{-1}$ for 0 equiv TMSCl, and then 360 $\mu$S cm$^{-1}$ for 1 and 2 equiv TMSCl (Figure 46C). Given that non-zero conductivity exists as a result of the presence of TMSCl, these collective observations support that ion pair 25 is the new species in solution, rather than neutral species 24. When corresponding titrations are performed with 1 equiv TBSCl and Ph$_3$SiCl with respect to FeCl$_3$, we observe no change in conductance from FeCl$_3$ alone, consistent with our titration-IR observations in Figure 46C.

Closer examination of the data yields additional insights. Comparison of the three carbonyls in the presence of 2 equiv TMSCl displays a trend of conductivity with 2$>23>22$ (Figure 46D). This trend suggests that there may be a relationship between the ability to form solvent-separated ion pairs and resonance contributors of the carbonyls, with 2 having the largest number of resonance contributors and 22 having the fewest. This trend is consistent with the formation of 25. Additionally, the data show that 22 is forming more ions in the presence of TMSCl than under baseline conditions. Importantly, this effect is reduced compared with 2 and 23, yielding the question: Is there a similar subtle impact on the titration-IR data for the 22 experiments?
Reevaluation of 22.

To examine if there is a subtle impact of TMSCl on the solution behavior of FeCl$_3$ and 22, we employed the procedure used to generate Figure 47B. We preformed the FeCl$_3$-22 Lewis pair (Figure 47, dashed line). We then titrated TMSCl to the system. Upon close examination of the data, an isosbestic point is apparent at 1612 cm$^{-1}$. However, it is nowhere near as pronounced as the point observed for 2. When combined with the subtle change in solution conductivity, the
subtle change in the IR spectrum suggests that 22 does induce the formation of 25, but to a lesser degree than either 2 or 23. This decreased presence is consistent with our proposal that resonance contributors impact the formation of 25.

Figure 47. Solution IR data for the titration of FeCl$_3$ (1 mmol in 6 mL DCE) and 22 (0.8 mmol) with TMSCl. Black dashed line indicates solution data in the absence of TMSCl (A). Magnified view of isosbestic point at 1612 cm$^{-1}$ (B). Titration proceeds from red to green with increasing amounts of titrant. (A and B: [22] = 0.132 M. [TMSCl] = 0 M (black dashed line), 0.180 M, 0.328 M, 0.47 M, 0.629 M.)

Examination of GaCl$_3$.

There are two key observations which are central to our proposal in Figure 46E: 1) the fact that FeCl$_3$ is insoluble in anhydrous DCE and the TMSCl appears to be incapable of improving this physical property, and 2) FeCl$_3$ mixtures in DCE do not typically induce solution conductivity when FeCl$_3$ is in excess. However, FeCl$_3$ does display solution conductivity when carbonyl is present in excess due to the formation of 1:4 FeCl$_3$-carbonyl complexes. We have previously utilized GaCl$_3$ as a comparative tool for characterizing the solution behavior of FeCl$_3$. Like FeCl$_3$, GaCl$_3$ forms pairwise interactions with carbonyls that do not induce solution conductivity. Unlike FeCl$_3$, GaCl$_3$ is 1) highly soluble in anhydrous DCE, and 2) incapable of
forming solution aggregates that induce solution conductivity when combined with simple carbonyls. With this collection of qualities, we examined the spectroscopic and colligative properties of GaCl₃ combined with TMSCl and simple carbonyls.

Figure 48. Solution IR data for titration of GaCl₃ (1 mmol in 6 mL DCE) with 0-1 equiv 2 (A). Solution IR data for titration of GaCl₃ (1 mmol in 6 mL DCE) with 0-0.6 equiv 2 in the presence of 1 equiv TMSCl (B) and 0.6-1 equiv 2 in the presence of 1 equiv TMSCl (C). Solution conductance for the titration of GaCl₃ (1 mmol in 6 mL DCE) with 0-1 equiv 2 (D, black ▲) and with 0-1 equiv 2 in the presence of 1 equiv TMSCl (B, gold ■). Comparative proposal of solution equilibria for FeCl₃ (E) and GaCl₃ (F).

To establish the baseline interaction of GaCl₃ in anhydrous DCE, we began by titrating a homogeneous solution of GaCl₃ in anhydrous DCE with 2.¹ Between 0-1 equiv 2 with respect to GaCl₃, we observe exclusive formation of vibrations at 1611, 1592, and 1570 cm⁻¹, and no free 2 (Figure 48A). We then performed a similar titration with 1 equiv TMSCl present in solution (Figure 48B). Intriguingly, we observe an immediate departure from the baseline observations;

¹ See Appendix B for more information.
the GaCl$_3$-TMSCl system initially displays new vibrations at 1585 and 1555 cm$^{-1}$ when 2 is introduced. These new vibrations form in the absence of both the GaCl$_3$-2 Lewis pair and free 2. This new species continues to increase in absorbance until 0.6 equiv 2 is introduced. After 0.6 equiv, the absorbance of the vibration at 1555 cm$^{-1}$ begins to decrease, concomitant with the growth of vibrations consistent with the GaCl$_3$-2 Lewis pair at 1611, 1592, and 1570 cm$^{-1}$, manifesting an isosbestic point at 1562 cm$^{-1}$ (Figure 48C). We observe no appreciable difference when 2 equiv TMSCl are present.

These spectroscopic observations suggest that when GaCl$_3$, TMSCl, and 2 are combined in anhydrous DCE with an excess of GaCl$_3$ and TMSCl, a new solution species forms. No free 2 or Lewis pair are detected, suggesting that this new species is some combination of all three molecules in solution. This new species is then consumed as the [2] increases, yielding the formation of the GaCl$_3$-2 Lewis pair. Further, this new species displays at least one vibration that is identical to what we observe in the analogous FeCl$_3$ system (Figure 44E): 1555 cm$^{-1}$.

We next examined the $\kappa$ of the GaCl$_3$ systems (Figure 48D). As we have previously reported, between 0-1 equiv added 2, we observed negligible values of $\kappa$ when TMSCl is absent (Figure 48D, black ▲).$^{31,73}$ In the presence of 1 equiv TMSCl, we observe a rapid increase in solution conductivity to a level beyond what we observe for the FeCl$_3$ system (gold ▼). This maximum of 858 $\mu$S cm$^{-1}$ manifests at 0.4 equiv. Interestingly, the $\kappa$ then decreases rapidly towards 0 $\mu$S cm$^{-1}$. From these data, it appears that the solution yields the most conductivity when the new species is present and the least conductivity when the new species either cannot form or is consumed at high [25].

An additional property that GaCl$_3$ possesses that is beneficial to our analysis is that it is diamagnetic, allowing for examination of whether or not an observable solution interaction exists.
between GaCl$_3$ and TMSCl in the absence of 2. Using $^1$H NMR, we examined the chemical shifts of the protons on the methyls of 0.1 mmol TMSCl in CDCl$_3$.\(^1\) In the absence of GaCl$_3$, we observe a chemical shift of 0.44 ppm. When combined with 0.1 mmol GaCl$_3$, we observe a downfield shift to 0.48 ppm. A downfield shift is analogous to Olah and Field’s report of the interaction between TMSCl and AlCl$_3$.$^{157}$ These data suggest that before 2 is introduced into the GaCl$_3$ and TMSCl solution, there is an interaction between GaCl$_3$ and TMSCl, consistent with Feng and coworkers’ proposal.$^{156}$ and our initial hypothesis for FeCl$_3$ (Figure 42).

**Impact on Carbonyl-Olefin Metathesis.**

The species observed via our spectroscopic and colligative investigations suggest that FeCl$_3$ may not be the Lewis acid that activates the carbonyl for the metathesis reaction.$^{28}$ Importantly, this new Lewis acid system may explain the dramatic increase in reaction rate we observe as a result of the introduction of TMSCl (Figure 43). To identify if a new catalyst is present in the reaction system, we examined the rate order of TMSCl and FeCl$_3$, respectively, using the reaction of 20 as a model.$^1$ We set [20] at 10 mM and [FeCl$_3$] at 0.8 mM to examine five concentrations of TMSCl (1, 2, 3, 4, and 5 mM). Across these reactions, we observe an order of 0.96 ± 0.03 for TMSCl. When we probe the rate order of FeCl$_3$, we were intrigued to find divergent rate orders depending on the relative amounts of TMSCl and FeCl$_3$. When TMSCl is in excess, we observe the order of FeCl$_3$ to be 0.98 ± 0.05. Alternatively, we observe a rate order of 2.5 ± 0.2 for FeCl$_3$ when FeCl$_3$ is in excess relative to TMSCl. These data suggest concentration of carbonyl is reached, the new species is consumed, resulting in the disappearance of its IR vibrations and the reduction of solution conductivity. As a result, we propose the following parallel interactions for FeCl$_3$ and GaCl$_3$ when that when TMSCl is in excess, 25 forms during

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$^1$ See Appendix B for more information.
the catalytic cycle. However, the presence of excess FeCl$_3$ modifies the catalytic cycle to employ a second molecule of FeCl$_3$, consistent with 29 (Figure 49). This proposal is consistent with Brown and coworkers’ analysis of identical 2nd order behavior with respect to GaCl$_3$ for C–Cl bond activation in GaCl$_3$-mediated Friedel-Crafts alkylation$^{160}$. Moreover, this proposal is additive to the work of Schindler and coworkers, whose effort shows that absent TMSCl, aliphatic ketones display second order behavior with respect to FeCl$_3$, and aromatic ketones do not.$^{79}$

Figure 49. Concentration-dependent rate orders.

**First Principles Models of TMSCl activation and Catalysis.**

These observations spurred us to use quantum chemistry to evaluate the utility of ion pair species as potential active catalysts for carbonyl-olefin metathesis, as well as possible mechanisms for formation of these ion pairs. Using density functional theory (DFT)$^2$ simulations first examined the possibility that species 25 and 29 were active in the catalytic cycle. We sought to compare a baseline FeCl$_3$ catalyst (no TMSCl, Cat1) to TMS[FeCl$_4$] (Cat2) and TMS[Fe$_2$Cl$_7$] (Cat3), proceeding through the same reaction mechanism for all three catalysts: Lewis-acid promoted cycloaddition to form an oxetane followed by cycloreversion to yield the metathesis product.

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$^2$ See Appendix B for full computational details
DFT simulations confirmed that the metathesis of substrate 20 is plausibly promoted by all three examined catalysts. The catalytic cycle, shown in Figure 50, consists of three elementary steps. From the starting state of Lewis acid bound to the substrate carbonyl, concerted asynchronous [2+2]-cycloaddition yields an oxetane intermediate. Each catalyst results in activation barriers in the range of 16-17 kcal/mol; therefore, the catalysts are similarly enabling of this step. Next, a stepwise ring opening breaks a C–O bond, giving a transient intermediate, followed by C–C cleavage to yield the metathesis product. Ring-opening barriers range from 15-18 kcal/mol for the three catalysts; therefore, the rate-limiting step will depend on catalyst identity (Table 1). In all, simulations indicate that the three catalysts are competent for carbonyl-olefin metathesis. In addition, the reaction mechanism follows prior simulations by the Zimmerman group on Fe(III)-catalyzed metathesis. Figure 10A and Table 1 compare key differences in the metathesis reaction mechanism for the three catalysts. In particular, Cat2 and Cat3 increase activation of the carbonyl bond compared to FeCl₃, with C=O bonds lengthening by 0.01 to 0.02 Å when TMS is involved. These differences in degree of substrate activation are further reflected in the rate-limiting barriers for each catalytic cycle, as shown in Table 1. The silyl cation and the FeCl₄ anion of Cat2 and Cat3 are associated with one another by a Si–Cl interaction, with distances of 3.79 and 3.74 Å, respectively, indicating a moderate Coulomb binding but not a covalent link. Overall, Cat2 and Cat3 can be reasonably described as cationic SiMe₃⁺ with an associated counteranion that does not directly participate in the reaction.
Having uncovered evidence from first principles simulations that carbonyl-olefin metathesis can be promoted by ion pairs such as 25 and 29, additional simulations studied the mechanism to transform the precatalyst species (TMSCl and FeCl₃) and substrate 20 into catalytically active ion pairs. Figure 51B shows the postulated mechanism for this activation. Based on the insolubility of FeCl₃ in the absence of carbonyl, the first step involves complexation of Fe(III) to the substrate. Next, TMSCl forms a complex with the Fe(III)-carbonyl, and further association of a second carbonyl leads to the crucial precomplex for ion pair formation. Overall, this complex has an enthalpy of binding of -3.7 kcal/mol and a free energy of binding that is slightly uphill, by 5.7 kcal/mol. This intermediate reacts in a single
elementary step by displacing the Fe-carbonyl bond, making a Si-carbonyl bond, and transferring chloride from the TMS to the Fe(III) at the same time. The total free energy barrier for this transformation is 9.9 kcal/mol, indicating a plausible overall reaction pathway for ion pair formation. The ion pair 31 can transform into 32 by reaction with a second equivalent of FeCl₃. This pathway, shown in Figure 51C, follows a qualitatively similar mechanism as the formation of 31. First, a complex forms between the ion pair 31 and the Fe(III)-carbonyl complex 30 with a weak Fe-Cl-Fe connection. From there, a stronger connection of Cl from FeCl₄⁻ to FeCl₃ bridges the two iron species and displaces the carbonyl from the FeCl₃ complex. The total barrier for this step, 11.5 kcal/mol in free energy compared to the starting species, results in the final ion pairing intermediate composed of [Fe₂Cl₇]⁺ and [TMS-carbonyl]⁺. In all, the quantum chemical simulations indicate two important aspects of the FeCl₃-TMSCl chemistry: 1) Reactions for the formation of silyl cations are plausible through chloride exchange, with the final ion pair identity depending strongly on the amount of Fe present. 2) That the two postulated ion pairs may invoke the carbonyl-olefin metathesis reaction, with barriers that are slightly lower (1-2 kcal/mol) than the FeCl₃ catalyst. Importantly, formation of the ion pair species precludes FeCl₃.

Table 1. Gibbs Free Energy of key species (in kcal/mol) for the catalytic cycle of Figure 9. Free energies were obtained at ωB97X-D3/def2-TZVP/PCPM(DCE) level of theory.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Cat1</th>
<th>Cat2</th>
<th>Cat3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated Substrate</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>TS1</td>
<td>17.2</td>
<td>17.2</td>
<td>16.1</td>
</tr>
<tr>
<td>Oxetane</td>
<td>2.3</td>
<td>11.1</td>
<td>10.0</td>
</tr>
<tr>
<td>TS2</td>
<td>13.1</td>
<td>15.3</td>
<td>15.0</td>
</tr>
<tr>
<td>INT1</td>
<td>12.9</td>
<td>3.5</td>
<td>6.9</td>
</tr>
<tr>
<td>TS3</td>
<td>18.4</td>
<td>14.9</td>
<td>16.9</td>
</tr>
<tr>
<td>Product + byproduct complex</td>
<td>1.5</td>
<td>-3.2</td>
<td>-0.1</td>
</tr>
<tr>
<td>Rate-determining barrier</td>
<td>18.4</td>
<td>17.2</td>
<td>16.9</td>
</tr>
</tbody>
</table>

For an analogous path, which involves only one carbonyl, we calculate a higher overall barrier. See Appendix B for details.
Overall Mechanistic Proposal.

This manuscript’s kinetic, spectroscopic, and conductance investigations yield the following results: 1) The rate of catalytic turnover increases when carbonyl-olefin metathesis is performed with FeCl₃ and TMSCl present. 2) This increase allows us to decrease the loading of the FeCl₃ catalyst by more than a factor of five. 3) When TMSCl is in excess relative to FeCl₃, the reaction is first order in TMSCl and FeCl₃. 4) When FeCl₃ is in excess relative to TMSCl, the
reaction is first order in TMSCl and second order in FeCl₃. 5) Titration of FeCl₃ in the presence of TMSCl with 0–1 equiv 2 and 23 results in the formation of a new solution species in equilibrium with the FeCl₃:carbonyl Lewis pair. 6) The concentration of this new species is dependent on the amount of TMSCl present relative to FeCl₃. 7) A much less pronounced interaction occurs via titration with 22. 8) Titration of GaCl₃ with 0–0.6 equiv 2 shows exclusive formation of a TMSCl-dependent species. 9) The conditions that produce the new species result in an increase in solution conductivity, consistent with the formation of a solvent-separated ion pair.

Quantum chemical simulations predict that: 1) FeCl₃ and Fe₂Cl₆ can transform TMSCl into a silylium-Fe ion pair via Si–Cl bond activation when carbonyl is present. 2) Lewis acidic silylium is capable of inducing carbonyl-olefin metathesis reactivity. 3) This Si-centered Lewis acid decreases the barrier of the turnover-limiting step by 1-2 kcal/mol. 4) The active ion-pair catalyst is less susceptible to deactivation from byproducts than the bare Fe(III) salt. These simulations allow us to address the question we raised via our initial kinetic experiments: How does the addition of TMSCl change the turnover-limiting step of carbonyl-olefin metathesis?

When reaction of 20 is mediated by 8 mol% FeCl₃ and 20 mol% TMSCl, we observe a similar rate to the reaction facilitated by 50 mol% FeCl₃. Our collected observations suggest that these conditions result in a Cat2-facilitated reaction. We predict that this catalytic cycle’s turnover-limiting step is 1.2 kcal/mol lower than the FeCl₃-catalyzed reaction, which is consistent with the rate increase we observe in our kinetic results. In effect, the silylium cation supplants FeCl₃ and improves the overall activity towards carbonyl-olefin metathesis.

Examples of Lewis acid-assisted Lewis acid catalysts have been reported in the literature.¹⁶¹,¹⁶² Like Schindler’s report of the homodimeric interaction of FeCl₃ for aliphatic
carbonyl-olefin metathesis substrates, many of these systems feature two equivalents of the same Lewis acid driving reactivity.\textsuperscript{79} Alternatively, reports of mixed Lewis acid interactions are known. In particular, the Yamamoto group described the Lewis acid activation of TMSOTf by an Al(III) complex.\textsuperscript{163} They report that this catalyst system “exhibits exceedingly high activity on the catalytic Mukaiyama aldol reaction.” Mukaiyama’s aldol conditions rely upon the Lewis acid-mediated activation of a carbonyl in the presence of an activated olefin.\textsuperscript{15,16} Our results suggest that the TMSCl/FeCl\textsubscript{3} system should display analogous behavior to Yamamoto’s system. Indeed, when silyl enol ether \textsuperscript{35} is combined with \textsuperscript{2} in the presence of a \textbf{Cat2}-producing conditions, we observe a 93\% yield of the addition product after only 30 minutes of reaction time (Figure 52). Importantly, this reaction only required filtration through silica gel for work-up. The ability of the TMSCl/FeCl\textsubscript{3} system to successfully catalyze the Mukaiyama aldol illustrates its potential in the area of carbonyl-based transformations. Notably, TMSCl and FeCl\textsubscript{3} are widely available and inexpensive.

Another feature of our FeCl\textsubscript{3}-activated silylium catalyst is its catalytic activity in the presence of additional Lewis bases. Schindler and coworkers previously examined the inhibition of carbonyl-olefin metathesis by the N-protecting group FTs, selecting it because of decreased interaction with the FeCl\textsubscript{3} catalyst.\textsuperscript{78} Nevertheless, this reaction requires 50 mol\% FeCl\textsubscript{3} for success. The transition to the silylium system increases the reactivity towards the carbonyl over the FTs group. Additionally, the aldol system in Eq. 1 forms an alcohol product, while

![Figure 52. Silylyium catalysis in the Mukaiyama aldol reaction.](image-url)
maintaining a low reaction time, and avoiding acid-mediated E1cb to the aldol condensation product. This observation for the aldol reaction is consistent with Feng’s report, where their silylium-forming conditions prevent a similar elimination from occurring.\textsuperscript{156}

**Conclusion**

We have shown that the addition of TMSCl to FeCl\textsubscript{3}-catalyzed carbonyl-olefin metathesis not only inhibits byproduct inhibition of the Fe(III) center, but rather, increases the rate of the metathesis reaction. Through kinetic, spectroscopic, and colligative experiments, we investigated the solution interactions that result from the inclusion of this additive. We observe preferential formation of a silylium-activated substrate complex over the corresponding Fe(III)-activated substrate complex we have previously reported for carbonyl-olefin metathesis.\textsuperscript{73} Furthermore, we developed a theoretical framework to determine the thermodynamic and kinetic implications of the transition to silylium catalysis. Our model predicts the rate increase for carbonyl-olefin metathesis we observe experimentally. This FeCl\textsubscript{3}-mediated Si–Cl activation is additive to Al(III)-mediated Si–O activation reported by the Yamamoto lab.\textsuperscript{162}

By examining the impact of the addition of TMSCl to FeCl\textsubscript{3}-catalyzed carbonyl-olefin metathesis, we have been able to report a silylium-based catalyst for reactions requiring carbonyl activation. Additionally, we have shown the benefit of this catalyst system for carbonyl-olefin metathesis and the Mukaiyama aldol reactions and used the collected data to explain the observations reported by Feng and coworkers.\textsuperscript{156} We are currently examining the scope of metal halides that induce Si–Cl activation. We have, also, begun studies of other reaction systems that can benefit from this easily accessible silylium ion. Importantly, the interaction of FeCl\textsubscript{3} with the TMSCl is distinct from Gansäuer’s and Flowers’s proposal.\textsuperscript{158} However, TMSCl does decrease the concentration of solution aggregates that result from the interaction of excess carbonyl
compounds with FeCl$_3$, typically found when FeCl$_3$ is employed as a catalyst. The addition of TMSCl could potentially be employed as a mechanistic probe to determine if an FeCl$_3$-catalyzed reaction depends on the formation of solution aggregates.
CHAPTER 4
DIASTEREOSELECTIVE SYNTHESIS OF OXABICYCLO[3.3.1]NONENES FROM ALDEHYDES AND α-PINENE: FE(III) AGGREGATE CATALYSIS

Introduction

The biological properties of oxabicyclo[3.3.1]nonanes have garnered significant attention. Derivatives of these stable, oxygen containing heterocycles show activity against both α and β estrogen receptors (Figure 53A),\textsuperscript{164,165} antileishmanial properties (Figure 53B),\textsuperscript{166} and potential as amantadine-resistant influenza A treatments (Figure 53C).\textsuperscript{167}

![Figure 53. Oxabicyclo[3.3.1]nonenes and derivatives with biologically relevant properties.](image)

Previous methods of synthesizing oxabicyclo[3.3.1]nonenes employ clays,\textsuperscript{168,169} as well as Brønsted\textsuperscript{170,171} and Lewis acids\textsuperscript{172-174} as catalysts. The Salakhutdinov lab pioneered the use of clays in the synthesis of these compounds with their report of the reaction between (+)-(1) and p-hydroxybenzaldehyde in the presence of askelite-aentonite clay, yielding compound (Figure 54A).\textsuperscript{169} The group expanded upon the clay catalysis method by employing K10 clay with
(+)-car-2-ene (3), and p-methoxybenzaldehyde to yield 4 (Figure 54A).\textsuperscript{168} Using BF\textsubscript{3}•OEt\textsubscript{2}, the Saikia group obtained 5a from the reaction of geraniol (6) and benzaldehyde (Figure 54B).\textsuperscript{173} They also utilized these cyclizations to form oxabicyclo[3.3.1]nonanone 9, from 8 and benzaldehyde (Figure 54B).\textsuperscript{172} Singaram & Marimuthu applied InCl\textsubscript{3} as a catalyst to the synthesis of 5a from 1 and benzaldehyde (Figure 54B).\textsuperscript{174} In two separate reports, Gusevskaya and coworkers detail a Brønsted acid catalyzed synthesis of 5a from various alkenes and benzaldehyde.\textsuperscript{170,171} Using HPW/SiO\textsubscript{2}, the group is able to achieve high conversions of (−)-α-pinene (7) and benzaldehyde.

Figure 54. Previous methods towards the synthesis of oxabicyclo[3.3.1]nonenes and analogous compounds.

A limiting factor of available methods is side product formation. This additional reactivity limits the yields of the desired oxabicyclo[3.3.1]nonene and appears to do so...
independent of the type of catalyst involved. Many reports describe the formation of undesired
tetrahydropyrans or polycyclic compounds, likely facilitated by an unselective interaction with
the acid catalyst. We hypothesize that controlling the observed reactivity in the
oxabicyclo[3.3.1]nonene systems described above may occur via tuning of the strength of the
acid catalyst employed.

Previously, our lab has explored the interactions of Lewis acids and carbonyls,
determining their effect on catalytic carbonyl-based reactions. Through in-situ IR
spectroscopy, we have been able to observe the formation of highly-ligated, octahedral Lewis
acid-carbonyl compounds, like 10 (Figure 5), with decreased acidity that inhibits reactivity of
carbonyl-olefin metathesis. These properties could help mitigate side product formation in the
production of oxabicyclo[3.3.1]nonenes. We predict that a Lewis acid like FeCl₃, which readily
forms 4:1 aggregate species under catalytic conditions, may successfully accomplish this
task. Herein, we describe an FeCl₃-catalyzed diastereoselective protocol for the formation of
oxabicyclo[3.3.1]nonenes from α-pinene and aldehydes in up to quantitative yields (Figure
5).

**Results and Discussion**

Our investigation began with initial combination of benzaldehyde and 7 in the presence
of 5 mol% FeCl₃. We were delighted to observe a quantitative yield of 5b (Figure 5). Interestingly, both 2D NMR and X-ray crystallography reveal the exclusive formation of the
endo diastereomer. We found this intriguing as previous methods in which the configuration of

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1 Examination of other Lewis acids that do not form octahedral complexes with benzaldehyde resulted in inferior yields, in support of our hypothesis (see Appendix C)
this structure was reported describe exclusive formation of exo diastereomer 5a. This observed difference in diastereoselectivity prompted further exploration.

We turned towards ¹H NMR chemical shifts of key protons in the molecule, primarily proton Hₐ and Hₜ (Table 1). For the endo diastereomer 5b, we note a chemical shift of 4.93 ppm for proton Hₐ and 5.49 ppm for proton Hₜ. The Saikia group describe the synthesis of 9, formed exclusively as the endo diastereomer, analogous to 5b.¹⁷² Similarly, they support their characterization with an X-ray crystal structure. While 9 does not have a proton comparable to Hₜ, the chemical shift of 4.92 ppm for Hₐ is comparable to our value of 4.93 ppm in 5b. The similarity in chemical shift, as well as the complementary chemical structure suggest that both our protocol and Saikia’s 2010 protocol are diastereoselective towards the endo product.

Figure 55. Comparison of key protons Hₐ and Hₜ between diastereomers 5b, 5a, and analogous compound 9.

In their 2011 report, Saikia and coworkers describe selective formation of exo diastereomer 5a.¹⁷³ Though the group does not obtain a crystal structure, they employ 2D NMR to support this characterization. Furthermore, Singaram & Marimuthu also illustrate the
formation of 5a, using NMR as support for this assignment. It is with these two reports that we begin to see some divergence in NMR shifts. For proton Hₐ, Saikia in 2011 describes a shift of 4.88 ppm while Singaram & Marimuthu observe a shift of 4.80 ppm. Not only are these shifts different between the two reports, but they vary from our observed value of 4.93 ppm for proton Hₐ in 5b. We see similar divergence when comparing the shifts for Hₖ: 5.49 ppm vs 5.40-5.44 ppm. Because of this seeming disagreement across interpretations of these data, we developed a computational model to help provide clarity.

Figure 56. Comparison plots of predicted NMR shifts of the endo diastereomer as a function of our experimentally observed shifts for 5b (a), predicted NMR shifts for the exo diastereomer as a function of experimentally observed shifts of 5a as reported by the Saikia group (b) and the predicted NMR shifts of the endo diastereomer as a function of the experimental shifts observed by the Saikia group for the exo diastereomer, 5a (c).

Using DFT level of theory,² the trend between theoretically predicted chemical shifts and those observed experimentally were analyzed. We first calculated the predicted chemical shifts

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² For additional information see Appendix C.
for all protons in the endo diastereomer 5b. Plotting the predicted chemical shifts versus our experimentally observed chemical shifts produced a linear correlation with an $R^2 = 0.9986$ (Figure 56A). This correlation allows us to compare both sets of data and suggests that the predicted chemical shifts are in strong agreement with experimental chemical shifts for the endo diastereomer 5b. Next, we calculated the predicted chemical shifts for all protons in the exo diastereomer 5a. Plotting the predicted chemical shifts as a function of those observed experimentally by the Saikia group in 2011 yields a linear correlation with an $R^2 = 0.9779$ (Figure 56B). Conversely, plotting the Saikia report’s signals versus the predicted chemical shifts for the endo diastereomer 5b yield a linear correlation with an $R^2 = 0.9960$ (Figure 56C). The correlation observed in Figure 56C suggests these acid-mediated systems are likely facilitating the exclusive formation of the endo diastereomer 5b rather than the exo diastereomer 5a.

With ideal conditions and full characterization in hand, we moved on to examine the scope of the reaction of 7 with a variety of aldehydes (Figure 57). Halogenated benzaldehydes perform well under reaction conditions, providing the corresponding oxabicyclo[3.3.1]nonenes 12a and 12b in yields of 88 and 95%, respectively. Further, the $\alpha$-Br group does not diminish product formation. Generally, electron donating groups are fairly well tolerated, including 12e, which contains a Lewis basic oxygen that can compete for access to the Fe(III) center. Increasing the size of the substituent at the 4-position, which would increase the volume of the octahedral

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3 For a similar graph comparing predicted shifts against those observed experimentally by Singaram & Marimuthu, see Appendix C.

4 For a similar graph comparing predicted shifts for the endo diastereomer against those observed experimentally by Singaram & Marimuthu, see Appendix C.
complexes, has little impact on the yield when comparing Me-(12c, 80%), Et-(12d, 76%), iPr-(12f, 77%), and tBu-(12g, 76%) substituted systems. However, increasing to 4-Ph resulted in modest yield of 12i, and increasing to 2-napthaldehyde (12j) completely halted reactivity. A crystal structure of 12i reveals identical diastereoselectivity as 5b, suggesting that steric bulk does not impact the stereochemical outcome.

![Reaction Scheme](image)

**Figure 57. Scope of aldehydes.**

Examining electron-withdrawing 12h unveiled a controlling feature of this reaction. A significantly diminished yield of 35% was obtained with this 3-nitro group bearing substrate. Contrasting this result with those of electron donor bearing rings 12b-g suggest that the buildup of positive charge is necessary for the reaction. Additionally, we have shown the importance of
positive charge stabilization in the formation of aggregates like 10. From these two observations, we would predict that conjugated aldehydes would perform well. Indeed, we obtain yields of 73% and 81% for 12k and 12l, and simultaneously, no reaction for aliphatic aldehydes that would result in 12m and 12n.

The FeCl₃-catalyzed formation of oxabicyclo[3.3.1]nonenes from aldehydes and α-pinene likely follows a mechanistic pathway similar to those reported by both the Saikia lab as well as Singaram & Marimuthu. Both groups describe a Lewis acid-catalyzed (3,5)-oxonium-ene reaction, with either BF₃•OEt₂ or InCl₃ employed as the Lewis acid. Our collected observations point towards an analogous mechanism catalyzed by Fe(III)-centered aggregates.

Multiple observations support the conclusion that the aggregate species 14 functions as the catalyst. First, we previously reported that 14 forms readily under conditions in which 11 is in excess to FeCl₃. When FeCl₃ and 11 are present in a 1:1 ratio, Lewis pair 13 is observed. However, when excess 11 is added to the system, 14 forms (Figure 58). An investigation of the loading of FeCl₃ shows that yields of 5b decrease with increasing amounts of FeCl₃. In other words, as the amount of FeCl₃ present in the system increases, the amount of excess 11, and therefore the amount of 14 decreases. The yield of 5b is quantitative at 5 mol% FeCl₃ but decreases to 10% at 50 mol% loading and is negligible at 100 mol% loading (Figure 58).

Further, our protocol involves the addition of 11 to a slurry of FeCl₃, followed by the addition of 7. If 7 is added before 11, we observe a decrease in yield from quantitative to 41% 5b, with full consumption of 7. These observations suggest that if 14 is not allowed time to form, FeCl₃ will

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5 See Appendix C for full screen.
react directly with 7 in an alternate pathway. This other reactivity occurring in the absence of 14 is consistent with our initial hypothesis.

![Diagram](image)

Figure 58. Solution equilibria of FeCl₃ and aldehydes & the impact on reaction yield.

![Diagram](image)

Figure 59. Catalytic cycle for the (3,5)-oxonium-ene cyclization mediated by Fe(III)-centered aggregate.

Taken together, the mechanism of the reaction likely follows this path: When 11 is added to FeCl₃, reactive aggregate 14 forms. The reaction initiates upon the addition of 7. A molecule of 7 will displace an equivalent of 11, yielding carbocation intermediate 15. A retro-4-exo-trig cyclization forms alkene-carbocation intermediate 16, which then undergoes intramolecular nucleophilic attack from a pendant molecule of 11, yielding oxonium ion intermediate 17.
Finally, the oxonium-ene reaction, via a 6-endo-trig and elimination, offers product 5b (Figure 59).

**Conclusion**

We have developed a method towards the synthesis of biologically relevant oxabicyclo[3.3.1]nonenes employing an Fe(III)-aldehyde aggregate species as the active catalyst. This procedure has proven to be diastereoselective towards the endo isomer. Through X-ray crystallography, $^1$H NMR analysis, and DFT computational studies, we were able to propose a reassignment of the configuration of previously characterized oxabicyclo[3.3.1]nonene compounds. A variety of aldehydes are tolerated under reaction conditions, yielding products with electron withdrawing, electron donating, alkyl, and halogen substituents on the aryl ring. Further, studies into the identity of the active catalyst species revealed higher yields of oxabicyclo[3.3.1]nonene products, when conditions favor the formation of 14. Similarly, a lower yield, and in some cases, no reaction is observed when conditions disfavor aggregate formation. In all, we have presented a diastereoselective method towards the synthesis of oxabicyclo[3.3.1]nonenes in up to quantitative yields using an inexpensive and abundant Lewis acid catalyst. Studies of additional systems into which these aggregates may be applied are ongoing.
CHAPTER 5
INVESTIGATION OF CHANGES TO SOLUTION BEHAVIOR
BETWEEN LEWIS ACIDS AND CARBONYLS IN THE PRESENCE OF TMSCL
ADDITIVE VIA INFRARED-MONITORED TITRATION

Introduction

Cases of Lewis acids activating one another toward catalysis have been previously reported in the literature. Brown and Dehaan observe second order behavior of the GaCl$_3$ catalyst in their Lewis acid-mediated Friedel-Crafts alkylation (Figure 60A). The group describes catalysis to occur via a Ga$_2$Cl$_6$ homodimeric species, which activates the C-Cl bond of methyl chloride. Similarly, Schindler and coworkers report the carbonyl-olefin metathesis reaction of aliphatic ketones to be 2$^{nd}$ order with respect to the FeCl$_3$ catalyst (Figure 60B). They conclude that the active catalyst is an Fe$_2$Cl$_6$ homodimer that coordinates to the carbonyl of the substrate.

Figure 60. Lewis acid activation via homodimers: Brown and Dehaan (A), and Schindler (B).
On the other hand, several reports of mixed Lewis acid activations have been described. Most notably, the Yamamoto group details a Mukaiyama aldol reaction in which the Lewis acid TMSOTf is activated by an Al(III) species (Figure 61).\(^{161-163}\) Employing this Lewis acid activation system, the group obtains high yields, short reaction times, and excellent syn:anti selectivity of aldol adducts.

![Figure 61. Mukaiyama aldol featuring activation of TMSOTf by Al(III) complex.](image)

Additionally, our group has detailed the activation of TMSCl by FeCl\(_3\) in carbonyl-olefin metathesis (Figure 62).\(^{175}\) Like the Yamamoto lab’s report, the FeCl\(_3\) activation of the Si-Cl bond yields a catalytically active silylium complex, which can successfully mediate both carbonyl-olefin metathesis and the Mukaiyama aldol reaction. When employing this activated silylium species, we observe a 5-fold increase in the rate of carbonyl-olefin metathesis. We have characterized the silylium species and its activation by FeCl\(_3\) through \textit{in-situ} IR titration and solution conductivity measurements. By employing similar methods of characterization, we were also able to observe analogous activation of TMSCl by GaCl\(_3\).

By utilizing \textit{in-situ} IR titration and conductivity measurements, our group has previously been able to detail a series of solution interactions between Lewis acids and Lewis basic
carbonyls.\textsuperscript{31,73} After investigating the activation of TMSCl by both GaCl\textsubscript{3} and FeCl\textsubscript{3},\textsuperscript{175} we set out to similarly characterize the interactions of a variety of Lewis acids with the silyl chloride.

![Diagram of reactions](image)

Figure 62. Devery group’s previous work in FeCl\textsubscript{3} activated silylium catalysis.

Our efforts began with the investigation of various Lewis acids and benzaldehyde (16) in the presence of 2 equiv TMSCl with respect to the acid. This representative system yields the most prominent deviations in solution behavior from baseline titrations in both the GaCl\textsubscript{3} and FeCl\textsubscript{3} systems. In cases where a Lewis acid in the presence of TMSCl does exhibit a deviation from baseline with 16, our exploration expanded to include other simple carbonyls: acetone (17) and crotonaldehyde (18). Carbonyl was incrementally titrated into a slurry or solution of Lewis acid and TMSCl in anhydrous DCE and interactions were observed via \textit{in-situ} IR spectroscopy (ReactIR) and solution conductivity measurements.

**Results**

When a variety of Lewis acids are combined with TMSCl and titrated with carbonyl, two distinct trends resolve. (1) The system displays no observable change in solution behavior when
TMSCl is present versus when it is absent. This solution behavior is not consistent with Si-Cl bond activation; we term this category “non-activating”. (2) The system exhibits changes in solution behavior when TMSCl is present versus when it is absent. These changes manifest as either the presence of new peaks in the IR spectra or the absence of all peaks associated with previously characterized Lewis acid-carbonyl monomeric species. Additionally, an increase in solution conductivity exists when TMSCl is present. These observations are consistent with Lewis acid-induced Si-Cl bond activation and this category is termed “activating”.

Non-Activating Lewis Acids.

Figure 63. Solution IR data for the titrations of ZnCl$_2$ with 0-1 equiv 16 (A) and of ZnCl$_2$ in the presence of TMSCl (2 mmol) with 0-1 equiv 16 (B). Solution conductivity measurements for the titration of ZnCl$_2$ with 0-1 equiv 16 (C), titration of ZnCl$_2$ and TMSCl (2 mmol) with 16 (▲, C).

Initially, our group observed negligible complexation between carbonyls and relatively weak Lewis acids like ZnCl$_2$, AgOTf, I$_2$, and CeCl$_3$.$^{31}$ To explore the impact of the TMSCl additive on these systems, we employed ZnCl$_2$ as a representative Lewis acid. Upon titrating a slurry of ZnCl$_2$ with 0-1 equiv 16 in the absence of TMSCl, we observe exclusively unbound 16 at 1704 cm$^{-1}$ (Figure 63A). Notably, the slurry remains heterogenous throughout the titration.

When an analogous experiment including 2 equiv TMSCl is performed, there appears to be little
change in the IR spectra from the baseline. Once again, we see the exclusive growth of a peak at 1704 cm\(^{-1}\), consistent with free 16, between 0-1 equiv carbonyl (Figure 63B). The slurry remains heterogeneous throughout the titration. Furthermore, both baseline and additive systems display negligible solution conductance between 0-1 equiv 16 (Figure 63C).

Interactions between relatively weak Lewis acids, like ZnCl\(_2\), and carbonyls have not been observed under the conditions probed by our group. The addition of TMSCl does not appear to change the way ZnCl\(_2\) interacts with carbonyls or create any other observable solution behavior. Previously, our group noted that shifting in the C=O region begins to manifest as Lewis acidity increases from weak to moderate. Loose binding Lewis acids like BF\(_3\)\(\cdot\)OEt\(_2\) appear to coordinate with simple carbonyls to a modest extent. In these systems, we observe Lewis pair and free carbonyl grow in concurrently, indicating that an equilibrium exists between the two species.\(^{31}\) When a solution of BF\(_3\)\(\cdot\)OEt\(_2\) in anhydrous DCE is titrated with 0-1 equiv 16, we observe the formation of peaks at 1577, 1599, and 1626 cm\(^{-1}\), likely associated with species 19, a monomeric complex between 1 molecule of 16 and one molecule of BF\(_3\). At this point in the titration, we also observe unbound 16 at 1704 cm\(^{-1}\) (Figure 64A). The unbound 16 grows in concomitant with the peaks associated with 19. Analogous behavior is observed in a system where 2 equiv TMSCl is present. Again, unbound 16 at 1704 cm\(^{-1}\) and the peaks associated with 19 grow in simultaneously between 0-1 equiv carbonyl (Figure 64B). The addition of TMSCl does not appear to change the interaction of this loose-binding acid with carbonyls, and no new peaks are present in the IR spectra. Solution conductance illustrates no significant activity in either the baseline system or the additive system (Figure 64C).
Figure 64. Solution IR data for the titrations of BF$_3$•OEt$_2$ with 0-1 equiv 16 (A), BF$_3$•OEt$_2$ in the presence of TMSCl (2 mmol) with 0-1 equiv 16 (B). Solution conductivity measurements for the titration of BF$_3$•OEt$_2$ with 0-1 equiv 16 (C, D), BF$_3$•OEt$_2$ and TMSCl (2 mmol) with 16 (△, C). Solution IR data for the titrations of BCl$_3$ with 0-1 equiv 16 (D), BCl$_3$ in the presence of TMSCl (2 mmol) with 0-1 equiv 16 (E). Solution conductivity measurements for the titration of BCl$_3$ with 0-1 equiv 16 (F, G), BCl$_3$ and TMSCl (2 mmol) with 16 (△, F). Solution IR data for the titrations of AlCl$_3$ with 0-1 equiv 16 (H, I), AlCl$_3$ in the presence of TMSCl (2 mmol) with 0-1 equiv 16 (H). Solution conductivity measurements for the titration of AlCl$_3$ with 0-1 equiv 16 (I, J), AlCl$_3$ and TMSCl (2 mmol) with 16 (△, J).

Unlike BF$_3$•OEt$_2$, when a solution of BCl$_3$ in DCE is titrated with 16, we do not observe free 16 between 0-1 equiv carbonyl. Instead, the exclusive growth of a species with signals at 1563 and 1589 cm$^{-1}$ is apparent. These signals are likely consistent with the formation of 20, a
BCl$_3$-$\text{16}$ Lewis pair (Figure 64D). When 2 equiv TMSCl is added to the solution at the start of a titration, the exclusive formation of $\text{20}$ is once again observed. There does not appear to be a significant difference in the shape of the IR spectra, or the intensity of the peaks associated with $\text{20}$ (Figure 64E). Additionally, neither BCl$_3$ system displays significant solution conductance, and there is very little deviation between baseline and additive systems (Figure 64, F).

AlCl$_3$ is a stronger Lewis acid than either ZnCl$_2$ or BF$_3$·OEt$_2$ and we have previously characterized it as tight binding due to its solution behavior in the presence of carbonyls.$^{31}$ Between 0-1 equiv carbonyl, AlCl$_3$ exclusively forms monomeric species $\text{21}$, which manifests as three vibrations at 1568, 1596, and 1614 cm$^{-1}$ that form between 0-1 equiv $\text{16}$. During this time, no free carbonyl is observed (Figure 64G). Notably, AlCl$_3$ is insoluble in DCE at the start of the titration but becomes soluble around 1 equiv added carbonyl. When analogous titrations including 2 equiv TMSCl are conducted, no deviation from baseline solution behavior is apparent. We once again observe the exclusive formation of the three vibrations at 1568, 1596, and 1614 cm$^{-1}$ that are consistent with $\text{21}$ (Figure 64H). Further, solution conductance measurements reveal little difference between the baseline and additive systems. Between 0-1 equiv $\text{16}$, both systems exhibit a small increase in solution conductance. However, the addition of TMSCl does not appear to affect the magnitude of this increase.

While both tight and loose binding Lewis acids appear to form 1:1 complexes like $\text{19}$, $\text{20}$, and $\text{21}$ between 0-1 equiv carbonyl, Lewis acids like ZrCl$_4$, SnCl$_4$, and TiCl$_4$ instead form dimeric complexes.$^1$ When 0-0.5 equiv $\text{16}$ is titrated into a slurry of ZrCl$_4$ in DCE, we observe the formation of a species with vibrations at 1573, 1596, and 1614 cm$^{-1}$, which is consistent with the formation of Lewis pair $\text{22}$. As the titration proceeds from 0.5-1 equiv $\text{16}$, the peak at 1614 cm$^{-1}$ begins to broaden as dimeric complex $\text{23}$ is formed in solution (Figure 65A).
Figure 65. Solution IR data for the titrations of ZrCl\textsubscript{4} with 0-1 equiv \textit{16} (A), ZrCl\textsubscript{4} in the presence of TMSCl (2 mmol) with 0-1 equiv \textit{16} (B). Solution conductivity measurements for the titration of ZrCl\textsubscript{4} with 0-1 equiv \textit{16} (\textbullet, C), ZrCl\textsubscript{4} and TMSCl (2 mmol) with \textit{16} (\textbullet, C). Solution IR data for the titrations of SnCl\textsubscript{4} with 0-1 equiv \textit{18} (D), SnCl\textsubscript{4} in the presence of TMSCl (2 mmol) with 0-1 equiv \textit{18} (E). Solution conductivity measurements for the titration of SnCl\textsubscript{4} with 0-1 equiv \textit{16} (\textbullet, F), SnCl\textsubscript{4} and TMSCl (2 mmol) with \textit{16} (\textbullet, F). Solution IR data for the titrations of TiCl\textsubscript{4} with 0-1 equiv \textit{18} (G), TiCl\textsubscript{4} in the presence of TMSCl (2 mmol) with 0-1 equiv \textit{18} (H). Solution conductivity measurements for the titration of TiCl\textsubscript{4} with 0-1 equiv \textit{16} (\textbullet, I), TiCl\textsubscript{4} and TMSCl (2 mmol) with \textit{16} (\textbullet, I).

ZrCl\textsubscript{4} is insoluble in DCE, and the system does not reach homogeneity at any point.

When examining the additive system, we observe analogous solution behavior. Again, the peaks at 1573, 1596, and 1614 cm\textsuperscript{-1} form at the onset of titration with the vibration at 1614 cm\textsuperscript{-1}.
broadening significantly from 0.5-1 equiv 16 (Figure 65B). Similarly, the TMSCl system does not reach homogeneity at any point. When conductance studies were performed, we observed that neither system exhibited significant solution conductivity, and the difference between the two systems was negligible (Figure 65C).

While ZrCl\textsubscript{4} forms 1:1 complex 22 at the onset of titration and dimeric complex 23 at higher equivalents of 16, SnCl\textsubscript{4} and TiCl\textsubscript{4} proceed directly to dimeric species 24 and 25.\textsuperscript{31} Though experiments thus far have employed 16 as a representative carbonyl, the SnCl\textsubscript{4} and TiCl\textsubscript{4} systems formed a precipitate that prevented accurate examination of solution behavior via IR titration. Therefore, we utilized 18 for the investigation of these two systems.

SnCl\textsubscript{4} is soluble in DCE and 18 was titrated directly into a homogenous solution. In baseline titrations between 0-1 equiv 18, we observe the exclusive formation of vibrations at 1599 and 1632 cm\textsuperscript{-1}. These vibrations are consistent with dimeric species 24 (Figure 65D). When 2 equiv TMSCl is added at the start of the titration, these observations do not appear to change. We again see the exclusive formation of 24 with peaks manifesting at 1599 and 1632 cm\textsuperscript{-1} (Figure 65E). The additive system is homogenous throughout the titration and no free 18 is observed in either system. Solution conductance investigations display negligible conductivity of both systems with no significant difference between the two (Figure 65F).

Similarly, TiCl\textsubscript{4} is highly soluble in DCE. When 0-1 equiv 18 is titrated into a solution of TiCl\textsubscript{4} and DCE, two peaks at 1614 and 1629 cm\textsuperscript{-1}, and a shoulder peak at 1588 cm\textsuperscript{-1}, grow in exclusively. These vibrations are likely consistent with dimeric species 25 (Figure 65G). An analogous titration with 2 equiv TMSCl with respect to TiCl\textsubscript{4} yielded no deviation from baseline. Once more, we observe the growth of two peaks at 1614 and 1629 cm\textsuperscript{-1} with a shoulder at 1588 cm\textsuperscript{-1}, and no free 18 (Figure 65H). Solution conductivity displays negligible difference between
the baseline and additive systems, both of which do not appear to conduct on their own (Figure 65I).

**Activating Lewis Acids.**

Unlike other loose binding Lewis acids, InCl₃ displays disparate behavior between the baseline and TMSCl titrations. Between 0-1 equiv carbonyl, we observe the concomitant growth of free carbonyl and peaks associated with a Lewis pair complex. When 17 is the titrant absent TMSCl, we observe free 17 at 1714 cm⁻¹ and Lewis pair 26 which manifests as one vibration at 1673 cm⁻¹ (Figure 66A). Similarly, when 18 is titrated into a slurry of InCl₃ in DCE, Lewis pair 27 exhibits vibrations at 1622 and 1635 cm⁻¹, and free 18 grows in at 1689 cm⁻¹ (Figure 66D). When 16 is the titrant, Lewis pair 28 manifests as vibrations at 1581, 1596, and 1637 cm⁻¹, along with free 16 at 1704 cm⁻¹ (Figure 66G). InCl₃ is insoluble in DCE and none of these systems reach homogeneity.

When analogous titrations are performed in the presence of 2 equiv TMSCl, deviations in solution behavior are apparent. When 0-1 equiv 17 is titrated into a slurry of InCl₃, TMSCl, and DCE, we observe the exclusive growth of the peak at 1714 cm⁻¹, consistent with free 17. The vibration at 1673 cm⁻¹ associated with 26, is not present to a significant extent at any point (Figure 66B). Further, when 18 and 16 are the titrant and 2 equiv TMSCl is added, we observe primarily free carbonyl. Between 0-1 equiv carbonyl, the peak at 1689 cm⁻¹, consistent with free 18, and the peak at 1704 cm⁻¹, consistent with free 16, are predominant in their respective systems. In the 18 system, the two peaks associated with 27 at 1622 and 1635 cm⁻¹ are present, but at a much lower intensity than in the baseline titration (Figure 66E). Similarly, in the 16 system, the three vibrations associated with 28 are visible at 1581, 1596, and 1637 cm⁻¹ with a significantly diminished intensity relative to baseline titrations (Figure 66H).
Figure 66. Solution IR data for the titrations of InCl$_3$ with 0-1 equiv 17 (A), InCl$_3$ in the presence of TMSCl (2 mmol) with 0-1 equiv 17 (B). Solution conductivity measurements for the titration of InCl$_3$ with 0-1 equiv 17 (○, C), InCl$_3$ and TMSCl (1 mmol) (○, C) (2 mmol) (▲, C) with 17. Solution IR data for the titrations of InCl$_3$ with 0-1 equiv 18 (D), InCl$_3$ in the presence of TMSCl (2 mmol) with 0-1 equiv 18 (E). Solution conductivity measurements for the titration of InCl$_3$ with 0-1 equiv 18 (○, F), InCl$_3$ and TMSCl (1 mmol) (○, F) (2 mmol) (▲, F) with 18. Solution IR data for the titrations of InCl$_3$ with 0-1 equiv 16 (G), InCl$_3$ in the presence of TMSCl (2 mmol) with 0-1 equiv 16 (H). Solution conductivity measurements for the titration of InCl$_3$ with 0-1 equiv 16 (○, I), InCl$_3$ and TMSCl (1 mmol) (○, I) (2 mmol) (▲, I) with 16.

The peaks associated with 27 and 28 appear to grow in at a slower rate when TMSCl is present. Like the baseline titrations, none of these systems completely reach homogeneity.
When TMSCl is added to any carbonyl system, we observe divergence in solution behavior from baseline titrations. The peaks associated with Lewis pair 26 are completely absent, while peaks corresponding to 27 and 28 exhibit significantly decreased intensities. It does not appear that 26, 27, and 28 are forming to the same extent in the presence of TMSCl. However, while the Lewis pair peaks are absent or less intense, we do not see a corresponding increase in free carbonyl. In Figure 66, graphs B, E, and H display a black dotted line to represent the intensity of the absorbance of free carbonyl that would be present at 1 equiv in a system where only free carbonyl is present. In all three cases, it is evident that some amount of free carbonyl is absent when TMSCl is present. Most notably is the 17 system. Though no peaks associated with 26 are present, the intensity of 1 equiv free 17 is not matched (Figure 66B, dotted line). This observation may indicate that there is some amount of 17, which would otherwise make up 26, participating in an alternate interaction upon the addition of TMSCl. At this time, we have not observed new peaks at any absorbance in the spectra of any carbonyl systems. Investigation into the nature of the interaction that is leading to the missing carbonyl is ongoing.

Solution conductance measurements reveal another departure from baseline solution behavior. When 17 is titrated into a slurry of InCl$_3$ in DCE, no conductance is observed between 0-1 equiv carbonyl. However, when TMSCl is included in either 1 or 2 equiv, a marked increase in solution conductance over the course of the titration is evident (Figure 65C). When 18 is titrated into a slurry of InCl$_3$ in DCE, a slight increase in conductance from 0-1 equiv carbonyl is observed. Again, when TMSCl is added in either 1 or 2 equiv, the magnitude of the solution conductance is much greater when compared to the baseline titration (Figure 65F). Finally, when 16 is titrated into a slurry of InCl$_3$ in DCE, negligible solution conductivity occurs between 0-1 equiv carbonyl. Once more, the presence of 1 or 2 equiv TMSCl yields much greater
conductance throughout the titration when compared to the baseline experiment (Figure 66I).

The greatest increase in solution conductivity between baseline and additive systems occurs with 17, which also displays the most dramatic deviation in IR spectra.

We’ve previously characterized GaCl₃ as a tight-binding Lewis acid due to its high-affinity interactions with carbonyls.³¹ GaCl₃ forms tightly bound Lewis pairs, with no observable free carbonyl between 0-1 equiv added carbonyl. Like loose-binding InCl₃, GaCl₃ also displays changes in solution behavior between baseline and additive systems. When 0-1 equiv 17 is added to a solution of GaCl₃ in DCE absent TMSCl, we observe the exclusive formation of Lewis pair, 29, which yields a single vibration at 1630 cm⁻¹ (Figure 67A). Adding 2 equiv TMSCl at the start of the titration results in a significantly different solution behavior. Between 0-1 equiv 17, a new peak at 1605 cm⁻¹ is present alongside the peak at 1630 cm⁻¹, consistent with 29 (Figure 67B). Breaking this titration into two parts reveals that, between 0-0.6 equiv 17, the exclusive formation of the peak at 1605 cm⁻¹ can be observed (Figure 67C). Once 0.6 equiv 17 has been surpassed, the species resulting in the peak at 1605 cm⁻¹ is consumed while 29 begins to grow in at 1630 cm⁻¹. Similar behavior is observed with 0-1 equiv 18, where Lewis pair, 30 forms exclusively, yielding two vibrations at 1595 and 1629 cm⁻¹ in the absence of TMSCl (Figure 67D).

When an analogous titration with 2 equiv TMSCl was performed, we observe the formation of the peaks consistent with 30, alongside two new vibrations at 1566 and 1619 cm⁻¹ (Figure 67E). Furthermore, the two new vibrations at 1566 and 1619 cm⁻¹ grow in exclusively from 0-0.6 equiv 18, at which point the peaks associated with 30 begin to dominate the spectra (Figure 67F). Titrations with 16 also yield analogous results.
Figure 67. The titrations of GaCl₃ with 0-1 equiv 17 (A), GaCl₃ and TMSCl (2 mmol) with 0-1 equiv 17 (B) and between 0-0.6 equiv 17 (C). GaCl₃ with 0-1 equiv 18 (D), GaCl₃ and (2 mmol) with 0-1 equiv 18 (E) and between 0-0.6 equiv 18 (F). GaCl₃ with 0-1 equiv 16 (G), GaCl₃ and (2 mmol) with 0-1 equiv 16 (H) and between 0-0.6 equiv 16 (I). Solution conductivity of GaCl₃ with 0-1 equiv 17 (▲, J), GaCl₃ and TMSCl (1 mmol) (○, J) (2 mmol) (▲, J) with 17. GaCl₃ with 0-1 equiv 18 (▲, K), GaCl₃ and TMSCl (1 mmol) (○, K) (2 mmol) (▲, K) with 18. GaCl₃ with 0-1 equiv 16 (▲, L), GaCl₃ and TMSCl (1 mmol) (○, L) (2 mmol) (▲, L) with 16.
In the absence of TMSCl, we observe the exclusive formation of peaks at 1573, 1596, and 1610 cm\(^{-1}\), consistent with Lewis pair 31 (Figure 67G). Employing 2 equiv TMSCl at the start of the titrations reveals the formation of these three peaks along with two new peaks at 1555 and 1585 cm\(^{-1}\) and a shoulder at 1604 cm\(^{-1}\) (Figure 67H). The two new peaks at 1555 and 1585 cm\(^{-1}\) and the shoulder at 1604 cm\(^{-1}\) once again grow in exclusively from the start of the titration until 0.6 equiv 16 is reached (Figure 67I). Like the other systems, these three vibrations are consumed after 0.6 equiv 16 and the peaks associated with 31 continue to form until 1 equiv 16.

Solution conductivity provided more insight into the behavior of these systems. In titrations absent TMSCl, 17, 18, and 16 display no conductivity with GaCl\(_3\). However, when TMSCl is present, all systems exhibit an immediate and intense increase in solution conductivity at the onset of titration. The solution conductivity continues to increase until roughly 0.4 equiv carbonyl. At this point, a rapid decrease is observed in each system, with the measurements approaching baseline by 1 equiv carbonyl (Figure 67J, 67K, 67L). These solution conductance data correlate with the previously discussed observations in the IR titrations. As the new peaks grow into the IR spectra, solution conductivity appears to also increase. When Lewis pair species 29, 30, or 31 begin to form and the corresponding peaks begin to dominate the IR spectra, solution conductivity decreases and returns to baseline.

Unlike GaCl\(_3\), FeCl\(_3\) is not soluble in DCE and the addition of TMSCl does not alter this observation. To establish a baseline, a slurry of FeCl\(_3\) in anhydrous DCE was titrated with 17, 18, and 16. Between 0-1 equiv 17, we observe the exclusive growth of a peak at 1633 cm\(^{-1}\), which is consistent with the formation of Lewis pair, 32 (Figure 68A). When an analogous titration including 2 equiv TMSCl is performed, we observe the exclusive formation of a peak at 1633 cm\(^{-1}\), with no significant deviation from baseline (Figure 68B).
Figure 68. Solution IR data for the titrations of FeCl₃ with 0-1 equiv 17 (A), FeCl₃ and TMSCl (2 mmol) with 0-1 equiv 17 (B). Solution conductivity measurements for the titration of FeCl₃ with 0-1 equiv 17 (○, C), FeCl₃ and TMSCl (1 mmol) (○, C) (2 mmol) (▲, C) with 17. Solution IR data for the titrations of FeCl₃ with 0-1 equiv 18 (D), and FeCl₃ in the presence of TMSCl (2 mmol) with 0-1 equiv 18 (E). Solution conductivity measurements for the titration of FeCl₃ with 0-1 equiv 18 (○, F), FeCl₃ and TMSCl (1 mmol) (○, F) (2 mmol) (▲, F) with 18. Solution IR data for the titrations of FeCl₃ with 0-1 equiv 16 (G), and FeCl₃ in the presence of TMSCl (2 mmol) with 0-1 equiv 16 (H). Solution conductivity measurements for the titration of FeCl₃ with 0-1 equiv 16 (○, I), FeCl₃ and TMSCl (1 mmol) (○, I) (2 mmol) (▲, I) with 16.

Notably, titrations involving 18 and 16 yield differing behavior between baseline and additive experiments. When 0-1 equiv 16 is titrated into a slurry of FeCl₃ in DCE absent TMSCl, two peaks with vibrations at 1593 and 1625 cm⁻¹ form (Figure 68D).
These vibrations are consistent with Lewis pair, 33. The two vibrations are also observed when an analogous titration including TMSCl is performed. In addition to these two peaks, the TMSCl system exhibits one additional peak that is not present in the baseline at 1566 cm\(^{-1}\) (Figure 68E). Similarly, when 16 is the titrant, the formation of Lewis pair 34 results in three vibrations at 1569, 1592, and 1610 cm\(^{-1}\) between 0-1 equiv added carbonyl (Figure 68 G). In the presence of TMSCl, these three peaks are observed alongside a fourth additional peak at 1555 cm\(^{-1}\) (Figure 68H). Once again, this peak is not present in the baseline titration. No free carbonyl is observed in any of the systems probed.

Solution conductance investigations carried out on these systems are telling. Absent TMSCl, all three carbonyls exhibit negligible solution conductivity between 0-1 equiv when titrated into a slurry of FeCl\(_3\) and DCE. In the 17 system, a slight increase is observed when 1 or 2 equiv TMSCl is present (Figure 68C). However, when 18 is titrated into a slurry of FeCl\(_3\) and 1 or 2 equiv TMSCl in DCE, a much larger increase in conductivity is observed (Figure 68F). This is consistent with the examination of IR data, which illustrates a very small change in the 17 systems between baseline and additive titrations, but a much larger change between both 18 systems. Further, the greatest change in conductivity is observed when 16 is titrated into a slurry of FeCl\(_3\) and 1 or 2 equiv TMSCl in DCE; this increase is larger when 2 equiv TMSCl is present as opposed to 1 equiv TMSCl (Figure 68I).

**Discussion**

Through *in-situ* IR titration and conductance measurements, we were able to observe the solution behavior of an array of Lewis acids and carbonyls in the presence of TMSCl. Compiling these observations allows us to categorize each Lewis acid investigated as either “non-activating” or “activating” of the Si-Cl bond in TMSCl under the conditions probed.
Lewis acids that fall under the “non-activating” category do not display any solution behavior indicative of Si-Cl bond activation or silylium formation. In all cases, when a slurry or solution of a “non-activating” Lewis acid is titrated with 0-1 equiv 16 in the presence of TMSCl, there is no observable deviation from analogous baseline titrations in the absence of TMSCl.

Figure 69. Non-activating Lewis acids and solution complexes observed with TMSCl additive.

Similarly, solution conductivity remains the same between 0-1 equiv 16, regardless of the amount of TMSCl present in the system. Notably, the “non-activating” category contains Lewis acids of varying strength that each exhibit very different types of interactions with carbonyls in baseline titrations.

The weakest Lewis acid examined, ZnCl₂, has not been observed to coordinate with simple carbonyls under these conditions.³¹ Although ZnCl₂ is a weak acid, even compounds of moderate or strong Lewis acidity can also fall into the “non-activating” category. We have previously characterized BF₃•OEt₂ as a moderate Lewis acid that exhibits modest binding interactions with carbonyls. The Lewis pair 19 (Figure 64A) exists in equilibria with free 16 between 0-1 equiv carbonyl. BF₃•OEt₂ similarly fails to display any change in solution behavior
when TMSCl is present. Stronger Lewis acids that exhibit high binding affinity with simple carbonyls, like BCl$_3$ and AlCl$_3$, also do not yield any evidence of Si-Cl bond activation or silylium formation. ZrCl$_4$, SnCl$_4$, and TiCl$_4$ may also be deemed stronger Lewis acids, and we have previously observed the formation of dimeric species 23, 24, and 25 (Figure 65) between 0-1 equiv simple carbonyls. Once again, this solution behavior appears unchanged by the addition of TMSCl. “Non-activating” Lewis acids do not display any observations consistent with Si-Cl bond activation, but it also appears that TMSCl does not disrupt baseline solution interactions in these systems. Under the conditions probed, ZnCl$_2$, BF$_3$•OEt$_2$, BCl$_3$, AlCl$_3$, ZrCl$_4$, SnCl$_4$, and TiCl$_4$ can all be classified as “non-activating” Lewis acids (Figure 69). The wide deviation in Lewis acidities and solution behaviors with simple carbonyls of the compounds in this category limit our ability to determine which factors play a role in determining if a given Lewis acid will be able to induce silylium formation.

Three Lewis acids of varying acidities can be categorized as “activating”. InCl$_3$, which aligns with BF$_3$•OEt$_2$ in terms of acidity, displays modest binding interactions with simple carbonyls. In the absence of TMSCl, in-situ IR titration reveals that Lewis pairs 26, 27, and 28 appear to be in equilibria with free carbonyl 17, 18, and 16 (Figure 66A, D, G). Importantly, when TMSCl is present, peaks associated with InCl$_3$-carbonyl Lewis pairs are completely absent or significantly less intense (Figure 66B, E, H). The absence of Lewis pair is not balanced by a corresponding increase in free carbonyl. Some amount of 17, 18, and 16 appears to be missing in each corresponding system. We propose that the missing 17, 18, and 16 activates the Si-Cl bond of TMSCl, yielding silylium complexes 35, 36, and 37 (Figure 70). There are no new peaks corresponding to these silylium complexes present in the IR, though it is possible these vibrations may be buried under background signals. Increases in solution conductivity when
TMSCl is present in all carbonyl systems also indicate the presence of solvent-separated ion pairs like 35, 36, and 37 (Figure 70). Studies into the behavior of InCl₃ with TMSCl and simple carbonyls are ongoing.

Figure 70. Activating Lewis acids and corresponding silylium ion complexes.

Previously, we’ve observed that FeCl₃ and GaCl₃ display high affinity interactions with simple carbonyls.³¹ Between 0-1 equiv carbonyl, exclusive formation of Lewis pairs are observed, with no detectable free carbonyl. When TMSCl is present in GaCl₃-carbonyl titrations,
new peaks are visible, which correspond to silylium species 38, 39, and 40. Additionally, solution conductance increases when TMSCl is added, consistent with solvent-separated ion pairs forming. Similarly, FeCl₃ systems with TMSCl also yield new peaks that correspond to 41, 42, and 43. As with InCl₃ and GaCl₃, a solution conductivity increase is also evident upon the addition of TMSCl to carbonyl-FeCl₃ systems.

In all, numerous Lewis acids and their interactions with carbonyls in the presence of TMSCl have been investigated. We have proposed a classification system consisting of two groups, activating and non-activating. Each Lewis acid can be placed in one of these two categories, depending on the presence or absence of solution behavior indicative of activation of the Si-Cl bond of TMSCl. Evidence indicating Si-Cl activation may include: the presence of peaks that do not correspond with previously observed carbonyl-Lewis acid monomers, the absence of peaks associated with these Lewis pairs without a corresponding increase in free carbonyl, and an increase in solution conductivity when TMSCl is present.

Yamamoto’s group previously explored the benefits of silylium catalysis with their exploration of Al(III) activated TMSOTf in the Mukaiyama aldol reaction. We present another path towards silylium catalysis through activation of the Si-Cl bond on TMSCl, which numerous Lewis acids may successfully accomplish. The silylium species formed through activation of TMSCl by FeCl₃ (41, 42, 43) have been shown to successfully catalyze carbonyl-olefin metathesis and the Mukaiyama aldol reaction. Analogous species formed through activation of TMSCl by GaCl₃ (38, 39, 40) are also capable of catalyzing carbonyl-olefin metathesis. Further efforts will focus on expanding the scope of silylium catalysis to other carbonyl-based organic transformations and exploring the potential of other activating Lewis acids.
APPENDIX A

SUPPLEMENTARY INFORMATION FOR CHAPTER 2
General Information

General Laboratory Procedures.

All moisture-sensitive reactions were performed under an atmosphere of argon in flame-dried round bottom flasks or glass vials fitted with rubber septa. Stainless steel syringes were used to transfer air or moisture-sensitive liquids.

Materials and Instrumentation.

All chemicals were purchased from Alfa Aesar, VWR, Matheson Coleman and Bell, Beantown Chemicals, or Acros. All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques or in an M. Braun UNIlab Pro glovebox. Glassware was dried at 150 °C overnight. Diethyl ether, \( n \)-pentane, tetrahydrofuran, and toluene were purified using a Pure Process Technology solvent purification system. Before use, an aliquot of each solvent was tested with a drop of sodium benzophenone ketyl in THF solution. All reagents were purchased from commercial vendors and used as received. \( \text{HCz}^{\text{Bu}}(\text{Pyr}^{\text{Pr}})_2 \) was prepared according to a modified literature procedure.\(^7\) \(^{1}\text{H} \) NMR data were recorded on a Varian Inova 500 MHz spectrometer at 22 °C. Resonances in the \(^{1}\text{H} \) NMR spectra are referenced to residual \( \text{CD}_2\text{Cl}_2 \) at \( \delta = 5.32 \) ppm or \( \text{CDCl}_3 \) at \( \delta = 7.27 \) ppm. Solution magnetic susceptibilities were determined using the Evans method.\(^{26}\) Continuous-wave (CW) EPR spectra were recorded at 77 K on a Bruker EMX plus X-band EPR spectrometer equipped with a liquid \( \text{N}_2 \) cold-finger Dewar flask. Cyclic voltammetry was conducted \( \text{via} \) a CH-Instruments electrochemical analyzer (model 620E), employing a 3 mm glassy carbon working electrode, a silver wire pseudo reference electrode, and a platinum coiled wire counter electrode. All measurements were performed using either \( \text{CH}_2\text{Cl}_2 \) or THF solutions containing 1 mM analyte and 0.1 M \( \text{Bu}_4\text{NPF}_6 \) as the supporting electrolyte. The potentials were referenced to a ferrocene/ferrocenium redox couple.
analyses were conducted by Midwest Microlab, LLC (Indianapolis, IN). Acetone was dried over K₂CO₃. DCE was dried and stored over 3 Å Molecular sieves. Infrared (IR) spectra were obtained using a Mettler Toledo ReactIR 15. IR data are represented as frequency of absorption (cm⁻¹). Conductivity measurements were obtained using a VWR Portable Conductivity Meter. Conductivity data are represented as microsiemens per centimeter (μS cm⁻¹).

**Abbreviations Used.**

DCE = 1,2-dichloroethane, K₂CO₃ = potassium carbonate, KCl = potassium chloride, THF = tetrahydrofuran

**X-ray Crystallography**

**Table S1.** Selected Bond Distances (Å) and Angles (°) for 1 and 3.

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<td>Fe1–N1</td>
</tr>
<tr>
<td>Fe1–N3</td>
<td>1.940(5)</td>
<td>Fe1–N3</td>
</tr>
<tr>
<td>Fe1–N5</td>
<td>2.171(5)</td>
<td>Fe1–N5</td>
</tr>
<tr>
<td>Fe1–Cl1</td>
<td>2.253(2)</td>
<td>Fe1–Cl1</td>
</tr>
<tr>
<td>Fe1–Cl2</td>
<td>2.224(2)</td>
<td>Fe1–Cl1#1</td>
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</tbody>
</table>

N1–Fe1–N3  88.4(2)  N1–Fe1–N3  87.2(3)  N1–Fe1–N5  88.6(2)  N3–Fe1–N5  86.5(3)  N1–Fe1–N5  175.1(2)  N1–Fe1–N5  173.7(2)  N3–Fe1–Cl1  117.0(2)  N3–Fe1–Cl1  124.16(4)  N3–Fe1–Cl1  124.16(4)  N3–Fe1–Cl1  124.16(4)  Cl1–Fe1–Cl2  123.37(7)  Cl1–Fe1– Cl1#1  111.67(8)  Cl1#1

τ₅    0.86  s  0.83

---

¹ Numbers in parentheses are standard uncertainties in the last significant figures. Atoms are labeled as indicated in Figures 1 and S1. ² Symmetry operations: #1 = x, 3/2-y, z.
Table S2. X-ray Crystallographic Data for 1 and 2.

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<td>Chemical formula</td>
<td>C$<em>{32}$H$</em>{40}$Cl$_2$FeN$_5$</td>
<td>C$<em>{26}$H$</em>{28}$Cl$_2$FeN$_5$·C$_4$H$_8$O</td>
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<td>$M_r$</td>
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<td>609.39</td>
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<td>Monoclinic, $P2_1/m$</td>
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<td>150</td>
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<td>16.501 (3)</td>
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<td>90</td>
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<tr>
<td>$\gamma$ (°)</td>
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<td>Radiation type</td>
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<td>Cu $K\alpha$</td>
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<td>$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}}$ (e Å$^{-3}$)</td>
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<td>1.03, -1.26</td>
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</table>

Special refinement details.

For complex 3, the crystal under investigation was found to be non-merohedrally twinned. The orientation matrices for the two components were identified using the program Cell_Now, with the two components being related by a 180° rotation around the real $a$-axis. Twinning is close to pseudo-merohedral, emulating a $c$-centered lattice with $a = 13.8210$, $b = 30.2830$, $c = 7.1443$, but with a substantial offset for the gamma angle from 90 degrees (91.6%).
Integration and refinement are possible, but R values are about doubled compared to refinement in $P2_1/m$ (ca 19% for R1 and 39% for wR2).

The two components were integrated using Saint and corrected for absorption using twinabs, resulting in the following statistics:

2186 data (1007 unique) involve domain 1 only, mean I/sigma 16.4

2232 data (1016 unique) involve domain 2 only, mean I/sigma 17.0

6449 data (2393 unique) involve 2 domains, mean I/sigma 35.3

1 data (1 unique) involve 3 domains, mean I/sigma 103.5

The exact twin matrix identified by the integration program was found to be:

\[
\begin{bmatrix}
0.99912 & 0.00225 & -0.00190 \\
0.00054 & -1.00000 & -0.00013 \\
-0.92713 & -0.00046 & -0.99912
\end{bmatrix}
\]

The structure was solved using direct methods with only the non-overlapping reflections of component one. The structure was refined using the hklf 5 routine with all reflections of both components (including the overlapping ones), resulting in a BASF value of 0.491(4).

The R$_{int}$ value given is for all reflections and is based on agreement between observed single and composite intensities and those calculated from refined unique intensities and twinfractions (TWINABS (Sheldrick, 2012)).

A THF molecule is disordered across a mirror plane. Chemically equivalent bond distances were restrained to be similar. U$_{ij}$ components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar.

**Hydrogen atom treatment.**
For both structures, H atoms attached to carbon atoms were positioned geometrically and constrained to ride on their parent atoms. C-H bond distances were constrained to 0.95 Å for aromatic and alkene C-H moieties, and to 1.00, 0.99 and 0.98 Å for aliphatic C-H, CH$_2$ and CH$_3$ moieties, respectively. Methyl CH$_3$ were allowed to rotate but not to tip to best fit the experimental electron density. U$_{iso}$(H) values were set to a multiple of U$_{eq}$(C) with 1.5 for CH$_3$ and 1.2 for C-H, CH$_2$ units, respectively.

**Figure S1.** Molecular structure of 3 with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Color key: orange = Fe, blue = N, gray = C, green = Cl.

**Cyclic Voltammetry**

**Figure S2.** Cyclic voltammograms of 0.1 mM 1 in CH$_2$Cl$_2$ (0.1 M nBu$_4$PF$_6$) at scan rates of 100, 200, 300, 400, and 500 mV s$^{-1}$. Inset: Plot of anodic, $I_{pa}$, and cathodic, $I_{pc}$, peak current, versus...
square root of scan rate for the first (●, blue; R² = 0.9977) and second oxidation (◆, orange; R² = 0.9986).

**Figure S3.** Cyclic voltammograms of 0.1 mM 2 in CH₂Cl₂ (0.1 M nBu₄PF₆) at scan rates of 100, 200, 300, 400, and 500 mV s⁻¹. Inset: Plot of anodic, Iₚa, and cathodic, Iₚc, peak current, versus square root of scan rate for the first (●, blue; R² = 0.9994) and second oxidation (◆, orange; R² = 0.9986).

**Figure S4.** Cyclic voltammograms of 0.1 mM of 1 (blue), 2 (green), and 3 (red) in acetone (0.1 M nBu₄PF₆) at scan rates of 100 mV s⁻¹.

**EPR Spectroscopy**
Figure S5. EPR spectrum of 2 (solid) at room temperature.

Figure S6. EPR spectrum of 3 (solid) at room temperature.

Figure S7. EPR spectrum of 2 (solid) at 77 K.
Figure S8. EPR spectrum of 3 (solid) at 77 K.

Figure S8. EPR spectrum of 1 (solid) at room temperature.

Figure S9. EPR spectrum of 1 (solid) at 77 K.
Figure S10. EPR spectrum of 2 in CH₂Cl₂ at room temperature.

Figure S11. EPR spectrum of 3 in CH₂Cl₂ at room temperature.

Figure S12. EPR spectrum of 2 in CH₂Cl₂ at 77 K.
Figure S13. EPR spectrum of 3 in CH$_2$Cl$_2$ at 77 K.

**IR Titrations**

**General procedure.**

Lewis acid (1.00 mmol) was added to a flame-dried 25 mL 2-neck round bottom flask with a rice stir bar. The flask was sealed with septa and an Ar balloon was inserted. The flask was placed into an oil bath heated to 30 °C. Anhydrous DCE (6 mL) was added. The solution was stirred for 15 minutes to reach temperature. Acetone was added in 10 μL increments to the 2$^{\text{nd}}$ equivalence point of carbonyl, then 20 μL increments were added until 4$^{\text{th}}$ equivalence point was reached. Complexation was analyzed via real time infrared spectroscopy, using a Mettler Toledo ReactIR 15. IR titration was performed for complexes 1, 2, and 3.

Figure S14. Solution IR data for titration of 1 with 0-4.2 equiv acetone. Titration proceeds from black to violet with increasing amounts of acetone.
**Figure S15.** Solution IR data for second trial titration of 1 with 0–4.2 equiv acetone. Titration proceeds from black to violet with increasing amounts of acetone.

**Figure S16.** Spectral deconvolution of solution with 1 and 0.664 M acetone. Observed spectrum (solid black), simulated total (dashed black), simulated acetone (red), simulated complex (blue).

**Figure S18.** Solution IR data for titration of 2 (with 0–4.2 equiv acetone. Titration proceeds from black to violet with increasing amounts of acetone
Figure S19. Solution IR data for titration of 3 (1 mmol in 6 mL DCE) with 0-4.2 equiv acetone. Titration proceeds from black to violet with increasing amounts of acetone ([acetone] = 0 M, 0.045 M, 0.089 M, 0.178 M, 0.330 M, 0.499 M, 0.664 M).

**Conductance Analysis**

A VWR Portable Conductance Meter was calibrated with standard solutions of KCl (10 mM and 0.5 mM) of known conductivity (1411 μS cm\(^{-1}\) and 74 μS cm\(^{-1}\), respectively). Then the probe was rinsed with water and finally with DCE several times before taking measurements. Before each experiment, the conductance meter was recalibrated with the standard solutions.

**Procedure for conductance of 1 with acetone.**

In a glove box, 1 (1.27 g, 2.0 mmol) was added to a flame-dried 20 mL scintillation vial charged with a stir bar. Anhydrous DCE was added (12 mL, 166 mM). The conductance of the mixture was observed via a VWR Portable Conductance Meter. Acetone was incrementally titrated until 4 equivalents of acetone were reached. The conductance after each addition of acetone was observed and recorded as an average of three measurements. Between each reading, the probe was rinsed with DCE. Plotting was performed with Microsoft Excel.
Table S3: Conductivity measured between acetone and 1.

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Procedure for conductance of 2 with acetone.

In a glove box, 2 (550 mg, 1.0 mmol) was added to a flame-dried 20 mL scintillation vial charged with a stir bar. Anhydrous DCE was added (6 mL, 166 mM). Acetone was incrementally titrated until 2.2 equivalents of acetone were reached. The conductance after each addition of acetone was observed and recorded as an average of three measurements. Between each reading, the probe was rinsed with DCE. Plotting was performed with Microsoft Excel.

Table S4: Conductivity measured between acetone and 2.

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Procedure for conductance of 3 with acetone.

In a glove box, 3 (700 mg, 1.3 mmol) was added to a flame-dried 20 mL scintillation vial charged with a stir bar. Anhydrous DCE was added (8 mL, 163 mM). The conductance of the mixture was observed via a VWR Portable Conductance Meter. Acetone was incrementally titrated until 2.2 equivalents of acetone were reached. The conductance after each addition of acetone was observed and recorded as an average of three measurements. Between each reading the probe was rinsed with DCE. Plotting was performed with Microsoft Excel.]

Table S5: Conductivity measured between acetone and 3.

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APPENDIX B

SUPPLEMENTARY INFORMATION FOR CHAPTER
General Information

General Laboratory Procedures.

All moisture-sensitive reactions were performed under an atmosphere of argon in flame-dried round bottom flasks fitted with rubber septa. Stainless steel syringes were used to transfer air or moisture-sensitive liquids. Flash chromatography was performed using silica gel Silia Flash® 40-63 micron (230-400 mesh) from Silicycle.

Materials and Instrumentation.

All chemicals were purchased from Alfa Aesar, VWR, Matheson Coleman and Bell, Beantown Chemicals, or Acros. All ketones were dried over 3 Å molecular sieves and purified via distillation. Acetone was dried over K₂CO₃. DCE was dried and stored over 3 Å molecular sieves in inert atmosphere glovebox. Infrared (IR) spectra were obtained using a Mettler Toledo ReactIR 15. Plotting was performed with GraphPad Prism 9. IR data are represented as frequency of absorption (cm⁻¹). Conductivity measurements were obtained using a VWR Portable Conductivity Meter. Conductivity data are represented as Microsiemens per centimeter (µS cm⁻¹). Proton Nuclear Magnetic Resonance (¹H NMR) spectra were recorded on a Bruker Avance 500 mHz spectrometer equipped with a prodigy cryoprobe.

Abbreviations used.

DCE = 1,2-dichloroethane, DCM = dichloromethane, K₂CO₃ = potassium carbonate, MeCN = acetonitrile.

IR Titrations

General procedure – FeCl₃ with additives. FeCl₃ (162 mg, 1 mmol) was added to a flame-dried 25 mL 2-neck round bottom flask under inert atmosphere with a stir bar. The flask was
sealed with a septa, taken out of the glovebox, and an argon balloon was inserted. The flask was placed in a hot plate set to 30 °C. Anhydrous DCE was added (6 mL, 166.7 mM). Distilled chlorosilane was added, and the solution was stirred for 15 minutes to reach temperature. Dry 22, 23 was added in 10 µL increments to the 2\textsuperscript{nd} equivalence point of carbonyl, then 20 µL increments were added until 4\textsuperscript{th} equivalence point was reached.

**Figure S1:** Titration of 22 with FeCl\textsubscript{3} and 1 equiv TMSCl at 30 °C (0.127 mL, 166.7 mM) from 0-0.217 M 22.

**Figure S2:** Titration of 22 with FeCl\textsubscript{3} and 1 equiv TMSCl at 30 °C (0.127 mL, 166.7 mM) from 0.217-0.651 M 22. Select data points omitted from Figure 3, D for clarity.
**Figure S3:** Titration of 22 with FeCl₃ and 2 equiv TMSCl at 30 °C (0.254 mL, 333.3 mM) from 0-0.192 M 22.

**Figure S4:** Titration of 22 with FeCl₃ and 2 equiv TMSCl at 30 °C (0.254 mL, 333.3 mM) from 0.192-0.638 M 22. Select data points omitted from Figure 3, G for clarity.

**Figure S5:** Titration of 2 with FeCl₃ and 1 equiv TMSCl at 30 °C (0.127 mL, 166.7 mM) from 0-0.173 M 2.
**Figure S6:** Titration of 2 with FeCl$_3$ and 1 equiv TMSCl at 30 °C (0.127 mL, 166.7 mM) from 0.173-0.629 M 2. Select data points omitted from Figure 3, E for clarity.

**Figure S7:** Titration of 2 with FeCl$_3$ and 2 equiv TMSCl at 30 °C (0.254 mL, 333.3 mM) from 0-0.166 M 2.

**Figure S8:** Titration of 2 with FeCl$_3$ and 2 equiv TMSCl at 30 °C (0.254 mL, 333.3 mM) from 0.166-0.606 M 2. Select data points omitted from Figure 3, H for clarity.
Figure S9: Titration of 2 with FeCl$_3$ and 3 equiv TMSCl at 30 °C (0.381 mL, 500.0 mM) from 0-0.148 M 2.

Figure S10: Titration of 2 with FeCl$_3$ and 3 equiv TMSCl at 30 °C (0.381 mL, 500.0 mM) from 0.148-0.594 M 2.

Figure S11: Titration of 2 with FeCl$_3$ and 4 equiv TMSCl at 30 °C (0.508 mL, 666.7 mM) from 0-0.146 M 2.
**Figure S12:** Titration of 2 with FeCl₃ and 4 equiv TMSCl at 30 °C (0.508 mL, 666.7 mM) from 0.146-0.583 M 2.

**Figure 13:** Titration of 23 with FeCl₃ at 30 °C from 0-0.243 M 23. Select data points omitted from Figure 3, C for clarity.

**Figure S14:** Titration of 23 with FeCl₃ at 30 °C from 0.243-0.687 M 23.
Figure S15: Titration of 23 with FeCl$_3$ and 1 equiv TMSCl at 30 °C (0.127 mL, 166.7 mM) from 0-0.179 M 23. Select data points omitted from Figure 3, F for clarity.

Figure S16: Titration of 23 with FeCl$_3$ and 1 equiv TMSCl at 30 °C (0.127 mL, 166.7 mM) from 0.179-0.672 M 23. Select data points omitted from Figure 3, F for clarity.

Figure S17: Titration of 23 with FeCl$_3$ and 2 equiv TMSCl at 30 °C (0.254 mL, 333.3 mM) from 0-0.175 M 23. Select data points omitted from Figure 3, I for clarity.
**Figure S18:** Titration of 23 with FeCl₃ and 2 equiv TMSCl at 30 °C (0.254 mL, 333.3 mM) from 0.175-0.620 M 23. Select data points omitted from Figure 3, I for clarity.

**Figure S19:** Titration of 2 with FeCl₃ and 1 equiv TBSCl at 30 °C (0.214 mL, 205.9 mM) from 0-0.170 M 2.

**Figure S20:** Titration of 2 with FeCl₃ and 1 equiv TBSCl at 30 °C (0.214 mL, 205.9 mM) from 0.170-0.607 M 2.
**Figure S21**: Titration of 2 with FeCl₃ and 1 equiv Ph₃SiCl at 30 °C (0.296 g, 100.4 mM) from 0-0.161 M 2.

**Figure S22**: Titration of 2 with FeCl₃ and 1 equiv Ph₃SiCl at 30 °C (0.296 g, 100.4 mM) from 0.161-0.628 M 2.

**General procedure – GaCl₃ with TMSCl additive.**

GaCl₃ (176 mg, 1 mmol) was added to a flame-dried 25 mL 2-neck round bottom flask under inert atmosphere with a stir bar. The flask was sealed with a septa, taken out of the box, and an argon balloon was inserted. The flask was placed in a hot plate set to 30 °C. Anhydrous DCE was added (6 mL, 166.7 mM). In additive titrations, distilled TMSCl was then included, and the solution was stirred for 15 minutes to reach temperature. Dry 2 was added in 10 μL increments to the 2nd equivalence point of carbonyl, then 20 μL increments were added until 4th equivalence point was reached.
Figure S23: Titration of 2 with GaCl₃ and at 30 °C from 0-0.180 M 2. Select data points omitted from Figure 7, A for clarity.

Figure S24: Titration of 2 with GaCl₃ and at 30 °C from 0.180-0.666 M 2. Select data points omitted from Figure 7, A for clarity.

Figure S25: Titration of 2 with GaCl₃ and 1 equiv TMSCl at 30 °C (0.127 mL, 166.7 mM) from 0-0.173 M 2. Select data points omitted from Figure 7, B and C for clarity.
Figure S26: Titration of 2 with GaCl₃ and 1 equiv TMSCl at 30 °C (0.127 mL, 166.7 mM) from 0.173-0.928 M 2. Select data points omitted from Figure 7, B and C for clarity.

Figure S27: Titration of 2 with GaCl₃ and 2 equiv TMSCl at 30 °C (0.255 mL, 333.3 mM) from 0-0.172 M 2.

Figure S28: Titration of 2 with GaCl₃ and 2 equiv TMSCl at 30 °C (0.255 mL, 333.3 mM) from 0.172-0.639 M 2.

General Procedure – Titration of FeCl₃-carbonyl Lewis pair solutions with TMSCl.
FeCl₃ (162 mg, 1 mmol) was added to a flame-dried 25 mL 2-neck round bottom flask under inert atmosphere with a stir bar. The flask was sealed with septa, taken out of the box, and an argon balloon was inserted. The flask was placed in a hot plate set to 30 °C. Anhydrous DCE was added. Dry 22, 2, or 23 was added. In titrations of FeCl₃ and 1 or less than 1 equiv carbonyl, TMSCl was added in 20 µL increments to the 4th equivalence point. In titrations involving greater than 1 equiv carbonyl relative to FeCl₃, TMSCl was added in 20 µL increments to the 5th equivalence point, then 100 µL increments were added until the 10th equivalence point.

**Figure S29**: Titration of 2 (0.102 mL, 0.164 M) and FeCl₃ with TMSCl at 30 °C from 0-0.322 M TMSCl. Select data points omitted from Figure 4, B for clarity.

**Figure S30**: Titration of 2 (0.102 mL, 0.164 M) and FeCl₃ with TMSCl at 30 °C from 0.322-0.619 M TMSCl. Select data points omitted from Figure 4, B for clarity.
Figure S31: Titration of 22 (0.0515 mL, 0.132 M) and FeCl₃ with TMSCl at 30 °C from 0-0.629 M TMSCl. Select data points omitted from Figure 6 for clarity.

Figure S32: Titration of 2 (0.204 mL, 0.322 M) and FeCl₃ with TMSCl at 30 °C from 0-0.653 M TMSCl.

Figure S33: Titration of 2 (0.204 mL, 0.322 M) and FeCl₃ with TMSCl at 30 °C from 0.653 M-1.40 M TMSCl.
Figure S34: Titration of 22 (0.149 mL, 0.325 M) and FeCl₃ with TMSCl at 30 °C from 0 M-0.344 M TMSCl.

Figure S35: Titration of 22 (0.149 mL, 0.325 M) and FeCl₃ with TMSCl at 30 °C from 0.344 M-1.41 M TMSCl.

Figure S36: Titration of 23 (0.083 mL, 0.167 M) and FeCl₃ with TMSCl at 30 °C from 0-0.418 M TMSCl.
Figure S37: Titration of 23 (0.083 mL, 0.167 M) and FeCl₃ with TMSCl at 30 °C from 0.418-0.621 M TMSCl.

Conductance Analysis

General procedure for conductance measurements:

In a glove box, FeCl₃ (162 mg, 1 mmol) was added to a flame-dried 20 mL scintillation vial charged with a stir bar. Anhydrous DCE was added (6 mL, 166.7 mM) along with chlorosilane additive, if applicable. The conductance of the mixture was observed via a VWR Portable Conductance Meter. Carbonyl was incrementally titrated until 5 equivalents of carbonyl were reached. Conductance after each of addition of carbonyl was observed and recorded as an average of three measurements. Between each reading probe was rinsed with DCE and solution was stirred for 10 minutes to allow equilibration. Control experiments in which a slurry of FeCl₃ is titrated with 22, 2 were previously reported.³¹ Control experiments in which a solution of GaCl₃ is titrated with 2 were previously reported.³¹ Plotting and trendline analysis were performed with Microsoft Excel.
**Figure S38:** Solution conductance FeCl$_3$ (1 mmol in 6 mL DCE) and TMSCl (0 mmol, 1 mmol, or 2 mmol) with increasing amounts of 22 at 25 °C.

**Figure S39:** Solution conductance FeCl$_3$ (1 mmol in 6 mL DCE) and TMSCl (0 mmol, 1 mmol, or 2 mmol) with increasing amounts of 2 at 25 °C.

**Figure S40:** Solution conductance FeCl$_3$ (1 mmol in 6 mL DCE) and TMSCl (0 mmol, 1 mmol, or 2 mmol) with increasing amounts of 23 at 25 °C.
Figure S41: Solution conductance GaCl$_3$ (1 mmol in 6 mL DCE) and TMSCl (0 mmol or 1 mmol) with increasing amounts of 2 at 25 °C.

Table S1: Conductivity measured between 22 and FeCl$_3$ found in Figure 5.$^2$

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**Table S2:** Conductivity measured between 22 and FeCl$_3$ with 1 equiv TMSCl found in Figure 5.

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**Table S3:** Conductivity measured between 22 and FeCl$_3$ with 2 equiv TMSCl found in Figure 5.

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Table S4: Conductivity measured between 2 and FeCl$_3$ with 1 equiv TBSCl.

Conductivity ($\mu$S/cm-1)

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<th>Average</th>
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Table S5: Conductivity measured between 2 and FeCl$_3$ with 1 equiv Ph$_3$SiCl.

Conductivity ($\mu$S/cm-1)

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<th>2 (equiv)</th>
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<th>Trial 3</th>
<th>Average</th>
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**Table S6**: Conductivity measured between 22 and TMSCl (0.127 mL, 1 mmol) in the absence of FeCl₃.

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**Table S7**: Conductivity measured between 2 and FeCl₃ found in Figure 5.²

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</thead>
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Table S8: Conductivity measured between 2 and FeCl₃ with 1 equiv TMSCl found in Figure 5.

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<th>Average</th>
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Table S9: Conductivity measured between 2 and FeCl₃ with 2 equiv TMSCl found in Figure 5.

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Table S10: Conductivity measured between 2 and TMSCl (0.127 mL, 1 mmol) in the absence of FeCl₃.

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Table S11: Conductivity measured between 23 and FeCl₃ found in Figure 5.

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<th>Trial 3</th>
<th>Average</th>
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Table S12: Conductivity measured between 23 and FeCl₃ with 1 equiv TMSCl found in Figure 5.

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Table S13: Conductivity measured between 23 and FeCl₃ with 2 equiv TMSCl found in Figure 5.

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<th>23 (equiv)</th>
<th>Conductivity (μS/cm)</th>
<th>Trial 1</th>
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<th>Trial 3</th>
<th>Average</th>
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Table S14: Conductivity measured between 2 and GaCl₃ found in Figure 7, D.

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Table S15: Conductivity measured between 2 and GaCl₃ with 1 equiv TMSCl found in Figure 7, D.

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<th>Average</th>
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</table>

General procedure for conductance measurements of representative COM reaction.
Figure S42: Representative COM reactions employed for conductance measurements. Baseline reaction employed 10 mol% FeCl₃ catalyst (conditions 1) while experimental reaction employed 10 mol% FeCl₃ and 10 mol% TMSCl catalyst (Conditions 2).

Starting material was synthesized according to previous literature procedure.¹⁷⁶ In an inert atmosphere glove box, FeCl₃ (10 mol%, 4.48 mg) was added to a flame-dried 20 mL scintillation vial charged with a stir bar. Anhydrous DCE was added (16.5 mL, 25 mM) along with distilled TMSCl (10 mol%, 5.24 µL), if applicable. The conductance probe was inserted into the solution, and baseline measurement absent substrate was recorded. Substrate (413 µmol, 92.2 µL) was added to initiate reaction and timer started concurrently. The conductance of the mixture was observed via a Fisher Traceable Portable Conductance Meter. Measurements were taken at 30 second intervals until 5 minutes, then at 60 second intervals until 10 minutes. After 10 minutes, additional measurements 15 and 20 minutes. Two trials for each set of reaction conditions were performed, and the average of the two are plotted in Figure S43. Plotting and trendline analysis were performed with Microsoft Excel and GraphPad Prism 9.
Figure S43: Solution conductance through time of COM reactions. Conditions 1 depicted with gold. Conditions 2 depicted with maroon.

Table S15: Conductivity trials measured for conditions 1 COM reaction.

<table>
<thead>
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<th>Time (sec)</th>
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</thead>
<tbody>
<tr>
<td></td>
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Table S16: Conductivity trials measured for conditions 2 COM reaction.

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<td>900</td>
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<tr>
<td>1200</td>
<td>28.80</td>
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Kinetic Analysis

Starting amino acid derivative was synthesized according to previous literature procedure.78

Procedure for FeCl₃ inhibition model.

50 mol% FeCl₃. FeCl₃ (15 mg, 92.3 µmol) was added to a flame-dried 25 mL round bottom flask under an inert atmosphere with a stir bar. The flask was sealed with a septum and moved to the hood and an argon line was inserted. Anhydrous DCE was added (18 mL, 10 mM final concentration). The flask was placed in a jacketed beaker connected to a circulator (0 °C). The slurry was stirred for 15 min to reach temperature. 20 was prepared as a stock solution of
185 μmol substrate per 0.5 mL anhydrous DCE. 20 solution was added (0.5 mL solution) via syringe to the reaction mixture. 50 μL aliquots were sampled via syringe. 10 μL reaction solution was dissolved 980 μL 2:1 MeCN:H₂O containing 10 μL of 1.25 mg/mL naphthalene in MeCN. Samples were further diluted by adding 100 μL to 900 μL of 2:1 MeCN:H₂O. Samples were analyzed via reverse-phase UPLC, using a Waters Acquity H-Class UPLC with a transmission UV/Vis detector and an Acquity UPLC BEH C8 1.7 μm column. Plotting and trendline analysis were performed with GraphPad Prism 9.

**Table S17**: Inhibition model kinetics with 50 mol% FeCl₃.

<table>
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<th>Time (s)</th>
<th>Trial 1 [20] (mM)</th>
<th>Trial 2 [20] (mM)</th>
<th>Trial 3 [20] (mM)</th>
<th>Average [20] (mM)</th>
<th>Standard Deviation</th>
<th>% Error</th>
</tr>
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<td>10</td>
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</table>
50 mol% FeCl₃ 50 mol% 2. FeCl₃ (15 mg, 92.3 µmol) was added to a flame-dried 25 mL round bottom flask under an inert atmosphere with a stir bar. The flask was sealed with a septum and moved to the hood and an argon line was inserted. Anhydrous DCE (18 mL, 10 mM final concentration) and 2 (9.80 mg, 9.42 µL, 92.3 µmol). The flask was placed in a jacketed beaker connected to a circulator (0°C). The slurry was stirred for 15 min to reach temperature. 20 was prepared as a stock solution of 185 µmol substrate per 0.5 mL anhydrous DCE. 20 solution was added (0.5 mL solution) via syringe to the reaction mixture. 50 µL aliquots were sampled via syringe. 10 µL reaction solution was dissolved 980 µL 2:1 MeCN:H₂O containing 10 µL of 1.25 mg/mL naphthalene in MeCN. Samples were further diluted by adding 100 µL to 900 µL of 2:1 MeCN:H₂O. Samples were analyzed via reverse-phase UPLC, using a Waters Acquity H-Class UPLC with a transmission UV/Vis detector and an Acquity UPLC BEH C8 1.7 µm column. Plotting and trendline analysis were performed with GraphPad Prism 9.

Table S18: Inhibition model kinetics with 50 mol% FeCl₃ and 50 mol% 2.
50 mol% FeCl₃ 50% 2

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<th>Trial 2 [20] (mM)</th>
<th>Trial 3 [20] (mM)</th>
<th>Average [20] (mM)</th>
<th>Standard Deviation</th>
<th>% Error</th>
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<td>5.5276</td>
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50 mol% 50 mol% 2 100 mol% TMSCl. FeCl₃ (15 mg, 92.3 µmol) was added to a flame-dried 25 mL round bottom flask under an inert atmosphere with a stir bar. The flask was sealed with a septum and moved to the hood and an argon line was inserted. Anhydrous DCE (18 mL, 10 mM final concentration), 2 (9.80 mg, 9.42 µL, 92.3 µmol), and TMSCl (20.1 mg, 23.4 µL, 185 µmol). The flask was placed in a jacketed beaker connected to a circulator (0°C). The slurry was stirred for 15 min to reach temperature. 20 was prepared as a stock solution of 185 µmol substrate per 0.5 mL anhydrous DCE. 20 solution was added (0.5 mL solution) via syringe to the reaction mixture. 50 µL aliquots were sampled via syringe. 10 µL reaction solution was
dissolved 980 μL 2:1 MeCN:H₂O containing 10 μL of 1.25 mg/mL naphthalene in MeCN.

Samples were further diluted by adding 100 μL to 900 μL of 2:1 MeCN:H₂O. Samples were analyzed via reverse-phase UPLC, using a Waters Acquity H-Class UPLC with a transmission UV/Vis detector and an Acquity UPLC BEH C8 1.7 μm column. Plotting and trendline analysis were performed with GraphPad Prism 9.

**Table S19**: Inhibition model kinetics with 50 mol% FeCl₃, 50 mol% 2 and 50 mol% TMSCl.

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![Graph showing inhibition model kinetics](image)
Procedure for FeCl\textsubscript{3}/TMSCl Rate Order Determination. FeCl\textsubscript{3} was added to a flame-dried 25 mL round bottom flask under an inert atmosphere with a stir bar. The flask was sealed with a septum and moved to the hood and an Argon line was inserted. Anhydrous DCE (18 mL, 10 mM final concentration) and TMSCl. The flask was placed in a jacketed beaker connected to a circulator (0°C). The slurry was stirred for 15 min to reach temperature. 20 was prepared as a stock solution of 185 µmol substrate per 0.5 mL anhydrous DCE. 20 solution was added (0.5 mL solution) via syringe to the reaction mixture. 50 µL aliquots were sampled via syringe. 10 µL reaction solution was dissolved 980 µL 2:1 MeCN:H\textsubscript{2}O containing 10 µL of 1.25 mg/mL naphthalene in MeCN. Samples were further diluted by adding 100 µL to 900 µL of 2:1 MeCN:H\textsubscript{2}O. Samples were analyzed via reverse-phase UPLC, using a Waters Acquity H-Class UPLC with a transmission UV/Vis detector and an Acquity UPLC BEH C8 1.7 µm column. Plotting and trendline analysis were performed with GraphPad Prism 9.

Table S20: Raw Data, 8 mol% FeCl\textsubscript{3} 10 mol% TMSCl.

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Table S22: Raw Data, 8 mol% FeCl₃ 30 mol% TMSCl.

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Table S23: Raw Data, 8 mol% FeCl₃ 40 mol% TMSCl.

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Table S24: Raw Data, 8 mol% FeCl₃ 50 mol% TMSCl.

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Table S26: Raw Data, 18 mol% FeCl₃ 30 mol% TMSCl.

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Table S27: Raw Data, 20 mol% FeCl₃ 30 mol% TMSCl.

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Table S29: Raw Data, 13.4 mol% FeCl₃ 10 mol% TMSCl.

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### Table S30: Raw Data, 18 mol% FeCl₃ 10 mol% TMSCl.

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### Table S31: Raw Data, 20 mol% FeCl₃ 10 mol% TMSCl.

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<th>%Error</th>
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Table S32: Raw Data, 25 mol% FeCl$_3$ 10 mol% TMSCl.

25 mol% FeCl$_3$ 10 mol% TMSCl

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Rate orders. The rate order for the various systems were determined using a Van’t Hoff plot. Rates were determined plotting the natural logarithm of concentration vs time and finding the slope of the line within the linear portion of the plot.

Table S33: Rate order determination of TMSCl and FeCl$_3$.

8 mol% FeCl$_3$ 10 mol% TMSCl

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<tr>
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<td><strong>Trial 3</strong></td>
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Figure S44: Plot of Ln [SM] (mM) vs time (s) of each system (left) and the corresponding Van’t Hoff plot (right).

Table S34: Order Determination FeCl$_3$ with varying amounts of excess TMSCl:

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20 mol% FeCl₃ 30 mol% TMSCl

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25 mol% FeCl₃ 30 mol% TMSCl

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Figure S45: Plot of Ln [SM] (mM) vs time (s) of each system (left) and the corresponding Van’t Hoff plot (right).

Table S35: Order Determination FeCl₃ with TMSCl and varying amounts of excess FeCl₃:

13.4 mol% FeCl₃ 10 mol% TMSCl

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**Procedure for GaCl₃/TMSCl Rate Order Determination.**

Anhydrous DCE (10 mM final concentration) was added to a flame dried 25ml round bottom flask under an inert atmosphere with a stir bar. Catalyst was prepared as a stock solution of 18.5 μmol GaCl₃ per 1 mL of anhydrous DCE. GaCl₃ and TMSCl was added to the flask and sealed. The flask was placed in a jacketed beaker connected to a circulator (0 °C). The solution was stirred for 15 min to reach temperature. 20 was prepared as a stock solution of 185 μmol substrate per 0.5 mL anhydrous DCE. 20 solution was added (0.5 mL solution) via syringe to the reaction mixture. 50 μL aliquots were sampled via syringe. 10 μL reaction solution was dissolved 990 μL 2:1 MeCN:H₂O containing 10 μL of 1.25 mg/mL naphthalene in 2:1 MeCN:H₂O. Samples were further diluted by adding 100 μL to 900 μL of 2:1 MeCN:H₂O. Samples were analyzed via reverse-phase UPLC, using a Waters Acquity H-Class UPLC with a transmission UV/Vis detector and an Acquity UPLC BEH C8 1.7 μm column. Plotting and trendline analysis were performed with GraphPad Prism 9.

**Raw Data.**

![Figure S46: Plot of Ln [SM] (mM) vs time (s) of each system (left) and the corresponding Van’t Hoff plot (right).](image-url)
**Table S36:** Raw data. 10 mol% GaCl₃ 10 mol% TMSCl.

![Chemical Structure](image_url)

### 10 mol% GaCl₃ 10 mol% TMSCl

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**Table S37:** Raw data. 10 mol% GaCl₃ 20.3 mol% TMSCl.

### 10 mol% GaCl₃ 20.3 mol% TMSCl

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161
Table S38: Raw data. 10 mol% GaCl$_3$ 30 mol% TMSCl.

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Rate Orders. The rate order for the various systems were determined using a Van’t Hoff plot. Rates were determined plotting the natural logarithm of concentration vs time and finding the slope of the line within the linear portion of the plot.

Table S39: Rate order determination GaCl$_3$ with varying amounts of TMSCl, processed data.

<table>
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<tr>
<th>Time (s)</th>
<th>Trial 1 LN ([20] (mM))</th>
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10 mol% GaCl$_3$ 10 mol% TMSCl Set 1 (July 18th 2022)

Rate Orders. The rate order for the various systems were determined using a Van’t Hoff plot. Rates were determined plotting the natural logarithm of concentration vs time and finding the slope of the line within the linear portion of the plot.

Table S39: Rate order determination GaCl$_3$ with varying amounts of TMSCl, processed data.
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<th>LN ([20] mM)</th>
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**10 mol% GaCl$_3$ 20.3 mol% TMSCl**

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**Table S40:** Second set of Data for 30-X mol% TMSCl.

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**10 mol% GaCl$_3$ 30 mol% TMSCl Set 1 (July 18th 2022)**

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10 mol% GaCl₃ 40.5 mol% TMSCl Set 2 (Aug 5th 2022)

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Figure S47: Plot of Ln [SM] (mM) vs time (s) of each system for data set 1 (top left) and data set 2 (top right) and the corresponding Van’t Hoff plots (bottom left).

**Synthetic Procedures**

**Procedures for FeCl₃/TMSCl Catalyzed Mukaiyama Aldol.**

![Chemical reaction diagram](image)

Figure S48: Synthesis of acetophenone-derived silyl enol ether.
Sodium iodide (31 mmol) was dissolved in acetonitrile (0.806 M). The resulting solution was added dropwise over 45 minutes to a mixture of S1 (25 mmol), TMSCl (31 mmol), and half the triethylamine (16.6 mmol) in hexanes (1 M). The solution was stirred for 1 hour at room temperature. Then the other portion of triethylamine (16.6 mmol) was added. The reaction was then allowed to stir for about 1.5 hours or until judged complete by TLC. Reaction mixture was added to separatory funnel and acetonitrile phase was extracted with 2 X 50 mL of hexanes. The hexanes phases were washed with 2 X 50 mL of DI water and 2 X 50 mL of saturated NH₄Cl. Organic phases were dried Na₂SO₄ and concentrated under reduced pressure. The crude product was purified via fractional distillation under reduced pressure (b.p. 93-97 ºC) to afford silyl enol ether 35. ¹H NMR (500 mHz, CDCl₃): δ 0.32 (s, 9H), 4.48 (s, 1H), 4.99 (s, 1H), 7.41-7.34 (m, 3H), 7.69-7.67 (m, 2H)

Figure S49: Mukaiyama aldol with FeCl₃ and TMSCl.

In an inert atmosphere glovebox, FeCl₃ (0.2 mmol) was weighed into the reaction flask. A septa was placed in the flask and it was removed from the glovebox. Once attached to the Schlenk line, dry DCM (0.1 M) from a solvent purification system was added. Flask was placed in an isopropanal and dry ice bath and allowed to cool to -78 ºC. Once cooled, distilled TMSCl (0.2 mmol) was added. After 5 minutes of stirring, 2 (1 mmol) distilled over sieves was added to the flask via syringe. Finally, 35 (1.2 mmol) was added and reaction was allowed to stir at -78 ºC until judged complete by TLC (approximately 30 minutes). Completed reaction mixture was passed through a silica plug and concentrated under reduced pressure yielding Mukaiyama Aldol
product 36 in 93% yield. (500 MHz, CDCl$_3$): $\delta =$ 3.39 (d, J = 10 Hz, 2H), 3.74 (s, J = 1H), 5.38 (dd, J = 5 Hz, 10 Hz, 1H), 7.29 − 7.31 (m, 1H), 7.37 − 7.41 (m, 2H), 7.44 − 7.47 (m, 4H), 7.57 − 7.61 (m, 1H), 7.95 − 7.97 (m, 2H).

NMR Spectra

GaCl$_3$ $^1$H NMR
**General procedure for sample preparation.** Flame dried NMR tubes were brought into an inert atmosphere glove box for sample prep. In 25 mL glass vials inside the glovebox, GaCl$_3$ (0.1 mmol) was added to 0.5 mL CDCl$_3$ followed by relevant additives, 2 (0.6 mmol) and/or TMSCl (0.1 mmol). NMR tubes were capped and removed from inert atmosphere glovebox.

![Figure S50: 1H NMR spectra overlay of the region between 0.34 and 0.86 ppm from top to bottom: 0.1 mmol GaCl$_3$ with 0.6 equiv 2 and 1 equiv TMSCl. 0.1 mmol GaCl$_3$ with 0.6 equiv 2. 0.1 mmol GaCl$_3$ with 1 equiv TMSCl. 0.1 mmol TMSCl with 0.6 equiv 2. 0.6 mmol 2. 0.1 mmol TMSCl.](image)

**Computational Details**

All quantum chemical calculations utilize density functional theory (DFT) as implemented in the Q-Chem 5.1 electronic structure program.$^{177}$ Geometry optimizations were carried out using the B97-D density functional employing the double-$\zeta$, 6-31+G* basis set. Initial transition state (TS) searches were performed using the reaction discovery tools of the Zimmerman group, in particular, the double-ended Growing String Method (GSM). GSM locates minimum energy reaction paths and the associated transition states, without requiring detailed prior knowledge of the transition state structures.$^{178}$ To ascertain the true nature of all stationary
points, normal mode analysis was conducted at the B97-D/6-31+G* level of theory. These frequency computations were further used to assign theoretical IR spectra of the predicted structures. Following this, single point solvent phase calculation on the gas phase optimized geometries were performed using the CPCM solvent model, with 1,2-dichloroethane (DCE) as the solvent. CPCM energies were computed using the ωB97X-D3 density functional and the def2-TZVP basis set in the ORCA quantum chemical package.¹⁷⁹

Thermal corrections to enthalpies ($H_{freq}$) and Gibbs free energies ($G_{freq}$) were obtained from frequency calculations in the gas phase. For the solvent phase free energies, entropic corrections are significantly quenched in the solvent phase as compared to those in the gas phase. Experiments have shown solutes lose about 50%-60% of their entropy on going from the gas phase to the solution phase. Therefore, the correction scheme based on works by Wertz and Ziegler and others was used, where the entropy of any solute is estimated to be 0.5 $S(g)$, with $S(g)$ being the entropy of the solute in the gas phase.¹⁸⁰,¹⁸¹ Reported energies for intermediates and activation barriers are solvent phase (DCE) free energies obtained using the ωB97X-D3/def2-TZVP/CPCM level of theory in the sextet spin state unless mentioned otherwise.

The gas-phase entropy is given by

$$-S(g) = \frac{[G(g) - H(g)]}{T} = \frac{[G_{freq} - H_{freq}]}{T}$$

$$S(l) = 0.5 \times S(g)$$

$$H(l) = E(l) + Hcorr$$, $E(l)$ is solvent phase total energy.

Therefore, $G(l) = [H(l) + T \times S(l)]$
**Figure S52.** Possible aggregation behavior of carbonyl byproduct with active catalyst. Free energies in kcal/mol are shown with enthalpies in parentheses. The uphill thermodynamics makes these pathways unfavorable.

**Table S41: XYZ Coordinates for All Structures.**

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H   1.51169867  7.26064183  4.04695470
H   2.00872858  5.10624452  4.10654842
H   1.51169867  7.26064183  4.04695470
Si   2.37842383  0.10897596 -0.73937223
C   2.24858007  0.52154777  1.08438877
H   2.38598848 -0.40648347  1.66084583
H   3.01350211  1.24293987  1.41423931
H   1.26090676  0.93877649  1.32984452
C   0.89672040 -0.76989993 -1.48822837
H   1.01640430 -0.91385047 -2.57405084
H   0.77864638 -1.75514051 -1.01364958
H  -0.01753636 -0.18436857 -1.30812521
C   4.05911009  0.52461441  1.30734446
H   4.10966875  0.60165471 -2.40563832

aggregate-complex2
Cl -0.88472542  2.32729678  0.30417601
Fe  1.14120185  3.97525408  2.19972216
Cl  1.43345557  5.81495805  0.46924696
Cl  2.34909692  3.17784540  2.91388823
C   2.03143247  2.84640510 -1.12698241
H   1.92925735  2.94399842 -0.03908304
C   1.90728619  4.01686100 -1.94406879
C   1.62608403  5.24895457 -1.29596023
C   2.04616091  3.96276990  3.3520556
C   1.48526041  6.41174075  2.05685756
H   1.50529741  5.27620307 -0.21316704
C   1.90887857  5.12969075  4.10344624
C   2.25167543  3.00577285 -3.83766426
C   1.62755152  6.35189176 -3.45323482
H   1.24809718  7.35419634 -1.56389329
H   2.00872858  5.10103641 -5.18925842
H   1.51169867  7.26064183 -4.04695470
Si   2.37842383  0.10897596 -0.73937223
C   2.24858007  0.52154777  1.08438877
H   2.38598848  0.40648347  1.66084583
H   3.01350211  1.24293987  1.41423931
H   1.26090676  0.93877649  1.32984452
C   0.89672040  0.76989993 -1.48822837
H   1.01640430  0.91385047 -2.57405084
H   0.77864638 -1.75514051 -1.01364958
H  -0.01753636 -0.18436857 -1.30813251
C   4.05911009 -0.52461441 -1.30734446
H   4.10966875  0.60165471 -2.40563832
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<th></th>
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<td>1.60192713</td>
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<td>H</td>
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APPENDIX C

SUPPLEMENTARY INFORMATION FOR CHAPTER 4
General Information

General Laboratory Procedures.

All moisture-sensitive reactions were performed under an atmosphere of argon in flame-dried round bottom flasks or glass vials fitted with rubber septa. Stainless steel syringes were used to transfer air or moisture-sensitive liquids. Flash chromatography was performed using silica gel Silia Flash® 40-63 micron (230-400 mesh) from Silicycle. Nuclear magnetic resonance (NMR) spectra (\(^1\)H, \(^13\)C, 135 DEPT, H-H COSY, HMBC, HSQC, NOESY) were recorded with a Bruker Topspin 500 MHz instrument equipped with a Prodigy Cryoprobe in CdCl₃. Chemical shifts are reported in ppm and analysis was performed in Mnova. Fourier transform-infrared (FTIR) spectroscopy was performed using a Thermo Nicolet NEXUS 470 FTIR. HRCI MS was obtained with an Agilent 7200 GC-QTOF/MS.

Materials and Instrumentation.

All chemicals were purchased from Alfa Aesar, VWR, Matheson Coleman and Bell, Beantown Chemicals, TCI, Pfaltz & Bauer, or Acros.

Reaction Conditions Screens

General Procedure for reaction screens.

In an Inert atmosphere glovebox, Lewis acid was weighed directly into 7 mL vial which was then capped and removed from the glovebox. Solvent was then added to a 1 M concentration. Vial was set on a stir plate and 1 mmol of benzaldehyde was added. Reaction was allowed to stir for 5 minutes. Then, 1 mmol of \(\alpha\)-pinene was added. Reactions were tracked with TLC until completion. Yields were determined via \(^1\)H NMR analysis against DMF as an internal standard unless otherwise noted.
Table S1. Solvent and temperature screens.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Temperature (°C)</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH₂Cl₂</td>
<td>25</td>
<td>6%</td>
</tr>
<tr>
<td>2</td>
<td>Et₂O</td>
<td>25</td>
<td>3%</td>
</tr>
<tr>
<td>3</td>
<td>Toluene</td>
<td>25</td>
<td>1%</td>
</tr>
<tr>
<td>4</td>
<td>MeCN</td>
<td>25</td>
<td>0%</td>
</tr>
<tr>
<td>5</td>
<td>MeOH</td>
<td>25</td>
<td>0%</td>
</tr>
<tr>
<td>6</td>
<td>DCE</td>
<td>-10</td>
<td>44%</td>
</tr>
<tr>
<td>7</td>
<td>DCE</td>
<td>0</td>
<td>53%</td>
</tr>
<tr>
<td>8*</td>
<td>DCE</td>
<td>25</td>
<td>99%</td>
</tr>
<tr>
<td>9</td>
<td>DCE</td>
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*Isolated yield reported

Table S2. Lewis acid screen.

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<tr>
<td>1</td>
<td>ZnCl₂</td>
<td>9%</td>
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<tr>
<td>2*</td>
<td>InCl₃</td>
<td>65%</td>
</tr>
<tr>
<td>3</td>
<td>AlCl₃</td>
<td>3%</td>
</tr>
<tr>
<td>4</td>
<td>AgOTf</td>
<td>8%</td>
</tr>
<tr>
<td>5*</td>
<td>FeCl₃</td>
<td>99%</td>
</tr>
<tr>
<td>6</td>
<td>BCl₃</td>
<td>10%</td>
</tr>
<tr>
<td>7</td>
<td>BF₃•OEt₂</td>
<td>77%</td>
</tr>
<tr>
<td>8*</td>
<td>GaCl₃</td>
<td>87%</td>
</tr>
<tr>
<td>9</td>
<td>FeOTf</td>
<td>35%</td>
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<tr>
<td>10</td>
<td>I₂</td>
<td>7%</td>
</tr>
<tr>
<td>11</td>
<td>TiCl₄</td>
<td>4%</td>
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<tr>
<td>12</td>
<td>CeCl₃</td>
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<td>13</td>
<td>SnCl₄</td>
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<td>14</td>
<td>CuCl₂</td>
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<td>15*</td>
<td>FeCl₃•6H₂O</td>
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*Isolated yield reported
**Table 3. Lewis acid loading mol% screen.**

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<th>Lewis acid</th>
<th>Loading (mol%)</th>
<th>Yield %</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>FeCl₃</td>
<td>1</td>
<td>29%</td>
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<td>2*</td>
<td>FeCl₃</td>
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<td>99%</td>
</tr>
<tr>
<td>3*</td>
<td>FeCl₃</td>
<td>10</td>
<td>99%</td>
</tr>
<tr>
<td>4*</td>
<td>FeCl₃</td>
<td>20</td>
<td>15%</td>
</tr>
<tr>
<td>5</td>
<td>FeCl₃</td>
<td>50</td>
<td>10%</td>
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<tr>
<td>6</td>
<td>FeCl₃</td>
<td>75</td>
<td>4%</td>
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<td>7</td>
<td>FeCl₃</td>
<td>100</td>
<td>3%</td>
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<tr>
<td>8</td>
<td>FeCl₃·6H₂O</td>
<td>1</td>
<td>20%</td>
</tr>
<tr>
<td>9*</td>
<td>FeCl₃·6H₂O</td>
<td>5</td>
<td>82%</td>
</tr>
<tr>
<td>10</td>
<td>FeCl₃·6H₂O</td>
<td>10</td>
<td>75%</td>
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*Isolated yield reported

**NMR Data & Analysis NMR Analysis Methods**

Theoretical shifts were calculated using DFT (see computational details section). Theoretical shifts were compared with experimental shifts obtained on a Bruker Topspin 500 MHz NMR instrument for 5b. Experimental shifts for 5a were obtained from the reports of Saikia¹⁷² and Singaram & Mariumuthu.¹⁷⁴ In the case that a chemical shift was reported as a range of ppm values, the median value was used for analysis.
Table 4. Experimental and theoretical chemical shifts for 5b.

<table>
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<tr>
<th>Proton</th>
<th>Experimental Shift (ppm)</th>
<th>Theoretical shift</th>
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<tbody>
<tr>
<td>H_a</td>
<td>0.91</td>
<td>0.71</td>
</tr>
<tr>
<td>H_b</td>
<td>1.44</td>
<td>1.40</td>
</tr>
<tr>
<td>H_c</td>
<td>1.38</td>
<td>1.35</td>
</tr>
<tr>
<td>H_d</td>
<td>4.93</td>
<td>5.18</td>
</tr>
<tr>
<td>H_e</td>
<td>1.61</td>
<td>1.48</td>
</tr>
<tr>
<td>H_f</td>
<td>2.40</td>
<td>2.33</td>
</tr>
<tr>
<td>H_g</td>
<td>1.78</td>
<td>1.87</td>
</tr>
<tr>
<td>H_h</td>
<td>2.25</td>
<td>2.16</td>
</tr>
<tr>
<td>H_i</td>
<td>5.49</td>
<td>5.66</td>
</tr>
<tr>
<td>H_j</td>
<td>2.45</td>
<td>2.41</td>
</tr>
<tr>
<td>H_k</td>
<td>2.13</td>
<td>2.07</td>
</tr>
<tr>
<td>Ph1</td>
<td>7.22</td>
<td>7.28</td>
</tr>
<tr>
<td>Ph2</td>
<td>7.31</td>
<td>7.36</td>
</tr>
<tr>
<td>Ph3</td>
<td>7.36</td>
<td>7.44</td>
</tr>
</tbody>
</table>

Table 5. Experimental shifts (as reported by Saikia\cite{172} and Singaram & Marimuthu\cite{174}) and theoretical shifts for compounds 5a.

<table>
<thead>
<tr>
<th>Proton</th>
<th>Experimental Shift (Saikia) (ppm)</th>
<th>Experimental Shift (Singaram &amp; Marimuthu) (ppm)</th>
<th>Theoretical shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_a</td>
<td>0.86</td>
<td>0.87</td>
<td>1.99</td>
</tr>
<tr>
<td>H_b</td>
<td>1.40</td>
<td>1.31</td>
<td>1.49</td>
</tr>
<tr>
<td>H_c</td>
<td>1.34</td>
<td>1.28</td>
<td>1.29</td>
</tr>
<tr>
<td>H_d</td>
<td>4.88</td>
<td>4.80</td>
<td>5.00</td>
</tr>
<tr>
<td>H_e</td>
<td>1.56</td>
<td>1.46</td>
<td>2.50</td>
</tr>
<tr>
<td>H_f</td>
<td>2.375</td>
<td>2.305</td>
<td>2.15</td>
</tr>
<tr>
<td>H_g</td>
<td>1.73</td>
<td>1.73</td>
<td>1.33</td>
</tr>
<tr>
<td>H_h</td>
<td>2.20</td>
<td>2.13</td>
<td>1.95</td>
</tr>
<tr>
<td>H_i</td>
<td>5.42</td>
<td>5.42</td>
<td>6.77</td>
</tr>
<tr>
<td>H_j</td>
<td>2.375</td>
<td>2.305</td>
<td>1.99</td>
</tr>
<tr>
<td>H_k</td>
<td>2.08</td>
<td>2.08</td>
<td>2.07</td>
</tr>
<tr>
<td>Ph1</td>
<td>7.185</td>
<td>7.185</td>
<td>7.26</td>
</tr>
<tr>
<td>Ph2</td>
<td>7.265</td>
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</tr>
<tr>
<td>Ph3</td>
<td>7.315</td>
<td>7.32</td>
<td>7.48</td>
</tr>
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</table>

Figure 1. Theoretical shifts vs experimental shifts for 5a as reported by Singaram & Marimuthu.\cite{174}
Computational Details

All chemical calculations utilize density functional theory (DFT) as implemented in the Spartan 20 computational program. Geometry optimizations and NMR shift predictions were carried out using the ωB97X-D level of theory, employing the 6-31G* basis set.

Experimental Procedures

General procedure for the synthesis of oxabicyclo[3.3.1]nonenes from aldehydes.

On the benchtop, FeCl₃ (5 mol%) was weighed into a 7 mL vial. DCE (1 mL, 1 M) was then added to the vial. The vial was placed on a stir plate and allowed to stir as aldehyde (1 mmol) was added. The solution was allowed to stir for 5 minutes to allow the FeCl₃-aldehyde aggregate species to form. The FeCl₃ should be homogenous at the end of the 5 minutes. Next, (±)-α-pinene (1 mmol) was added to the solution and the reaction was allowed to stir overnight at room temperature. Reaction was checked on TLC for completion (1:10 Ethyl acetate:hexanes). Once completed, the solution was run through a silica plug, eluted with DCM, to remove the FeCl₃. Solvent was evaporated using reduced pressure.

(1R,4R,5R)-2,2,6-trimethyl-4-phenyl-3-oxabicyclo[3.3.1]non-6-ene (5b). General synthesis procedure was employed using benzaldehyde (1 mmol), producing 5b as a clear,

Figure 2. Theoretical shifts for 5b vs experimental shifts for 5a as reported by Singaram & Marimuthu.¹⁷⁴
colorless oil. No purification was required (99% yield). \( ^1H \text{NMR} \) (500 MHz, CDCl\(_3\)) \( \delta \) 0.91 (m, 3 H), 1.39 (s, 3 H), 1.44 (s, 3 H), 1.61 (m, 1 H), 1.78 (dt, J = 10 and 5 Hz, 1H), 2.13 (ddt, J = 20, 10, and 5 Hz, 1 H), 2.25 (m, 1 H), 2.40 (m, 1 H), 2.45 (m, 1 H), 4.93 (m, 1 H), 5.49 (m ,1 H), 7.20-7.24 (m, 1 H), 7.29-7.32 (m, 2 H), 7.35-7.37 (m, 2 H); \(^{13}C \text{NMR} \) (500 MHz, CDCl\(_3\)) \( \delta \) 24.0, 24.1, 27.8, 28.4, 28.7, 34.0, 41.6, 74.2, 74.4, 123.3, 125.7, 126.6, 127.9, 133.2, 142.9; IR (cm\(^{-1}\)):
2930, 1449, 1378, 1228, 1102, 1084, 1055, 1029, 942

(1\(R\),4\(R\),5\(R\))-4-(4-fluorophenyl)-2,2,6-trimethyl-3-oxabicyclo[3.3.1]non-6-ene (12a).
General synthesis procedure was employed using \( p \)-fluorobenzaldehyde (1 mmol). Purification by flash chromatography eluting with EtOAc/hexanes yielded 12a as a clear yellow oil (88%).

\( ^1H \text{NMR} \) (500 MHz, CDCl\(_3\)) \( \delta \) 0.93 (m, 3 H), 1.38 (s, 3 H), 1.43 (s, 3 H), 1.60 (m, 1 H), 1.76-1.79 (dt, J = 15 and 5 Hz, 1 H), 2.10-2.16 (ddt, J = 20, 5, and 5 Hz, 1 H) 2.20 (m, 1 H), 2.36-2.40 (m, 1 H), 2.44 (m, 1 H), 4.90 (m, 1 H), 5.50 (m, 1 H), 6.99-7.03 (m, 2 H), 7.32-7.35 (m, 2 H);

\(^{13}C \text{NMR} \) (500 MHz, CDCl\(_3\)) \( \delta \) 23.9, 24.2, 27.7, 28.2, 28.7, 33.9, 41.6, 73.7, 75.5, 114.6, 114.7, 123.6, 127.2, 132.8, 138.7, 160.8, 162.8;

(1\(R\),4\(R\),5\(R\))-4-(2-bromophenyl)-2,2,6-trimethyl-3-oxabicyclo[3.3.1]non-6-ene (12b).
General synthesis procedure was employed using 2-bromobenzaldehyde (1 mmol). Purification by flash chromatography eluting with EtOAc/hexanes yielded 12b as a clear pale-yellow oil (95%). \( ^1H \text{NMR} \) (500 MHz, CDCl\(_3\)) \( \delta \) 0.88-0.89 (m, 1 H), 1.37 (s, 3 H), 1.45 (s, 3 H), 1.59-1.62 (m, 1 H), 1.74-1.78 (dt, J = 15 and 5 Hz, 1 H), 2.11-2.17 (ddt, J = 15, 5, and 5 Hz, J = 1 H), 2.38-2.41 (m ,1 H), 2.43-2.47 (m, 1 H), 2.58-2.59 (m, 1 H), 5.11 (m, 1 H), 5.51 (m, 1 H), 7.08-7.12 (m, 1 H), 7.25-7.28 (m, 1 H), 7.49-7.52 (m, 2 H); \(^{13}C \text{NMR} \) (500 MHz, CDCl\(_3\)) \( \delta \) 23.9, 24.1, 27.7, 27.8, 28.7, 33.9, 37.3, 73.5, 75.7, 121.4, 123.7, 127.2, 128.2, 132.0, 132.9, 141.4; IR (cm\(^{-1}\)
(1R,4R,5R)-2,2,6-trimethyl-4-(p-tolyl)-3-oxabicyclo[3.3.1]non-6-ene (12c). General synthesis procedure was employed using p-tolualdehyde (1 mmol). Purification by flash chromatography eluting with EtOAc/hexanes yielded 12c as a clear colorless oil (80%). $^1$H NMR (500 MHz, CDCl$_3$) δ 0.97-0.98 (m, 3 H), 1.41 (s, 3 H), 1.46 (s, 3 H), 1.61-1.63 (m, 1 H), 1.78-1.81 (dt, J = 15 and 5 Hz, 1 H), 2.13-2.19 (ddt, J = 15, 5, and 5 Hz, 1 H), 2.25 (m, 1 H), 2.37 (s, 3 H), 2.39-2.43 (m, 1 H), 2.45-2.49 (m, 1 H), 4.92 (m, 1 H), 5.51 (m, 1 H), 7.13-7.15 (m, 2 H), 7.27-7.28 (m, 2 H); $^{13}$C NMR (500 MHz, CDCl$_3$) δ 21.2, 24.1, 24.3, 27.8, 28.4, 28.8, 34.1, 41.6, 74.2, 75.3, 123.2, 125.6, 128.5, 133.4, 135.9, 139.9.

(1R,4R,5R)-4-(4-ethylphenyl)-2,2,6-trimethyl-3-oxabicyclo[3.3.1]non-6-ene (12d). General synthesis procedure was employed using p-ethylbenzaldehyde (1 mmol). Purification by flash chromatography eluting with EtOAc/hexanes yielded 12d as a clear colorless oil (76%). $^1$H NMR (500 MHz, CDCl$_3$) δ 0.98-0.99 (m, 3 H), 1.26-1.29 (t, 3 H), 1.42 (s, 3 H), 1.46 (s, 3 H), 1.62-1.64 (m, 1 H), 1.79-1.83 (dt, J = 10 and 5 Hz, 1 H), 2.14-2.27 (ddt, J = 20, 10 and 5 Hz, 1 H), 2.26 (m, 1 H), 2.41-2.44 (m, 1 H), 2.47-2.50 (m, 1 H), 2.66-2.71 (q, 2 H), 4.94 (m, 1 H), 5.53 (m, 1 H), 7.17-7.19 (m, 2 H), 7.31-7.32 (m, 2 H); $^{13}$C NMR (500 MHz, CDCl$_3$) δ 15.9, 24.0, 24.3, 27.8, 28.5, 28.7, 28.8, 34.1, 41.6, 74.2, 75.3, 123.2, 125.7, 133.4, 140.23, 142.6; IR (cm$^{-1}$): 2968, 2925, 1453, 1382, 1237, 1074, 1021; HRCI cald. for C$_{19}$H$_{26}$O [M+NH$_4$]$^+$ requires 288.2328; found 288.2315.

(1R,4R,5R)-4-(4-methoxyphenyl)-2,2,6-trimethyl-3-oxabicyclo[3.3.1]non-6-ene (12e). General synthesis procedure was employed using p-anisaldehyde (1 mmol). Purification by flash
chromatography eluting with EtOAc/hexanes yielded 12e as a clear, colorless oil (79%).\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 0.93-0.94 (m, 3 H), 1.35 (s, 3 H), 1.41 (s, 3 H), 1.56-1.59 (m, 1 H), 1.72-1.76 (dt, J = 15 and 5 Hz, 1 H), 2.08-2.14 (ddt, J = 20, 10 and 5 Hz, 1 H), 2.17 (m, 1 H), 2.34-2.38 (m, 1 H), 2.40-2.45 (m, 1 H), 3.80 (s, 3 H), 4.86 (m, 1 H), 5.47 (m, 1 H), 6.83-6.85 (m, 2 H), 7.25-7.26 (m, 2 H); \textsuperscript{13}C NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 24.0, 24.2, 27.7, 28.3, 28.7, 33.9, 41.6, 55.3, 73.9, 75.3, 113.3, 123.2, 133.4, 135.3, 158.4

\((1R,4R,5R)-4-(4-isopropylphenyl)-2,2,6-trimethyl-3-oxabicyclo[3.3.1]non-6-ene\) (12f).

General synthesis procedure was employed using cuminaldehyde (1 mmol). Purification by flash chromatography eluting with EtOAc/hexanes yielded 12f as a clear colorless oil (77%).\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 0.97-0.98 (m, 3 H), 1.28-1.30 (dd, J = 5 Hz, 6 H), 1.41 (s, 1 H), 1.46 (s, 1 H), 1.61-1.64 (m, 1 H), 1.78-1.82 (dt, J = 10 and 5 Hz, 1 H), 2.13-2.19 (ddt, J = 25, 10, and 5 Hz, 1 H), 2.26 (m, 1 H), 2.40-2.44 (m, 1 H), 2.46-2.50 (m, 1 H), 2.9-2.98 (h, 1 H), 4.93 (m, 1 H), 5.52 (m, 1 H), 7.19-7.20 (m, 2 H), 7.31-7.33 (m, 2 H); \textsuperscript{13}C NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 24.0, 24.2, 24.3, 27.8, 28.4, 28.8, 33.9, 34.1, 34.4, 41.6, 74.2, 75.3, 123.2, 125.7, 125.9, 133.4, 140.3, 147.3

\((1R,4R,5R)-4-(4-(tert-butyl)phenyl)-2,2,6-trimethyl-3-oxabicyclo[3.3.1]non-6-ene\) (12g). General synthesis procedure was employed using 4-(tert-butyl)benzaldehyde (1 mmol). Purification by flash chromatography eluting with EtOAc/hexanes yielded 12g as a clear colorless oil (76%).\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 0.97 (m, 3 H), 1.37 (s, 9 H) 1.41 (s, 3 H), 1.45 (s, 3 H), 1.62 (m, 1 H), 1.78-1.82 (m, 1 H), 2.16 (m, 1 H), 2.26 (m, 1 H), 2.41-2.43 (m, 1 H), 2.46-2.50 (m, 1 H), 4.93 (m, 1 H), 5.52 (m, 1 H), 7.31-7.33 (m, 2 H), 7.36-7.37 (m, 2 H); \textsuperscript{13}C NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 24.1, 24.3, 27.8, 28.4, 8.8, 31.5, 34.1, 34.4, 41.5, 74.1, 75.2, 123.2,
124.7, 125.4, 133.4, 139.9, 149.5; \textbf{IR} (cm$^{-1}$): 2931, 1708, 1599, 1327, 1205, 1088, 1007, 967; HRCI cald. for C$_{21}$H$_{30}$O [M+NH$_4$]$^+$ requires 316.2641; found 316.2624

$(1R,4R,5R)$-2,2,6-trimethyl-4-(3-nitrophenyl)-3-oxabicyclo[3.3.1]non-6-ene (12h).

General synthesis procedure was employed using 3-nitrobenzaldehyde (1 mmol). Purification by flash chromatography eluting with EtOAc/hexanes yielded 12h as a clear pale-yellow oil (35%).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 0.83-0.84 (m, 3 H), 1.37 (s, 3 H), 1.41 (s, 3 H), 1.59-1.61 (m, 1 H), 1.76-1.80 (dt, J = 15 and 5 Hz, 1 H), 2.08-2.15 (m, 1 H), 2.26 (m, 1 H), 2.36-2.40 (m, 1 H), 2.41-2.44 (m, 1 H), 4.97 (m, 1 H), 5.49 (m, 1 H), 7.44-7.47 (m, 1 H), 7.68-7.70 (m, 1 H), 8.06-8.09 (m, 1 H), 8.20 (m, 1 H); $^{13}$C NMR (500 MHz, CDCl$_3$) $\delta$ 23.9, 24.2, 27.6, 28.2, 28.6, 33.8, 41.3, 73.6 75.9, 120.9, 121.7, 124.5, 128.6, 131.7, 132.1, 145.3; \textbf{IR} (cm$^{-1}$): 3705, 1680, 2936, 2921, 1527, 1345, 1228, 1055, 1032, 1013, 906; HRCI cald. for C$_{17}$H$_{21}$NO$_3$ [M+NH$_4$]$^+$ requires 338.1120; found 338.1102

$(1R,4R,5R)$-4-([1,1'-biphenyl]-4-yl)-2,2,6-trimethyl-3-oxabicyclo[3.3.1]non-6-ene (12i). General synthesis procedure was employed using [1,1'-biphenyl]-4-carbaldehyde (1 mmol). Purification by flash chromatography eluting with EtOAc/hexanes yielded 12i as a white solid (40%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 0.95-0.96 (m, 3 H), 1.38 (s, 3 H), 1.43 (s, 3 H), 1.57 (m ,1 H), 1.59-1.62 (m, 1 H), 1.76-1.80 (dt, J = 10 and 5 Hz, 1 H), 2.10-2.16 (m, 1 H), 2.27 (m, 1 H), 2.38-2.41 (m, 1 H), 2.42-2.47 (m, 1 H), 4.95 (m, 1 H), 5.49 (m, 1 H), 7.32-7.36 (m, 1 H), 7.41-7.46 (m, 4 H), 7.53-7.55 (m, 2 H), 7.60-7.62 (m, 2 H); $^{13}$C NMR (500 MHz, CDCl$_3$) $\delta$ 24.0, 24.2, 27.8, 28.4, 31.5, 34.0, 34.4, 41.5, 74.1, 75.2, 123.2, 124.7, 125.3, 133.5, 139.9, 149.5. \textbf{IR} (cm$^{-1}$): 2926, 1458, 1361, 1293, 1280, 1122, 1094, 1076, 813
(1R,4R,5R)-2,2,6-trimethyl-4-(naphthalen-2-yl)-3-oxabicyclo[3.3.1]non-6-ene (12j). General synthesis procedure was employed using 2-naphthaldehyde (1 mmol). No reaction was detected after 24 hours and starting materials were recovered.

(1R,4S,5R)-2,2,6-trimethyl-4-((E)-styryl)-3-oxabicyclo[3.3.1]non-6-ene (12k). General synthesis procedure was employed using cinnamaldehyde (1 mmol). Purification by flash chromatography eluting with EtOAc/hexanes yielded 12k as a clear colorless oil (73%). $^1$H NMR (500 MHz, CDCl$_3$) δ 1.36 (s, 3 H), 1.44 (s, 3 H), 1.58-1.60 (m, 1 H), 1.77 (m, 3 H), 2.14 (m, 1 H), 2.19 (m, 1 H), 2.30-2.32 (m, 1 H), 2.43-2.47 (m, 1 H), 4.53 (m, 1 H), 5.63 (m, 1 H), 6.22-6.26 (dt, J = 15 Hz, 1 H), 6.61-6.65 (m, 1 H), 7.23-7.26 (m, 1 H), 7.32-7.35 (m, 2 H), 7.42-7.43 (m, 2 H); $^{13}$C NMR (500 MHz, CDCl$_3$) δ 24.2, 25.2, 27.8, 28.1, 28.7, 34.1, 40.5, 74.5, 75.4, 123.9, 126.4, 127.3, 128.4, 128.8, 131.3, 133.3, 137.3

(1R,4S,5R)-2,2,6-trimethyl-4-((E)-prop-1-en-1-yl)-3-oxabicyclo[3.3.1]non-6-ene (12l). General synthesis procedure was employed using crotonaldehyde (1 mmol). Purification by flash chromatography eluting with EtOAc/hexanes yielded 12l as a clear colorless oil (73%). $^1$H NMR (500 MHz, CDCl$_3$) δ 1.26 (s, 3 H), 1.34 (s, 3 H), 1.49-1.52 (m, 1 H), 1.64-1.67 (m, 1 H), 1.68-1.70 (m, 3 H), 1.71-1.72 (m, 3 H), 1.96 (m, 1 H), 2.05-2.12 (m, 1 H), 2.18-2.22 (m, 1 H), 2.34-2.38 (m, 1 H), 4.25 (m, 1 H), 5.42-5.47 (m, 1 H), 5.54 (m, 1 H), 5.64-5.71 (m, 1 H); $^{13}$C NMR (500 MHz, CDCl$_3$) δ 17.7, 24.1, 25.1, 27.7, 27.9, 28.7, 33.9, 40.2, 74.5, 75.0, 123.5, 125.3, 132.7, 133.5

(1R,4S,5R)-2,2,6-trimethyl-4-(6-methylhept-5-en-2-yl)-3-oxabicyclo[3.3.1]non-6-ene (11m). General synthesis procedure was employed using melonal (1 mmol). No reaction was detected after 24 hours and starting materials were recovered.
*(1R,4S,5R)-4-(2,5-dimethylhex-4-en-1-yl)-2,2,6-trimethyl-3-oxabicyclo[3.3.1]non-6-ene (11n).* General synthesis procedure was employed using citronellal (1 mmol). No reaction was detected after 24 hours and starting materials were recovered.

**X-ray Crystallographic Data**

Structural determination of *(1R,4R,5R)-2,2,6-trimethyl-4-phenyl-3-oxabicyclo[3.3.1]non-6-ene (5b).*

![Crystal structure of 5b.](image)

**Figure 3.** Crystal structure of 5b.

*Crystallization of 5b (2236978).* Pure sample of 5b was added to a 1 mL vial and dissolved in hexanes. This vial was placed inside of a 20 mL vial and left uncapped. To the outer vial, ethyl acetate was added. The outer vial was sealed with parafilm and stored at -18 °C. After roughly one week, colorless, clear crystals had formed in the inner vial.

**Experimental.** Single crystals of C17H22O were supplied. A suitable crystal was selected and the crystal was mounted on a MITIGEN holder With Paratone oil on a XtaLAB Synergy, Single source at home/near, HyPix diffractometer. The crystal was kept at 250.00(10) K during data collection. Using Olex2, the structure was solved with the ShelXT structure solution.
program using Intrinsic Phasing and refined with the XL\textsuperscript{184} refinement package using Least Squares minimization.

Crystal structure determination of [5b]

Crystal Data for C\textsubscript{17}H\textsubscript{22}O (\(M = 242.34\)): orthorhombic, space group P2\textsubscript{1}2\textsubscript{1}2\textsubscript{1} (no. 19), \(a = 6.5185(5) \ \text{Å}, b = 7.4747(5) \ \text{Å}, c = 28.7382(17) \ \text{Å}, V = 1400.23(17) \ \text{Å}^3, Z = 4, T = 250.00(10) \ \text{K}, \mu(\text{CuKα}) = 0.528 \ \text{mm}^{-1}, D_{\text{calc}} = 1.150 \ \text{g/mm}^3, 13593 \ \text{reflections measured (12.236} \leq 2\Theta \leq 158.01), 2873 \ \text{unique (}R_{\text{int}} = 0.0638, R_{\text{sigma}} = 0.0588) \ \text{which were used in all calculations. The final} \ R_1 \ \text{was 0.0544 (}I > 2\sigma(I)) \ \text{and} \ wR_2 \ \text{was 0.1430 (all data).}

**Refinement Details.** No special refinement necessary.

**Solvent Treatment Details.** N/A

**Table 6.** Crystal data and structure refinement for 5b

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<td>Crystal size / \text{mm}^3</td>
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2Θ range for data collection
12.236 to 158.01°

Index ranges
-8 ≤ h ≤ 6, -9 ≤ k ≤ 9,
-35 ≤ l ≤ 36

Reflections collected
13593

Independent reflections
2873 [R(int) = 0.0638]

Data/restraints/parameters
2873/0/167

Goodness-of-fit on F²
1.031

Final R indexes [I>2σ (I)]
R₁ = 0.0544, wR₂ = 0.1134

Final R indexes [all data]
R₁ = 0.0947, wR₂ = 0.1430

Largest diff. peak/hole / eÅ³
0.143/-0.158

Table 7. Fractional Atomic Coordinates (×10⁴)
and Equivalent Isotropic Displacement Parameters (Å²×10³) for 5b. Uₑq is defined as 1/3 of the trace of the orthogonalised Uᵢᵢ tensor.

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Table 8. Anisotropic Displacement Parameters (Å²×10³) for 5b. The Anisotropic displacement factor exponent takes the form: -
2π²[h²a*b¹11+2hka*b¹U₁₂+…].

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242
### Table 9. Bond Lengths for 5b.

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### Table 10. Bond Angles for 5b.

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Table 11. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å²×10^3) for 5b.\textsuperscript{182}

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Structural determination of (1R,4R,5R)-4-([1,1'-biphenyl]-4-yl)-2,2,6-trimethyl-3-oxabicyclo[3.3.1]non-6-ene (12i).
Figure 4. Crystal structure of 12i.

Crystallization of 12i (2236980). Pure sample of 11h was added to a 1 mL vial and dissolved in hexanes. This vial was placed inside of a 20 mL vial and left uncapped. To the outer vial, ethyl acetate was added. The outer vial was sealed with parafilm and stored at -18 °C. After roughly one week, colorless, clear crystals had formed in the inner vial.

Experimental. Single crystals of C$_{23}$H$_{26}$O were supplied. A suitable crystal was selected and the crystal was mounted on a MITIGEN holder with Paratone oil on a XtaLAB Synergy, Single source, HyPix diffractometer. The crystal was kept at 250.00(10) K during data collection. Using Olex2$^{182}$, the structure was solved with the ShelXT$^{183}$ structure solution program using Intrinsic Phasing and refined with the XL$^{184}$ refinement package using Least Squares minimization.

Crystal structure determination of [12i]. Crystal Data for C$_{23}$H$_{26}$O (M =318.44):
orthorhombic, space group P2$_1$2$_1$2$_1$ (no. 19), $a = 6.58615(13)$ Å, $b = 7.53808(16)$ Å, $c = 35.8241(6)$ Å, $V = 1778.56(6)$ Å$^3$, $Z = 4$, $T = 250.00(10)$ K, $\mu$(CuKα) = 0.537 mm$^{-1}$, $D_{calc}$ = 1.189 g/mm$^3$, 17367 reflections measured (9.876 ≤ 2Θ ≤ 159.614), 3726 unique ($R_{int} = 0.0412$, $R_{sigma} = 0.0318$) which were used in all calculations. The final $R_1$ was 0.0421 (I > 2σ(I)) and $wR_2$ was 0.0997 (all data).

Refinement Details. No special refinement necessary.

Solvent Treatment Details. N/A

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<td>Temperature / K</td>
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Crystal system: orthorhombic
Space group: P2₁2₁2₁
a / Å, b / Å, c / Å: 6.58615(13), 7.53808(16), 35.8241(6)
α/°, β/°, γ/°: 90, 90, 90
Volume / Å³: 1778.56(6)
Z: 4
ρcalc / mg mm⁻³: 1.189
µ / mm⁻¹: 0.537
F(000): 688
Crystal size / mm³: 0.063 × 0.05 × 0.009
2Θ range for data collection: 9.876 to 159.614°
Index ranges: -8 ≤ h ≤ 7, -9 ≤ k ≤ 9, -45 ≤ l ≤ 45
Reflections collected: 17367
Independent reflections: 3726[R(int) = 0.0412]
Data/restraints/parameters: 3726/0/220
Goodness-of-fit on F²: 1.051
Final R indexes [I>2σ (I)]: R₁ = 0.0421, wR₂ = 0.0948
Final R indexes [all data]: R₁ = 0.0510, wR₂ = 0.0997
Largest diff. peak/hole / e Å⁻³: 0.117/-0.154

Table 13. Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for 12i. Ueq is defined as 1/3 of the trace of the orthogonalised Uij tensor.

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Table 14. Anisotropic Displacement Parameters (Å²×10³) for 12i. The Anisotropic displacement factor exponent takes the form: 
\[ -2\pi^2 [h^2a^*U_{11}+2hka^*b^*U_{12}+. . .] \].

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\textsuperscript{1}H and \textsuperscript{13}C NMR Spectra

\textsuperscript{1}H NMR Spectra – 5b.
$^{13}$C NMR Spectra – 5b

$^1$H NMR Spectra – 12a
$^{13}$C NMR Spectra – 12a

$^1$H NMR Spectra – 12b
$^{13}$C NMR Spectra – 12b

$^1$H NMR Spectra – 12c
$^{13}$C NMR Spectra – 12c

$^1$H NMR Spectra – 12d
$^{13}$C NMR Spectra – 12d

$^1$H NMR Spectra – 12e
$^{13}$C NMR Spectra – 12e

$^{1}$H NMR Spectra – 12f
$^{13}$C NMR Spectra – 12f

$^1$H NMR Spectra – 12g
$^{13}$C NMR Spectra – 12g

$^1$H NMR Spectra – 12h
$^{13}$C NMR Spectra – 12h

$^1$H NMR Spectra – 12i
$^{13}$C NMR Spectra – 12i

$^1$H NMR Spectra – 12k
$^{13}$C NMR Spectra – 12k

$^1$H NMR Spectra – 12l
$^{13}$C NMR Spectra – 12l

8.) 2D NMR Spectra – 5b
$^1$H-$^{13}$C HSQC

$^1$H-$^1$H NOESY
General Information

General Laboratory Procedures.

All moisture-sensitive reactions were performed under an atmosphere of argon in flame-dried round bottom flasks or glass vials fitted with rubber septa. Stainless steel syringes were used to transfer air or moisture-sensitive liquids. Flash chromatography was performed using silica gel Silia Flash® 40-63 micron (230-400 mesh) from Silicycle.

Materials and Instrumentation.

All chemicals were purchased from Alfa Aesar, VWR, Matheson Coleman and Bell, Beantown Chemicals, or Acros. All ketones were dried over 3 Å molecular sieves and purified via distillation. Acetone was dried over K₂CO₃. DCE was dried and stored over 3 Å Molecular sieves. Infrared (IR) spectra were obtained using a Mettler Toledo ReactIR 15. IR data are represented as frequency of absorption (cm⁻¹). Conductivity measurements were obtained using a VWR Portable Conductivity Meter or a Mettler Toledo portable Seven2Go™ Pro-conductivity meter. Conductivity data are represented as Microsiemens per centimeter (µS cm⁻¹).

IR Titrations

General procedure for ZnCl₂ complexation.

ZnCl₂ (1.00 mmol) was added to a flame-dried 25 mL 2-neck round bottom flask under inert atmosphere with a stir bar. The flask was sealed with septa, taken out of the box, and an Ar balloon was inserted. The flask was placed in a heating mantle set to 30 °C. Anhydrous DCE was added (6 mL, 167.3 mM). If applicable, TMSCl was then added (0.254 mL, 2.00 mmol). The solution was stirred for 15 minutes to reach temperature. 16 was added in 10 µL increments to the 2nd equivalence point of carbonyl, then 20 µL increments were added until 4th equivalence
point was reached. Complexation was analyzed via real time infrared spectroscopy, using a Mettler Toledo ReactIR 15.

![Figure S1](image1.png)

**Figure S1**: Titration of ZnCl$_2$ with 16 from $0 \rightarrow 0.178$ M. Select data points omitted from Figure 4A for clarity.

![Figure S2](image2.png)

**Figure S2**: Titration of ZnCl$_2$ and TMSCl (0.254 mL, 333.3 mM) with 16 from $0 \rightarrow 0.178$ M. Select data points omitted from Figure 4B for clarity.

**General procedure for BF$_3$•OEt$_2$ complexation.**

BF$_3$•OEt$_2$ (1.00 mmol) was added to a flame-dried 25 mL 2-neck round bottom flask under inert atmosphere with a stir bar. The flask was sealed with septa, taken out of the box, and an Ar balloon was inserted. The flask was placed in a heating mantle set to 30 °C. Anhydrous DCE was added (6 mL, 167.3 mM). If applicable, TMSCl was then added (0.254 mL, 2.00 mmol). The solution was stirred for 15 minutes to reach temperature. 16 was added in 10 µL increments to
the 2nd equivalence point of carbonyl, then 20 μL increments were added until 4th equivalence point was reached. Complexation was analyzed via real time infrared spectroscopy, using a Mettler Toledo ReactIR 15.

Figure S2: Titration of BF$_3$•OEt$_2$ with 16 from 0 – 0.162 M. Select data points omitted from Figure 5A for clarity.

Figure S4: Titration of BF$_3$•OEt$_2$ and TMSCl (0.254 mL, 333.3 mM) with 16 from 0 – 0.178 M. Select data points omitted from Figure 5B for clarity.

General procedure for BCl$_3$ complexation. BCl$_3$ (1 mL of 1M solution in DCM, 1.00 mmol) was added to a flame-dried 25 mL 2-neck round bottom flask under inert atmosphere with a stir bar. The flask was sealed with septa, taken out of the box, and an Ar balloon was inserted. The flask was placed in a heating mantle set to 30 °C. Anhydrous DCE was added (5 mL, 167.3
mM). If applicable, TMSCl was then added (0.254 mL, 2.00 mmol). The solution was stirred for 15 minutes to reach temperature. 16 was added in 10 μL increments to the 2\textsuperscript{nd} equivalence point of carbonyl, then 20 μL increments were added until 4\textsuperscript{th} equivalence point was reached. Complexation was analyzed via real time infrared spectroscopy, using a Mettler Toledo ReactIR 15.

**Figure S13**: Titration of BCl\textsubscript{3} with 16 from 0 – 0.178 M. Select data points omitted from Figure 5D for clarity.

**Figure S14**: Titration of BCl\textsubscript{3} and TMSCl (0.254 mL, 333.3 mM) with 16 from 0 – 0.171 M. Select data points omitted from Figure 5E for clarity.
General procedure for AlCl₃ complexation. AlCl₃ (1.00 mmol) was added to a flame-dried 25 mL 2-neck round bottom flask under inert atmosphere with a stir bar. The flask was sealed with septa, taken out of the box, and an Ar balloon was inserted. The flask was placed in a heating mantle set to 30 °C. Anhydrous DCE was added (6 mL, 167.3 mM). If applicable, TMSCl was then added (0.254 mL, 2.00 mmol). The solution was stirred for 15 minutes to reach temperature. 16 was added in 10 μL increments to the 2nd equivalence point of carbonyl, then 20 μL increments were added until 4th equivalence point was reached. Complexation was analyzed via real time infrared spectroscopy, using a Mettler Toledo ReactIR 15.

![Figure S5](image)

**Figure S5**: Titration of AlCl₃ with 16 from 0 – 0.130 M. Select data points omitted from Figure 5G for clarity.
Figure S6: Titration of AlCl$_3$ and TMSCl (0.254 mL, 333.3 mM) with 16 from 0 – 0.110 M. Select data points omitted from Figure 5H for clarity.

**General procedure for ZrCl$_4$ complexation.** ZrCl$_4$ (1.00 mmol) was added to a flame-dried 25 mL 2-neck round bottom flask under inert atmosphere with a stir bar. The flask was sealed with septa, taken out of the box, and an Ar balloon was inserted. The flask was placed in a heating mantle set to 30 °C. Anhydrous DCE was added (6 mL, 167.3 mM). If applicable, TMSCl was then added (0.254 mL, 2.00 mmol). The solution was stirred for 15 minutes to reach temperature. 16 was added in 10 μL increments to the 2$^{\text{nd}}$ equivalence point of carbonyl, then 20 μL increments were added until 4$^{\text{th}}$ equivalence point was reached. Complexation was analyzed via real time infrared spectroscopy, using a Mettler Toledo ReactIR 15.

![Graph](image1.png)

Figure S7: Titration of ZrCl$_4$ with 16 from 0 – 0.141 M. Select data points omitted from Figure 6A for clarity.

![Graph](image2.png)

Figure S8: Titration of ZrCl$_4$ and TMSCl (0.254 mL, 333.3 mM) with 16 from 0 – 0.171 M. Select data points omitted from Figure 6B for clarity.
**General procedure for SnCl₄ complexation.** SnCl₄ (1.00 mmol) was added to a flame-dried 25 mL 2-neck round bottom flask under inert atmosphere with a stir bar. The flask was sealed with septa, taken out of the box, and an Ar balloon was inserted. The flask was placed in a heating mantle set to 30 °C. Anhydrous DCE was added (6 mL, 167.3 mM). If applicable, TMSCl was then added (0.254 mL, 2.00 mmol). The solution was stirred for 15 minutes to reach temperature. 18 was added in 10 μL increments to the 2nd equivalence point of carbonyl, then 20 μL increments were added until 4th equivalence point was reached. Complexation was analyzed via real time infrared spectroscopy, using a Mettler Toledo ReactIR 15.

**Figure S11:** Titration of SnCl₄ with 18 from 0 – 0.180 M. Select data points omitted from Figure 6D for clarity.

**Figure S12:** Titration of SnCl₄ and TMSCl (0.254 mL, 333.3 mM) with 18 from 0 – 0.178 M. Select data points omitted from Figure 6E for clarity.
**General procedure for TiCl₄ complexation.** TiCl₄ (1.00 mmol) was added to a flame-dried 25 mL 2-neck round bottom flask under inert atmosphere with a stir bar. The flask was sealed with septa, taken out of the box, and an Ar balloon was inserted. The flask was placed in a heating mantle set to 30 °C. Anhydrous DCE was added (6 mL, 167.3 mM). If applicable, TMSCl was then added (0.254 mL, 2.00 mmol). The solution was stirred for 15 minutes to reach temperature. 18 was added in 10 μL increments to the 2nd equivalence point of carbonyl, then 20 μL increments were added until 4th equivalence point was reached. Complexation was analyzed via real time infrared spectroscopy, using a Mettler Toledo ReactIR 15.

![Graph](image1)

**Figure S9:** Titration of TiCl₄ with 18 from 0 – 0.180 M. Select data points omitted from Figure 6G for clarity.

[Graph](image2)

**Figure S10:** Titration of TiCl₄ and TMSCl (0.254 mL, 333.3 mM) with 18 from 0 – 0.180 M. Select data points omitted from Figure 6H for clarity.
**General procedure for InCl₃ complexation.** InCl₃ (1.00 mmol) was added to a flame-dried 25 mL 2-neck round bottom flask under inert atmosphere with a stir bar. The flask was sealed with septa, taken out of the box, and an Ar balloon was inserted. The flask was placed in a heating mantle set to 30 °C. Anhydrous DCE was added (6 mL, 167.3 mM). If applicable, TMSCl was then added (0.254 mL, 2.00 mmol). The solution was stirred for 15 minutes to reach temperature. Carbonyl was added in 10 μL increments to the 2nd equivalence point of carbonyl, then 20 μL increments were added until 4th equivalence point was reached. Complexation was analyzed via real time infrared spectroscopy, using a Mettler Toledo ReactIR 15.

![Graph](image)

**Figure S15:** Titration of InCl₃ with 17 from 0 – 0.178 M. Select data points omitted from Figure 7A for clarity.

![Graph](image)

**Figure S16:** Titration of InCl₃ and TMSCl (0.254 mL, 333.3 mM) with 17 from 0 – 0.171 M. Select data points omitted from Figure 7B for clarity.
Figure S17: Titration of InCl$_3$ with 18 from 0 – 0.180 M. Select data points omitted from Figure 7D for clarity.

Figure S18: Titration of InCl$_3$ and TMSCl (0.254 mL, 333.3 mM) with 18 from 0 – 0.173 M. Select data points omitted from Figure 7E for clarity.

Figure S19: Titration of InCl$_3$ with 16 from 0 – 0.162 M. Select data points omitted from Figure 7G for clarity.
General procedure for GaCl$_3$ complexation. GaCl$_3$ (1.00 mmol) was added to a flame-dried 25 mL 2-neck round bottom flask under inert atmosphere with a stir bar. The flask was sealed with septa, taken out of the box, and an Ar balloon was inserted. The flask was placed in a heating mantle set to 30 °C. Anhydrous DCE was added (6 mL, 167.3 mM). If applicable, TMSCI was then added (0.254 mL, 2.00 mmol). The slurry was stirred for 15 minutes to reach temperature. Carbonyl was added in 10 µL increments to the 2$^{nd}$ equivalence point of carbonyl, then 20 µL increments were added until 4$^{th}$ equivalence point was reached.

**Figure S20:** Titration of InCl$_3$ and TMSCI (0.254 mL, 333.3 mM) with 16 from 0 – 0.156 M. Select data points omitted from Figure 7G for clarity.

**Figure S27:** Titration of GaCl$_3$ with 17 from 0 – 0.178 M. Select data points omitted from Figure 8A for clarity.
**Figure S28:** Titration of GaCl$_3$ and TMSCl (0.254 mL, 333.3 mM) with 17 from 0 – 0.192 M. Select data points omitted from Figure 8B, 8C for clarity.

**Figure S29:** Titration of GaCl$_3$ with 18 from 0 – 0.160 M. Select data points omitted from Figure 8D for clarity.

**Figure S30:** Titration of GaCl$_3$ and TMSCl (0.254 mL, 333.3 mM) with 18 from 0 – 0.135 M. Select data points omitted from Figure 8E, 8F for clarity.
Figure S31: Titration of GaCl$_3$ with 16 from 0 – 0.163 M. Select data points omitted from Figure 8G for clarity.

Figure S32: Titration of GaCl$_3$ and TMSCl (0.254 mL, 333.3 mM) with 16 from 0 – 0.186 M. Select data points omitted from Figure 8H, 8I for clarity.

**General procedure for FeCl$_3$ complexation.** FeCl$_3$ (1.00 mmol) was added to a flame-dried 25 mL 2-neck round bottom flask under inert atmosphere with a stir bar. The flask was sealed with septa, taken out of the box, and an Ar balloon was inserted. The flask was placed in a heating mantle set to 30 °C. Anhydrous DCE was added (6 mL, 167.3 mM). If applicable, TMSCl was then added (0.254 mL, 2.00 mmol). The slurry was stirred for 15 minutes to reach temperature. Carbonyl was added in 10 μL increments to the 2nd equivalence point of carbonyl, then 20 μL increments were added until 4th equivalence point was reached. Complexation was analyzed via real time infrared spectroscopy, using a Mettler Toledo ReactIR 15.
Figure S21: Titration of FeCl₃ with 17 from 0 – 0.178 M. Select data points omitted from Figure 9A for clarity.

Figure S22: Titration of FeCl₃ and TMSCl (0.254 mL, 333.3 mM) with 17 from 0 – 0.174 M. Select data points omitted from Figure 9B for clarity.

Figure S23: Titration of FeCl₃ with 18 from 0 – 0.243 M. Select data points omitted from Figure 9D for clarity.
Figure S24: Titration of FeCl₃ and TMSCl (0.254 mL, 333.3 mM) with 18 from 0 – 0.179 M. Select data points omitted from Figure 9E for clarity.

Figure S25: Titration of FeCl₃ with 16 from 0 – 0.180 M. Select data points omitted from Figure 9G for clarity.

Figure S26: Titration of FeCl₃ and TMSCl (0.254 mL, 333.3 mM) with 16 from 0 – 0.166 M. Select data points omitted from Figure 9H for clarity.

**Conductance analysis**
General procedure for conductance measurements.

In a glove box, Lewis acid (1 mmol) was added to a flame-dried 20 mL scintillation vial charged with a stir bar. Anhydrous DCE was added (6 mL, 166.7 mM) along with chlorosilane additive, if applicable (1 or 2 mmol). The conductance of the mixture was observed via a VWR Portable Conductance Meter or a Mettler Toledo portable Seven2Go™ Pro-conductivity meter. Carbonyl was incrementally titrated until 4 equivalents of carbonyl were reached. Conductance after each of addition of carbonyl was observed and recorded as an average of three measurements. Between each reading probe was rinsed with DCE and solution was stirred for 10 minutes to allow equilibration. Plotting and trendline analysis were performed with Microsoft Excel and graphpad Prism 9.

Figure S27. Conductivity measurements of ZnCl$_2$ (1 mmol in 6 mL DCE) and 16 (Control – black square) and of ZnCl$_2$ (1 mmol in 6 mL DCE), TMSCl (2 mmol), and 16 (maroon square).

---

1 Comparison experiments reveal little deviation in solution conductivity measurements between the two probes when calibrated correctly at 25 °C with a 1411 µS/cm stock solution of KCl.
Table S1. Conductivity measurements of control experiment with ZnCl₂.

<table>
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<th>Equiv</th>
<th>Conductivity (µS/Cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
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<td>0.060 0.070 0.060 0.063</td>
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<td>5.0</td>
<td>23.000 24.400 25.100 24.167</td>
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</table>

Table S2. Conductivity measurements of experiment with ZnCl₂ and TMSCl (2 mmol).

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<thead>
<tr>
<th>Equiv</th>
<th>Conductivity (µS/Cm)</th>
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</thead>
<tbody>
<tr>
<td>16</td>
<td></td>
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<tr>
<td>0.0</td>
<td>0.060 0.050 0.050 0.053</td>
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<tr>
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<td>0.090 0.090 0.100 0.093</td>
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<tr>
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<tr>
<td>0.6</td>
<td>0.300 0.310 0.300 0.303</td>
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<td>0.530 0.510 0.490 0.510</td>
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<td>5.0</td>
<td>26.500 27.000 27.800 27.100</td>
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</table>
**Figure S28.** Conductivity measurements BF$_3$•OEt$_2$ (1 mmol in 6 mL DCE) and 16 (Control – black square) and of BF$_3$•OEt$_2$ (1 mmol in 6 mL DCE), TMSCl (2 mmol), and 16 (maroon square).

**Table S3.** Conductivity measurements of control experiment with BF$_3$•OEt$_2$.

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<th>Equiv 16</th>
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<th>Trial 2</th>
<th>Trial 3</th>
<th>Average</th>
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</thead>
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**Table S4.** Conductivity measurements of experiment with BF$_3$•OEt$_2$ and TMSCl (2 mmol).

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<th>Trial 2</th>
<th>Trial 3</th>
<th>Average</th>
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</thead>
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Figure S29. Conductivity measurements BCl₃ (1 mmol in 6 mL DCE) and 16 (Control – black square) and of BCl₃ (1 mmol in 6 mL DCE), TMSCl (2 mmol), and 16 (maroon square).

Table S5. Conductivity measurements of control experiment with BCl₃.

<table>
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<th>Equiv 16</th>
<th>Conductivity (µS/Cm)</th>
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<td>Trial 1</td>
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Table S6. Conductivity measurements of experiment with BCl₃ and TMSCl (2 mmol).

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Figure S30. Conductivity measurements AlCl₃ (1 mmol in 6 mL DCE) and 16 (Control – black square) and of AlCl₃ (1 mmol in 6 mL DCE), TMSCl (2 mmol), and 16 (maroon square).

Table S7. Conductivity measurements of control experiment with AlCl₃.

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Table S8. Conductivity measurements of experiment with AlCl₃ and TMSCl (2 mmol).

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<th>Equiv 16</th>
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<th>Trial 2</th>
<th>Trial 3</th>
<th>Average</th>
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Figure S31. Conductivity measurements ZrCl$_4$ (1 mmol in 6 mL DCE) and 16 (Control – black square) and of ZrCl$_4$ (1 mmol in 6 mL DCE), TMSCl (2 mmol), and 16 (maroon square).

Table S9. Conductivity measurements of control experiment with ZrCl$_4$.  

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Trial 1</td>
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<tr>
<td>0.0</td>
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Table S10. Conductivity measurements of experiment with ZrCl$_4$ and TMSCl (2 mmol).  

<table>
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<th>Conductivity ($\mu$S/Cm)</th>
</tr>
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<td>Trial 1</td>
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<tr>
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<tr>
<td>0.5</td>
<td>5.230</td>
</tr>
<tr>
<td>1.0</td>
<td>6.538</td>
</tr>
<tr>
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<td>2.0</td>
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<td>11.220</td>
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Figure S32. Conductivity measurements SnCl₄ (1 mmol in 6 mL DCE) and 18 (Control – black square) and of SnCl₄ (1 mmol in 6 mL DCE), TMSCl (2 mmol), and 18 (maroon square).

Table S11. Conductivity measurements of control experiment with SnCl₄.

<table>
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<tr>
<th>Equiv 16</th>
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<th>Trial 3</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
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Table S12. Conductivity measurements of experiment with SnCl₄ and TMSCl (2 mmol).

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<th>Trial 2</th>
<th>Trial 3</th>
<th>Average</th>
</tr>
</thead>
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<td>2.649</td>
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<td>9.510</td>
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<td>11.280</td>
<td>11.310</td>
<td>11.293</td>
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**Figure S33.** Conductivity measurements TiCl$_4$ (1 mmol in 6 mL DCE) and 18 (Control – black square) and of TiCl$_4$ (1 mmol in 6 mL DCE), TMSCl (2 mmol), and 18 (maroon square).

**Table S13.** Conductivity measurements of control experiment with TiCl$_4$.

<table>
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<td>Trial 1</td>
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<td>6.898</td>
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**Table S14.** Conductivity measurements of experiment with TiCl$_4$ and TMSCl (2 mmol).

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<th>Conductivity ($\mu$S/Cm)</th>
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<td>Trial 1</td>
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<td>10.070</td>
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Figure S34. Conductivity measurements InCl$_3$ (1 mmol in 6 mL DCE) and 17 (Control – black square) and of InCl$_3$ (1 mmol in 6 mL DCE), TMSCl (1 mmol, 2 mmol), and 17 (gold square, maroon square) [Top left]. Conductivity measurements InCl$_3$ (1 mmol in 6 mL DCE) and 18 (Control – black square) and of TiCl$_4$ (1 mmol in 6 mL DCE), TMSCl (1 mmol, 2 mmol), and 17 (gold square, maroon square) [Top right]. Conductivity measurements InCl$_3$ (1 mmol in 6 mL DCE) and 16 (Control – black square) and of InCl$_3$ (1 mmol in 6 mL DCE), TMSCl (1 mmol, 2 mmol), and 17 (gold square, maroon square) [bottom center].
**Table S15.** Conductivity measurements of control experiment with InCl$_3$ and 17.

<table>
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<th>Conductivity (µS/Cm)</th>
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<tbody>
<tr>
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**Table S16.** Conductivity measurements of experiment with InCl$_3$ and TMSCl (1 mmol) and 17.

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**Table S17.** Conductivity measurements of experiment with InCl$_3$ and TMSCl (2 mmol) and 17.

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Table S18. Conductivity measurements of control experiment with InCl$_3$ and 18.

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Table S19. Conductivity measurements of experiment with InCl$_3$ and TMSCl (1 mmol) and 18.

<table>
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Table S20. Conductivity measurements of experiment with InCl$_3$ and TMSCl (2 mmol) and 18.

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Table S21. Conductivity measurements of control experiment with InCl$_3$ and 16.

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Table S22. Conductivity measurements of experiment with InCl$_3$ and TMSCl (1 mmol) and 16.

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<th>Trial 2</th>
<th>Trial 3</th>
<th>Average</th>
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Table S23. Conductivity measurements of experiment with InCl$_3$ and TMSCl (2 mmol) and 16.

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<th>Trial 3</th>
<th>Average</th>
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Figure S35. Conductivity measurements GaCl₃ (1 mmol in 6 mL DCE) and 17 (Control – black square) and of GaCl₃ (1 mmol in 6 mL DCE), TMSCl (1 mmol, 2 mmol), and 17 (gold square, maroon square) [Top left]. Conductivity measurements GaCl₃ (1 mmol in 6 mL DCE) and 18 (Control – black square) and of GaCl₃ (1 mmol in 6 mL DCE), TMSCl (1 mmol, 2 mmol), and 17 (gold square, maroon square) [Top right]. Conductivity measurements GaCl₃ (1 mmol in 6 mL DCE) and 16 (Control – black square) and of GaCl₃ (1 mmol in 6 mL DCE), TMSCl (1 mmol, 2 mmol), and 17 (gold square, maroon square) [bottom center].
**Table S24.** Conductivity measurements of control experiment with GaCl₃ and 17.

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<tr>
<th>Equiv 17</th>
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**Table S25.** Conductivity measurements of experiment with GaCl₃ and TMSCl (1 mmol) and 17.

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<tr>
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<tr>
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<tr>
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<tr>
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**Table S26.** Conductivity measurements of experiment with GaCl₃ and TMSCl (2 mmol) and 17.

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### Table S27. Conductivity measurements of control experiment with GaCl₃ and 18.

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### Table S28. Conductivity measurements of experiment with GaCl₃ and TMSCl (1 mmol) and 18.

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### Table S29. Conductivity measurements of experiment with GaCl₃ and TMSCl (2 mmol) and 18.

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Table S30. Conductivity measurements of control experiment with GaCl₃ and 16.

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Table S31. Conductivity measurements of experiment with GaCl₃ and TMSCl (1 mmol) and 16.

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<th>Trial 3</th>
<th>Average</th>
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Table S32. Conductivity measurements of experiment with GaCl₃ and TMSCl (2 mmol) and 16.

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300
Figure S36. Conductivity measurements FeCl$_3$ (1 mmol in 6 mL DCE) and 17 (Control – black square) and of FeCl$_3$ (1 mmol in 6 mL DCE), TMSCI (1 mmol, 2 mmol), and 17 (gold square, maroon square) [Top left]. Conductivity measurements FeCl$_3$ (1 mmol in 6 mL DCE) and 18 (Control – black square) and of FeCl$_3$ (1 mmol in 6 mL DCE), TMSCI (1 mmol, 2 mmol), and 17 (gold square, maroon square) [Top right]. Conductivity measurements FeCl$_3$ (1 mmol in 6 mL DCE) and 16 (Control – black square) and of FeCl$_3$ (1 mmol in 6 mL DCE), TMSCI (1 mmol, 2 mmol), and 17 (gold square, maroon square) [bottom center].
Table S33. Conductivity measurements of control experiment with FeCl₃ and 17.

<table>
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<th>Average</th>
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<td>Trial 3</td>
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Table S34. Conductivity measurements of experiment with FeCl₃ and TMSCl (1 mmol) and 17.

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<td>Trial 3</td>
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**Table S35.** Conductivity measurements of experiment with FeCl₃ and TMSCl (2 mmol) and 17.

![Table S35](data:image/png;base64,iVBORw0KGgoAAAANSUhEUgAAAAEAAABeAQMAAABbF9QAABDeGh9odEAAAAAElFTkSuQmCC)

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**Table S36.** Conductivity measurements of control experiment with FeCl₃ and 18.

![Table S36](data:image/png;base64,iVBORw0KGgoAAAANSUhEUgAAAAEAAABeAQMAAABbF9QAABDeGh9odEAAAAAElFTkSuQmCC)

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Table S37. Conductivity measurements of experiment with FeCl$_3$ and TMSCl (1 mmol) and 18.

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Table S38. Conductivity measurements of experiment with FeCl$_3$ and TMSCl (2 mmol) and 18.

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Table S39. Conductivity measurements of control experiment with FeCl₃ and 16.

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Table S40. Conductivity measurements of experiment with FeCl₃ and TMSCl (1 mmol) and 16.

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### Table S41. Conductivity measurements of experiment with FeCl$_3$ and TMSCl (2 mmol) and 16.

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REFERENCE LIST

(16) Trost, B. M.; Jiang, C. Catalytic Enantioselective Construction of All-Carbon Quaternary


(43) Krishna Murthy, J.; Gross, U.; Rüdiger, S.; Venkat Rao, V.; Vijaya Kumar, V.; Wander, A.; Bailey, C. L.; Harrison, N. M.; Kemnitz, E. Aluminum Chloride as a Solid Is Not a


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(59) Gnuni, Karapetyan; Muhammad, Sher; Tariel, V. Ghochikyan; Ashot, Saghyan; Langer, Peter; T. T. D. Diversity-Oriented Synthesis of Functionalized Phenols by Regioselective [3+3] Cyclocondensations of 1,3-Bis(Silyloxy)-1,3-Butadienes with 3-Alkoxy-2-En-1-Ones and Related Substrates. Curr. Org. Chem. 2012, 16 (5), 557–565.


(69) Shirinian, V. Z.; Lvov, A. G.; Yanina, A. M.; Kachala, V. V.; Krayushkin, M. Synthesis

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VITA

Sophi R. Todtz received her undergraduate degree in synthetic organic chemistry from the University of San Francisco in San Francisco, California. While at the University of San Francisco, Dr. Todtz, under the direction of Dr. Jie Jack Li, worked towards the synthesis of chiral BINOL-type ligands for use in organic transformations. Dr. Todtz continued her education by pursuing a Ph.D. in physical organic chemistry at Loyola University Chicago under the guidance of Dr. James Devery. Since joining the Devery lab, Sophi Todtz has worked towards exploring the effects of ligand systems and additives on the solution interactions of Lewis acids and carbonyls. Dr. Todtz designed experiments to examine the impact of these effects on solution behavior in catalytic systems and applied these observations to develop a method towards the mitigation of byproduct inhibition in carbonyl-olefin metathesis. Dr. Todtz will be joining MilliporeSigma as an analytical development scientist in July of 2023 where she will work towards the development and implementation of new analytical methods, concepts, and technologies.