N-Heterocyclic and Mesoionic Carbene Complexes of Rhodium and Palladium:

Coordination Chemistry and Catalysis

by

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Abstract

Dimeric rhodium *N*-heterocyclic carbene (NHC) complexes $[Rh(NHC)(C_2H_4)Cl]_2$ react with a variety of other neutral donors to form heteroleptic complexes $[(L)Rh(NHC)(C_2H_4)Cl]$ (L = phosphine, pyridine) or $[(L)Rh(NHC)Cl]$ (L = 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen)). The reactivity of the resulting complexes towards O_2 was investigated. In particular, [(bipy)Rh(NHC)Cl] and [(phen)Rh(NHC)Cl] resulted in Rh^{III} peroxo complexes. In contrast, $[Rh(NHC)_2(O_2)Cl]$ display particularly short O-O bond lengths and are described as singlet oxygen species. Interestingly, the mode in which O_2 binds is associated with the coordination number about the transition metal complex, which is related to its reducing power.

$[Rh(IPr)(C_2H_4)Cl]_2$ reacts with phenyl pyridine derivatives at room temperature resulting in formal C-H activations. Upon the treatment of phenyl pyridine with pinacol borane (HBPin) in the presence of a weak base and a catalytic amount of $[Rh(IPr)(C_2H_4)Cl]_2$, C-H borylated products were obtained in high yield and selectivity. The borylated products can then be used as substrates in the palladium catalyzed Suzuki-Miyaura cross coupling with aryl halides.

1,2,3-Triazole mesoionic carbene (tMIC) ligands were generated upon treatment of corresponding triazolium salts with strong bases, and can be trapped in the presence of a transition metal. The synthesis of Ag-tMIC complexes proceeds by a facile and mild route upon treatment of the triazolium salt with Ag_2O. The resulting Ag-tMIC complexes undergo facile transmetallation to both Pd and Rh under very mild conditions resulting in air and moisture stable metal complexes. Triazolium salts can further be metallated to Pd

in the presence of weak bases, and the resulting Pd-tMIC complexes are active catalysts in the Mizoroki-Heck reaction with aryl iodides.

Benzylic trifluoromethyl sulfones are competent electrophilic substrates in palladium catalyzed cross coupling reactions, resulting in the formation of triarylmethanes in high yields under mild conditions. These substrates are conveniently synthesized and are highly reactive starting materials with phenyl boronic acids in the presence of a Pd-NHC catalyst. The structure of the Pd-NHC precatalyst is crucial, as only [(NHC)Pd(allyl)Cl] type complexes appear to be effective. These complexes can be conveniently synthesized upon the treatment of the corresponding imidazolium salt with a strong base and $[Pd(allyl)Cl]_2$.

Co-Authorship

I hereby declare that this thesis incorporates material that is the result of a joint research project as follows:

This thesis incorporates the outcome of research undertaken with the assistance of master's student Brandon D. Moore and postdoctoral research fellow Dr. Olena V. Zenkina. In all cases, the primary contributions, a majority of the experimental efforts and data analysis were performed by the author.

I certify that, with the above qualification, this thesis and the research to which it encompasses is the product of my own work.

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Statement of Originality

I hereby certify that all of the work described within this thesis is the original work of the author. Any published (or unpublished) ideas and/or techniques from the work of others are fully acknowledged in accordance with the standard referencing practices.

(Eric C. Keske)

(April, 2015)

List of Publications

1. Zenkina, O. V.; Keske, E. C.; Wang, R.; Crudden, C. M. "Double single-crystal-to-single-crystal transformation and small-molecule activation in rhodium NHC complexes" *Angew. Chem. Int. Ed.* **2011**, 50, 35, 8100-8104.

2. Zenkina, O. V.; Keske, E. C.; Wang, R.; Crudden, C. M. "Dimeric rhodium−ethylene NHC complexes as reactive intermediates for the preparation of tetra-heteroleptic NHC complexes" *Organometallics*, **2011**, 30, 23, 6423-6432.

3. Keske, E. C.; Zenkina, O. V.; Wang, R.; Crudden, C. M. "Synthesis and structure of silver and rhodium 1,2,3-Triazol-5-ylidene mesoionic carbene complexes." *Organometallics*, **2012**, 31, 1, 465-461.

4. Keske, E. C.; Zenkina, O. V.; Wang, R.; Crudden, C. M. "Synthesis and structure of palladium 1,2,3-Triazol-5-ylidene mesoionic carbene PEPPSI complexes and their catalytic applications in the Mizoroki−Heck Reaction" *Organometallics*, **2012**, 31, 17, 6215.

5. Cipot-Wechsler, J.; Covelli, D.; Praetorius, J. M.; Hearns, N.; Zenkina, O. V.; Keske, E. C.; Wang, R. Kennepohl, P.; Crudden, C. M. "Synthesis and characterization of cationic rhodium peroxo complexes" *Organometallics,* **2012**, 31, 21, 7306.

6. Zenkina, O. V.; Keske, E. C.; Kochhar, G. S.; Wang, R.; Crudden, C. M. "Heteroleptic rhodium NHC complexes with pyridine derived ligands: synthetic accessibility and reactivity towards oxygen" *Dalton Trans*. **2013**, 42, 2282.

7. Keske, E. C.; Zenkina, O. V.; Asadi, A.; Sun, H.; James, B. R.; Praetorius, J. P.; Allen, D. P.; Covelli, D.; Wang, R.; Kennepohl, P.; Crudden, C. M. "Dioxygen adducts of rhodium N-heterocyclic carbene Complexes" *Dalton Trans.* **2013**, 42, 7414.

8. Crudden, C.M.; Horton, J. H.; Ebralidze, I.; Zenkina, O. V.; McLean, A.B; Drevniok, B.; She, Z.; Kraatz, H-B.; Mosey, N.; Seki, T.; Keske, E.C.; Leake, J.D.; Rousina-Webb, A.; Wu, G. "Ultra stable self-assembled monolayers of N-heterocyclic carbenes on gold" *Nature Chem.* **2014**, 6, 409.

9. Keske, E. C.; Moore, B. D.; Zenkina, O. V.; Wang, R.; Crudden, C. M. "Directed dehydrogenative C-H borylation catalyzed by dimeric rhodium NHC complexes" *Chem. Commun*. **2014**, 50, 9889.

10. Eisenberger, P.; Bestvater, B. P.; Keske, E. C.; Crudden, C. M. "Hydrogenations at room temperature and atmosphereic pressure with mesoionic carbene-stabilized borenium catalysts." *Angew. Chem. Int. Ed.* **2015**, 54, 2567.

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List of Schemes

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List of Abbreviations

9-BBN	9-borabicyclo[3.3.1] nonane
Ac	acetyl
Ad	Adamantyl
acac	acetylacetonate
alk	alkyl
aNHC	abnormal *N*-heterocyclic carbene
atm	atmosphere(s)
Ar	aryl
B/L	branched-to-linear
BDE	bond dissociation energy
BIMe	1-methylbenzimidazole
BINAP	2,2’-bis(diphenylphosphino)-1,1’-binapthyl
bipy	2,2’-bipyridine
BITr	1-triphenylmethylbenzimidazole
bmim	1-butyl-3-methylimidazolium
bmim-y	1-butyl-3-methylimidazol-2-ylidene
Boc	*tert*-butoxycarbonyl
BQ	benzoquinone
Bu	butyl
°C	Celcius
Cat.	catalytic amount
cm	centimeter

CMD	concerted metallation deprotonation
COD	1,5-cyclooctadiene
COE	cyclooctene
Cp	cyclopentadienyl
Cp*	1,2,3,4,5-pentamethylcyclopentadienyl
Cy	cyclohexyl
dba	dibenzylideneacetone
DCE	1,2-dichloroethane
DCM	dichloromethane
DME	dimethoxyethane
Dipp	2,6-diisopropylphenyl
DFT	density functional theory
DMA	*N,N'*-dimethylacetamide
DMC	dimethylcarbonate
DMF	*N*,*N*'-dimethylformamide
D*o*M	directed ortho metallation
dpen	(*R*,*R*)-diphenylethylenediamine
EA	Elemental Analysis
ee	enantiomeric excess
EI-TOF	electron impact time of flight
Eq.	equation
ESI-TOF	electrospray ionization time of flight
Equiv.	equivalent(s)

Et	ethyl
eV	electron volt
GC	gas chromatography
h	hour(s)
HMDS	hexamethyldisilazide
HRMS	high-resolution mass spectrometry
Hz	hertz
IAd	1,3-diadamantylimidazol-2-ylidene
ICy	1,3-dicyclohexylimidazol-2-ylidene
IDM	1,3-dimethylimidazol-2-ylidene
IiPr	1,3-diisopropylimidazol-2-ylidene
IMes	1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene
IPent	1,3-bis(2,6-neopentylphenyl)imidazol-2-ylidene
iPr	isopropyl
IPr	1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene
IPr*	1,3-bis(2,6-bis(diphenylmethyl)-4-methylphenyl)imidazo- 2-ylidene
IR	infrared spectroscopy
ItBu	1,3-bis(*tert*-butyl)imidazol-2-ylidene
J	coupling constant
K	kelvin
L	ligand
L/B	linear-to-branched
Me	methyl

MeCN	acetonitrile
MeOH	methanol
Mes	2,4,6-trimethylphenyl
MeIiPr	1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene
MIC	mesoionic carbene
min	minute
MS	molecular sieves
ND	not determined
NHC	N-heterocyclic carbene
NMR	nuclear magnetic resonance
NR	no reaction
PEPPSI	pyridine enhanced precatalyst preparation stabilization and initiation
Ph	phenyl
Pin	pinacol
ppm	parts per million
Pr	propyl
psi	pounds per square inch
Qphos	1,2,3,4,5-pentaphenyl-1’-(di-tert-butylphosphino)ferrocene
RCM	ring-closing metathesis
RDS	rate determining step
ROMP	ring-opening metathesis polymerization
r	radius
r.t.	room temperature

SIMes	1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene
SIPr	1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene
SPhos	2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl
T	temperature
tBu	tertbutyl
TFAA	trifluoroacetic acid
THF	tetrahydrofuran
TMS	trimethylsilyl
TMEDA	*N*,*N*,*N*,*N*-tetramethylethylene diamine
TOF	turn over frequency
TON	turn over number
V_{Bur}	volume buried

Chapter 1

Introduction to N-Heterocyclic Carbenes as Ligands for Late Transition Metal Catalysis: Development, Synthesis, Structure, and Study

1.1 Introduction and Background on Ligand Development

The field of transition metal catalysis offers exciting possibilities in advancing synthetic organic chemistry, which has implications in fields ranging from pharmaceuticals to materials science.[1] In a fundamental sense, catalysis lowers reaction barriers, and can reduce chemical waste which offers a more environmentally friendly approach to organic synthesis. Possibly the most important feature of transition metal catalysis lies in the formation of new chemical bonds, which, in the absence of the metal, may not be feasible to construct.[2] As a result, this is currently an actively investigated field.[3] Within this field, the development of new ligands, and the fundamental study of their coordination chemistry is absolutely critical and of great importance in order to help tune transition metal catalysts for optimum performance.[4] Ligands are capable of stabilizing catalytically active species, thus improving catalyst turnovers, and decreasing catalyst loading. But in addition, different ligands can result in changes to the chemo-, regio-, and enantioselectivity of catalytic processes.

Without a doubt, phosphines have had the largest impact on homogeneous catalysis (Figure 1-1).[5] This is in part due to their ease of tunability with regard to both electronic and steric parameters, as well as their well-behaved coordination to most transition metals. However, phosphines have many limitations that have not gone unnoticed. The instability of phosphines, as well as many of their complexes, to oxidative conditions, combined with

the general lability of their bonds to transition metals has prevented the use of these ligands in some catalytic applications. As a result, many researchers have been actively exploring new avenues to make phosphines more powerful, universal and user-friendly, while increasing their oxidative stability.[6] Despite these efforts however, it is no surprise that as new families of ligands are developed, and it can be said that phosphines are continually being challenged for their supremacy.

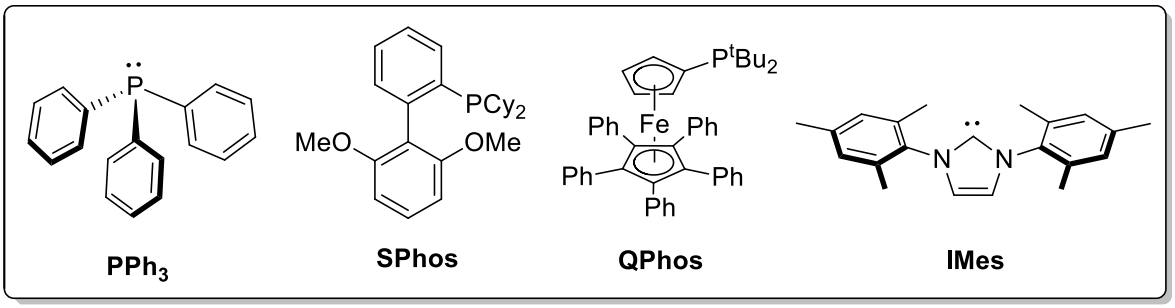


Figure 1-1: Various ligands described in the literature for homogeneous catalysis[4a]

The class of ligands that has had the biggest impact on organometallic chemistry in the last two decades is *N*-heterocyclic carbenes (NHCs).[7] Originally NHCs were merely laboratory curiosities, but after several key reports appeared detailing the isolation of these species[8] and their coordination to transition metals,[7b] researchers began investigating complexes of these ligands in catalysis.[9] Many highly active catalysts have been reported, and it appears that NHCs offer many distinct advantages over phosphines.[9] In particular, transition metal NHC complexes display substantially higher oxidative stability relative to phosphines.[10] In addition, NHCs produce very electron rich metal complexes, and typically bind very tightly to metals, and display much lower lability.[11] These ligands have enjoyed a remarkable development, and are now regarded as state of the art for transition metal

catalysis. Importantly, NHCs have displayed coordination not only to transition metals, but also to main group[12] as well as some F-block metals.[13] In addition, they have made a big impact in organocatalysis, and have even been implicated in biological systems involving Thiamine (vitamin B1).[14] In comparison to phosphines however, NHCs are still in their infancy. A brief background and history of carbenes and their coordination chemistry follows, along with some examples of their use in catalysis.

1.2 Background and History of Carbenes

Carbenes, which are defined as neutral species featuring a divalent carbon atom with only six valence electrons, have a long and extensive history in organic chemistry.[15] For decades, these species were commonly only encountered as reactive intermediates,[16] but in recent years, there have been numerous reports on the isolation of carbenes.[17] As a result, stable carbenes are now commonplace in modern literature. Their increased prevalence has resulted in the discovery of their extensive utility, not only as intermediates in organic chemistry, but also as ligands in organometallic chemistry.[18]

Carbenes can exist in either a singlet, or a triplet electronic state (Figure 1-2), and depending on the electronic configuration of the carbene, fundamentally different reactivity is observed.[17a] Specifically, triplet carbenes are sp hybridized, display linear geometry, and can be viewed as a diradical.[19] The unpaired electrons reside in two degenerate 2p non-bonding orbitals. This is in contrast to singlet carbenes, which are sp^2 hybridized and bent in structure. The non-bonding electrons exist as a pair, occupying a single, typically sp^2-hybridized orbital, leaving an empty orbital (commonly the p_π orbital) at 90° from the

occupied σ-orbital. Importantly, while triplet carbenes tend to be electrophilic in character, singlet carbenes are nucleophilic.[20]

The electronic configuration of the carbene is dictated dominantly by the substitutions on the carbon atom itself. Typically substituents which are capable of donating electrons into the empty p_π orbital raise the relative energy of this orbital, while leaving the σ orbital relatively untouched, favouring a singlet configuration.[19] Conversely, electropositive substituents destabilize this orbital and instead favour triplet configurations.[21]

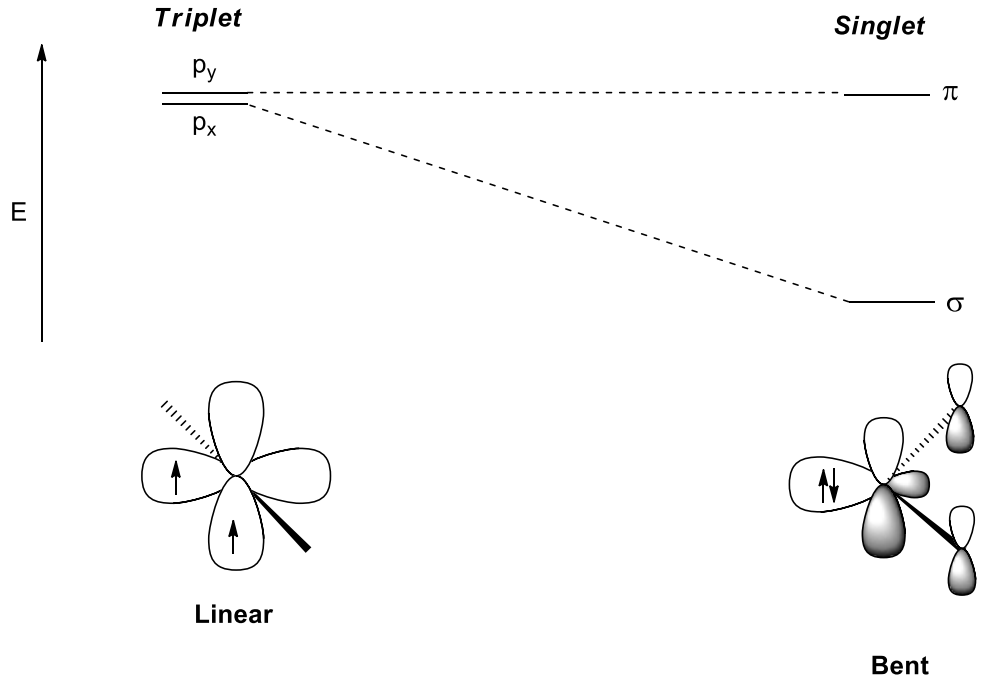
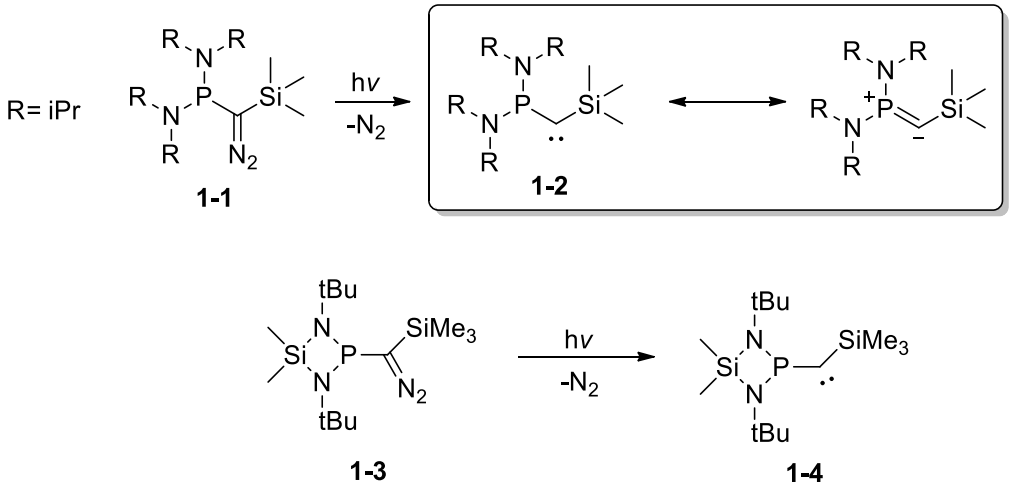


Figure 1-2: Graphical depiction of triplet and singlet carbenes

1.3 Isolation of Stable Carbenes

The first stable "bottleable" carbene was reported by Bertrand and coworkers in 1988, who described the synthesis and isolation of **1-2** by photolysis (300 nm) of **1-2** and,

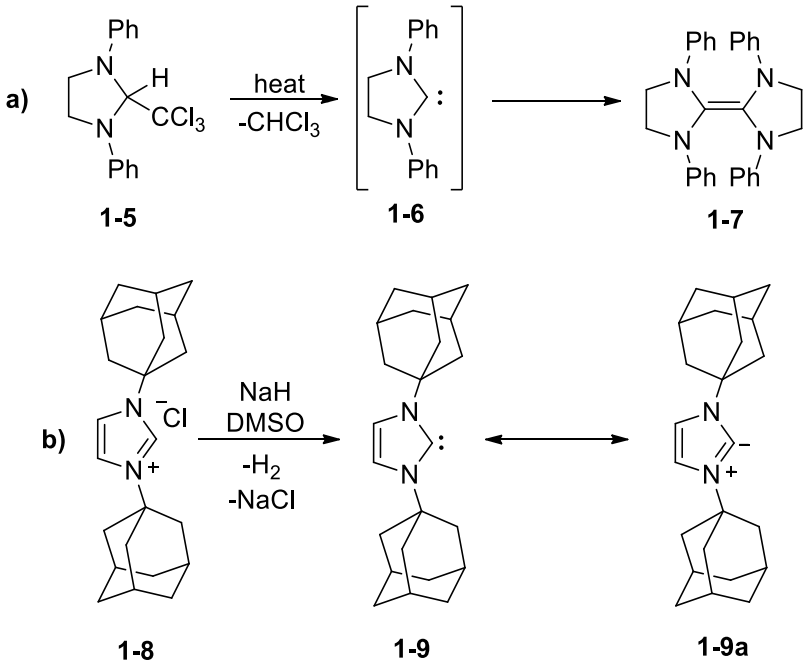
through a variety of experiments, demonstrated their carbene character (Scheme 1-1).[22] The key to the isolation of **1-2** was the pendant phosphino group that provided stabilization of the carbene atom by donation into the vacant p_π orbital. This effect helps to favour the singlet electronic state. The trimethylsilyl substituent also provided a beneficial weak interaction between the carbene lone pair, and the low-lying σ* orbital on the silyl group. While no crystal structure was originally reported, the crystal structure of related compound **1-4** was reported in 2000,[23] which indicated that this species may be better viewed as a vinyl ylide due to the substantial double bond character observed (P-C = 1.532(3) Å).



Scheme 1-1: Bertrand's synthesis of phosphoryl-silyl carbenes[22a, 23]

In 1991, Arduengo and coworkers used a different strategy to synthesize imidazolium-derived carbenes, that also resulted in the isolation of the free carbene (Scheme 1-2).[8a] These compounds, named *N*-heterocyclic carbenes (NHCs), were conveniently synthesized by deprotonation of their corresponding imidazolium salts. Decades earlier, Wanzlick had attempted to isolate the highly similar carbene **1-6** by a route

instead involving the loss of $CHCl_3$ from **1-5** upon heating.[24] Instead of the desired carbene, enetetramine **1-7** was obtained as the only product. It was proposed that the enetetramine may be in equilibrium with the free carbene, and this process was termed the 'Wanzlick equilibrium'.[25] In order to avoid the undesired Wanzlick equilibrium, Arduengo employed substantial steric bulk in the form of adamantyl groups on the flanking nitrogens to prevent the carbene from dimerizing. This approach was successful, and importantly, the resulting carbene, IAd (compound **1-9**), was crystalline, and its x-ray crystal structure was of crucial importance in confirming its description as a carbene. When compared to its imidazolium salt **1-8**, the C-N bond length was increased from 132 to 148.5 pm, and the C-N-C bond angle was decreased from 108 to 102.2°. These features suggest decreased π-delocalization compared to the imidazolium salt, which suggests significant carbene character, confirming the proposed structure of IAd. However it should be pointed out that vinyl ylide **1-9a** represents a valid resonance structure, and likely does contribute to the overall structure.



Scheme 1-2: a) Wanzlick's attempted synthesis of NHCs b) Arduengo's synthesis of free and stable NHCs

Since this initial report, a wide variety of other NHCs have been reported which vary in the nature of the heterocycle itself, as well as the steric parameters of the wingtip groups (Figure 1-3).[7b] It should be pointed out that while large wingtip groups generally increase the stability and thereby the lifetime of the carbene, depending on the nature of the heterocycle, these large groups are not necessarily required for stability. For example, imidazole derived carbenes with substantially smaller alkyl wingtip groups such as isopropyl (IiPr)[26] or even methyl (IDM)[27] groups also result in isolable carbenes despite their decreased steric protection and stability.

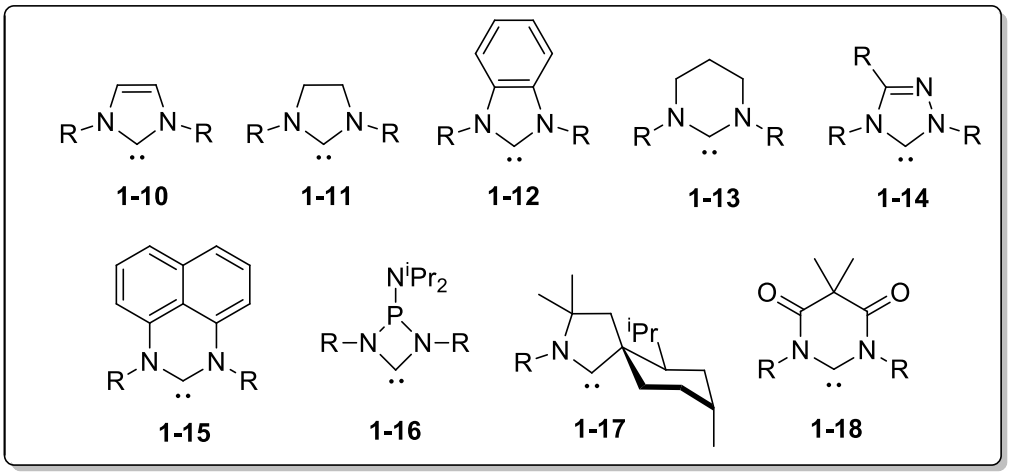
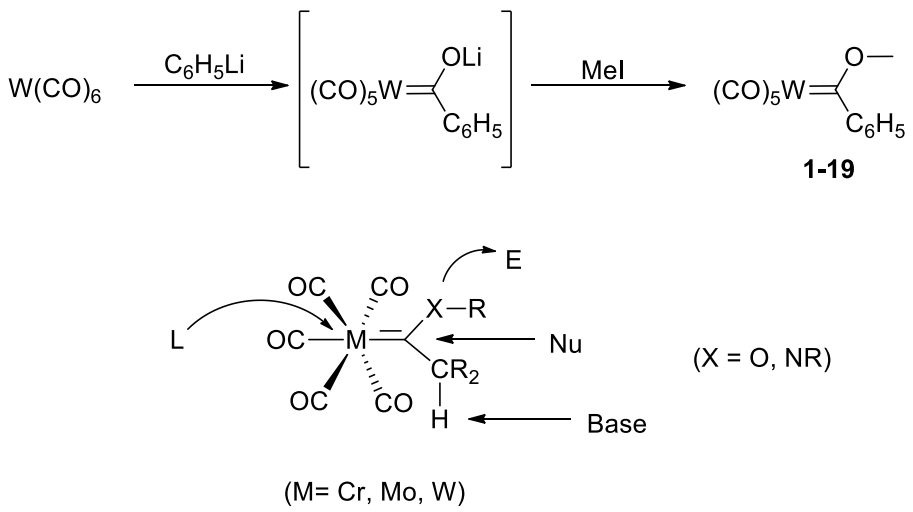


Figure 1-3: Selected examples of various heterocyclic carbenes reported in the literature[28]

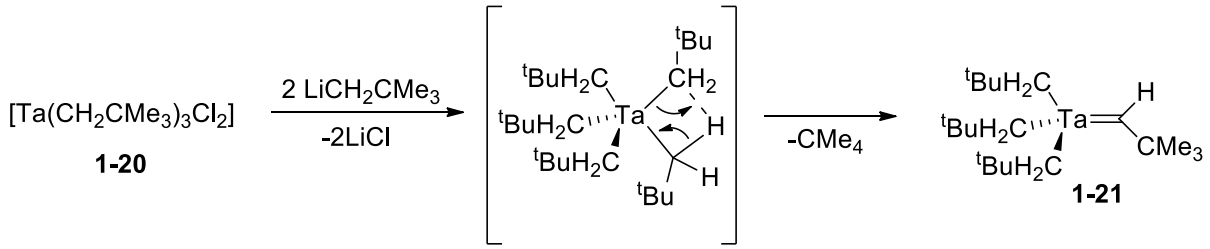
1.4 Carbenes as Ligands for Transition Metals

Despite the inherent instability of many free carbenes, their history as ligands for transition metals is well documented. In 1964, Fischer described what would be the first report of a well-defined transition metal carbene complex.[29] Treatment of $W(CO)_6$ with C_6H_5Li followed by MeI resulted in **1-19**, what would be soon known as the first Fischer carbene complex. After this report, similar reactivity was described employing chromium and molybdenum species.[30] The resulting complexes were studied extensively to probe the bonding structure of the carbene.[31] Generally, Fischer carbenes form strong bonds to low oxidation state (0 or +1) metals that are capable of substantial back bonding towards the carbene. Fischer carbenes exhibit true double bond character to a transition metal, with substantial overlap of empty p orbital on the carbene with the adjacent heteroatom.[32] Fischer carbene complexes characteristically display unique reactivity, most importantly they typically undergo nucleophilic attack at the carbene carbon (Scheme 1-3).[33]



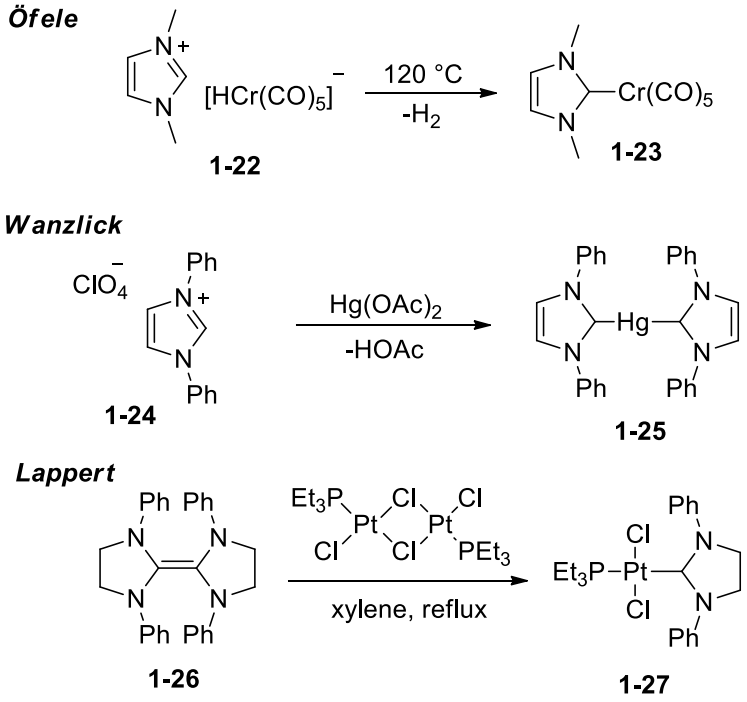
Scheme 1-3: Synthesis of the first Fischer carbene complex, and general reactivity of these complexes

In 1974, a report by Schrock appeared which detailed the synthesis of a very different kind of transition metal carbene complex.[34] Treatment of $[Ta(CH_2CMe_3)_3Cl_2]$, with $LiCH_2CMe_3$ resulted in the clean formation of carbene complex **1-21** in quantitative yield along with the formation of LiCl and neopentane (Scheme 1-4). This process involves an α-hydrogen elimination, which likely takes place by a sigma bond metathesis-type mechanism. In contrast to the reported Fischer type carbenes described previously, the carbene centre was totally lacking in heteroatom stabilization. In further contrast, they coordinate to high oxidation state metals that are not capable of back bonding. Another major difference was their general reactivity, as they display nucleophilic character.[35] These ligands were termed 'alkylidenes' and have a very different bonding structure than what was previously observed. While Fischer carbenes can be viewed in the singlet state and donate electrons towards the metal while receiving back donation from the metal into the empty π orbital, alkylidenes may be more appropriately viewed as existing in the triplet state, with the π-electrons equally distributed throughout.[31]



Scheme 1-4: Schrock's original synthesis of tantalum complex containing and alkylidene ligand

In addition to these reports, in 1968 Wanzlick[36] and Öfele[37] independently reported the synthesis and isolation of other carbene metal complexes which differed fundamentally from the earlier reports by Fischer or Schrock by virtue of the nature of the carbene itself (Scheme 1-5). By using imidazolium salts in the presence of either $[HCr(CO)_5]^-$ or $[Hg(OAc)_2]$, they observed the resulting complexes as the first examples of isolated transition metal complexes bound to NHCs (**1-23**, and **1-25** respectively). This was later followed up by a report from Lappert and coworkers, who described the synthesis of platinum NHC complex **1-27**, by the reaction of dimeric platinum precursors with enetetramine **1-26**. This synthetic strategy instead takes advantage of the Wanzlick equilibrium (*vide supra*), which generates free carbenes from enetetramines that are trapped in the presence of a metal.



Scheme 1-5: Early synthetic strategies to transition metal NHC complexes

In contrast to either Fischer or Schrock type carbenes, NHCs display remarkable stability and essentially no reactivity of the ligand under nucleophilic or electrophilic conditions. This is likely in part due to the substantial stabilization of the carbene via donation of π-electrons from the flanking N groups into the empty π-orbital on the carbene. In addition, while NHC complexes do exhibit some back-bonding from the transition metal, it is substantially less relative to Fischer carbene complexes.[38] Fundamentally, Fischer carbenes, alkylidenes and NHCs display different bonding structures to transition metals, which likely explains the difference in their reactivity. Simplified bonding structures of these metal ligand interactions are shown in Figure 1-4.

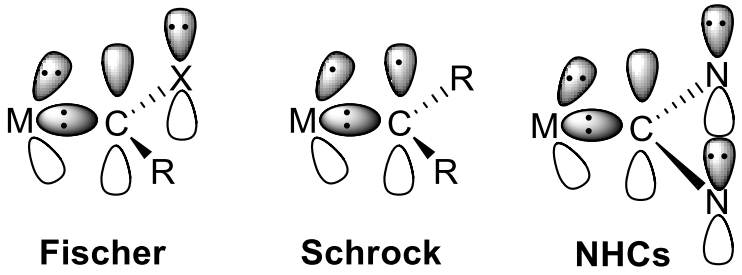


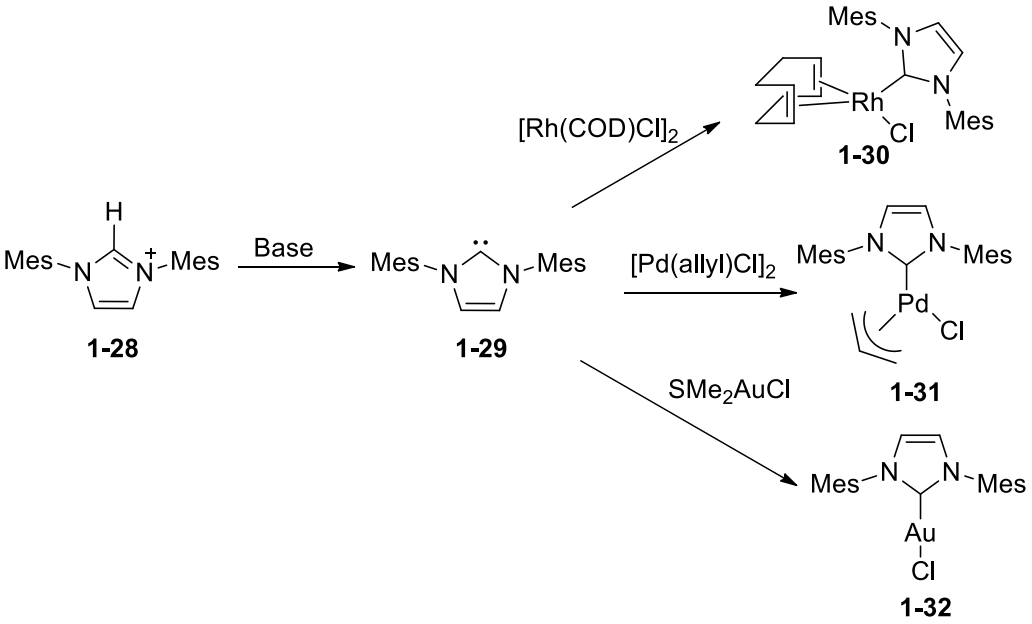
Figure 1-4: Graphical depiction of different bonding structure of carbenes

Despite these initial reports on transition metal NHC complexes, the field lay strangely dormant save for work by Lappert.[39] This is likely in part due to the problematic and inefficient synthetic protocols for the synthesis of these complexes. In this regard it should be then no surprise that after Arduengo's initial report on the isolation of stable NHCs, reports on the metallation of these ligands were numerous. In contrast to both Fischer and Schrock type carbenes, NHCs have been found to make stable complexes with almost every metal in the periodic table including main group metals and even some F-block metals.[13] Although decomposition reactions have been reported,[40] these ligands are fairly non-discriminate in their metallation.[7a, 18]

1.5 Modern Synthesis of NHC complexes

Several strategies have been reported for the synthesis of NHC complexes of transition metals, utilizing imidazolium salts as precursors. Conveniently, imidazolium salts can be deprotonated in the presence of a strong base resulting in the free carbene. As free carbenes have been effectively used as ligands towards a wide variety of metal precursors in order to generate metal NHC complexes, this is likely the most commonly used methodology for the synthesis of transition metal NHC complexes (Scheme 1-6).

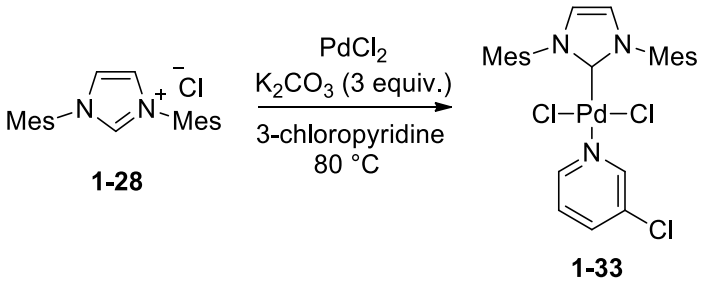
Conveniently, the free carbene can instead be prepared *in situ* in the presence of a transition metal under much milder conditions. For example, the free carbene IMes (**1-29**) can be combined with wide variety of transition metal precursors such as $[Rh(COD)Cl]_2$, $[Pd(allyl)Cl]_2$ or SMe_2AuCl to form NHC complexes **1-30**, **1-31**, and **1-32** respectively. In many cases however, the free carbene itself may not be indefinitely stable and may undergo a variety of decomposition reactions including the Wanzlick equilibrium. These side reactions can severely limit the use of free carbenes themselves, and several other methodologies have been developed.



Scheme 1-6: Synthesis of NHC metal complexes utilizing free carbenes

As the pKa of the imidazolium salt is estimated to be in the range of 22-25,[41] relatively strong bases are required for complete deprotonation of the imidazolium salt. Remarkably though, there have been several reports where far weaker bases such as K_2CO_3,[42] NEt_3[43] or NaOAc[44] are utilized to deprotonate imidazolium salts when the

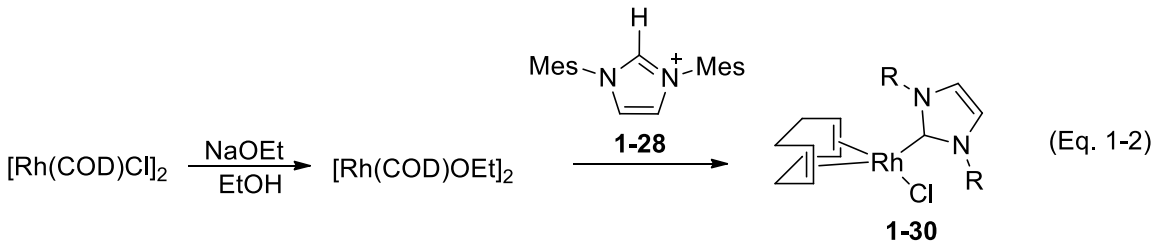
reaction is performed in presence of a metal. The conditions required are usually fairly harsh, including high temperatures and long reaction times. For example, complex **1-33** is synthesized by treatment of $PdCl_2$ with an imidazolium salt along with excess K_2CO_3 in refluxing 3-chloropyridine (Eq. 1-1).[42] Considering the pKa differences, it is unlikely that the free carbene is being generated to any appreciable degree, if at all. Although the mechanism of this transformation is unknown, it seems reasonable to suggest that an alternative explanation could involve a C-H activation protocol.[45] This is consistent with a wide body of literature on the functionalization of imidazoles at C2 by transition metal-catalyzed C-H functionalization. It has been suggested that the overall stability of the NHC complex provides a driving force for the overall metallation of the ligand.[46]



(Eq. 1-1)

Although these procedures provide exciting alternatives to the harsh requirement of strong bases, they can give inconsistent and low yielding results and are not as commonly employed in the preparation of isolated metal complexes. Alternatively, the use of metal precursors which have basic ligands such as $[Pd(OAc)_2]$,[47] $[Pd(acac)_2]$[48] or $[Rh(OEt)(COD)]_2$[49] can be a convenient alternative to the generation metal carbene complexes (Eq. 1-2). Formally these protocols were commonly encountered for forming well-defined transition metal NHC complexes, however these are inherently limited to metal precursors that contain basic ligands. This limitation prevents wider spread use of

this method. In addition, fairly harsh conditions are often also required, particularly with $Pd(OAc)_2$.[50] Nonetheless, this has been a particularly popular method.

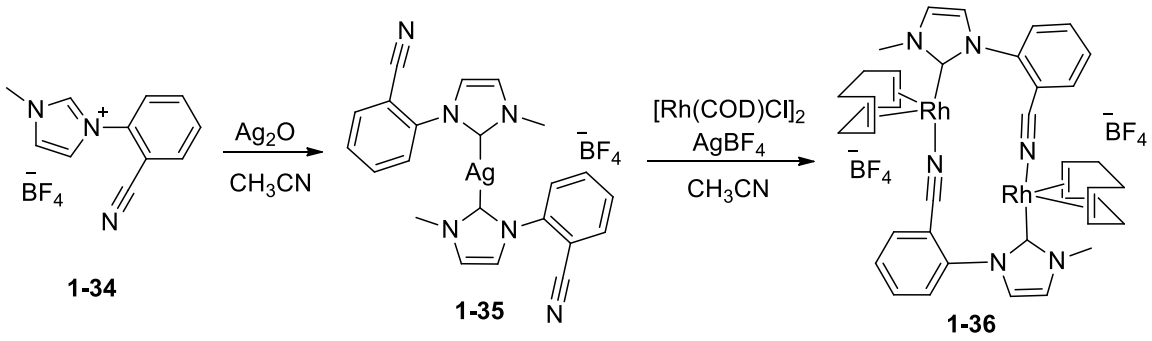


(Eq. 1-2)

Silver NHC complexes present a convenient alternative to the generation of free carbenes, as these species tend to be both air and moisture stable, but most importantly display facile transmetallation to other metals.[51] As a result of their facile transmetallation properties, Ag-NHCs are commonly thought of as free carbene surrogates. Commonly, Ag-NHCs can be conveniently prepared by the treatment of the imidazolium salt with a basic silver precursor such as Ag_2O or Ag_2CO_3 under ambient conditions. In contrast to some other methods, procedures featuring Ag_2O can be conducted at room temperature with no attempt to exclude air or moisture. Amazingly, Youngs and coworkers even described a synthesis in H_2O, displaying the remarkable stability of these precursors.[52] The silver NHC complexes need not be isolated, and are often immediately transmetallated following their synthesis. It should be noted however that a wide variety of Ag-NHC complexes are possible displaying a large range of complex architectures.[53] Most importantly, this method has proven to be general for a wide variety of carbene precursors that vary in the nature of the heterocycle itself.[54]

The use of Ag-NHCs as precursors for other transition metal NHC complexes is likely the most common route observed in the literature when the free carbene is inaccessible, or undesirable. For example, Morris and coworkers used the Ag-NHC

transmetallation methodology to synthesize rhodium nitrile-functionalized NHC complex **1-36** from Ag-NHC complex **1-35** (Scheme 1-7).[55] Due to the electrophilic character of the nitrile, attempts at synthesizing the free carbene of the ligand were met with failure. Instead, treatment with Ag_2O, followed by $[Rh(COD)Cl]_2$ resulted in the desired complex in high yield.



Scheme 1-7: Morris' use of the Ag-NHC transmetallation method to synthesize Rh-NHC complexes[55]

1.6 Properties of Transition Metal NHC Complexes

One key factor which sets NHCs apart from other ligands is their ability to produce particularly electron rich metal complexes.[11] In order to quantify the electron donating properties of NHCs, a variety of methods have been developed. As a more electron rich transition metal will transmit more electron density onto a strongly π-accepting ligand such as CO, the IR spectrum of a carbonyl-containing complex will provide information on the extent of back donation occurring. The lower the stretching frequency of the CO, the more basic the ligand *trans* to it.[56] Therefore, this method can be used to compare the amount of electron density donated by ligands, provided that their structures are otherwise analogous. Most commonly, the IR spectrum of rhodium or iridium complexes of general structure $[(NHC)M(CO)_2Cl]$ (M= Rh, Ir), or nickel complexes of general formula $[(NHC)Ni(CO)_3]$

can be used to compare various ligands. As a result of the simplicity of these tests, they are routinely preformed on newly described NHCs.

In 2006, Herrmann reported an exhaustive study where the CO stretches of several rhodium carbonyl complexes of general formula [(NHC)Rh(CO)$_2$Cl] were investigated.[27a] A wide selection of NHCs varying in the nature of the heterocycle were selected, and in order to properly compare the NHCs, the steric parameters of these ligands were held as close to one another as possible. From this investigation, it was observed that there is little electronic difference between saturated and unsaturated imidazole NHCs (Figure 1-5). It was also observed that carbenes derived from 1,2,4-triazoles and tetrazoles showed substantially lower donor strength compared to imidazole-derived carbenes. This is likely due to an increased inductive effect from the additional nitrogen atoms within the ring on the carbene carbon.

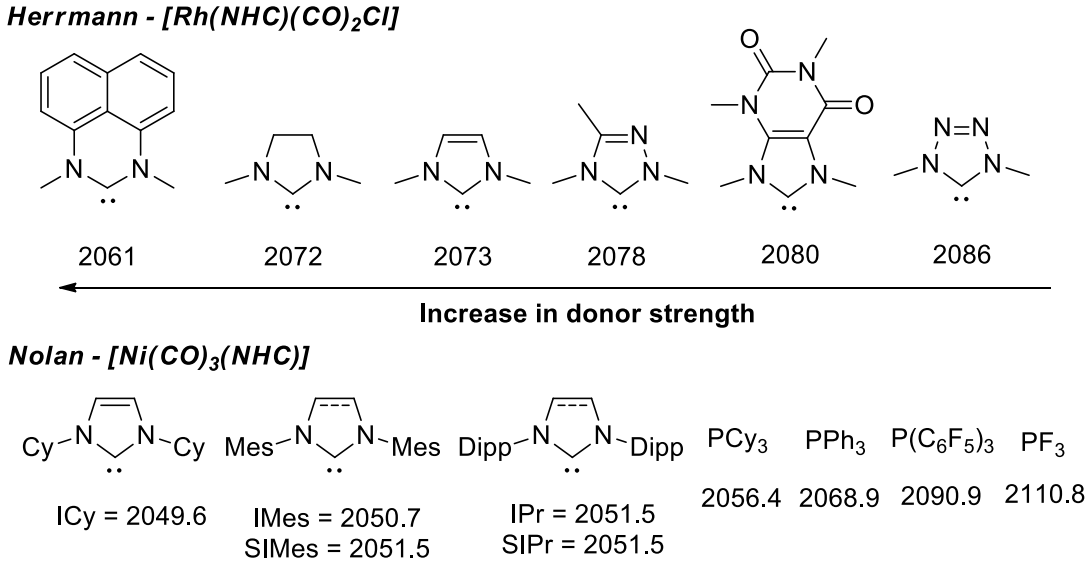


Figure 1-5: Electronic properties of NHCs as determined by Hermann and Nolan by IR spectroscopy (cm^{-1}).[27a, 57]

Nolan and Cavallo further examined the electronic character of different NHCs, probing the effect of different wingtip substituents on Ni carbonyl complexes.[57] In general, NHCs with alkyl wingtip groups, such as ICy, displayed higher basicity than NHCs with aromatic wingtip groups. This study further demonstrated that NHCs display a fairly narrow range of electron donating abilities, which is in contrast to phosphines that display a wide range. This can be easily explained as the substituents are not directly bound to the carbene itself, whereas they are directly bound to the phosphine, clearly having a more substantial effect. Importantly, these methods have indicated that most NHCs are typically more electron rich than even the most basic phosphines such as PCy_3. Similar trends have been observed by Huynh and coworkers, who instead measured the ^{13}C NMR signal of the carbene in palladium benzimidazole complexes.[58]

The steric parameters of an NHC are less straightforward to compare. While phosphines typically display cone like geometries as the substituents point away from the metal centre,[56] the wingtip groups on NHCs insteadpoint more towards the metal centre, and thus display very different parameters which have been described as fan, or fence-like.[59] In order to describe the steric parameters of different NHCS in a numerical manner, Cavallo and Nolan developed the % buried volume (% V_{bur}) comparison.[60] This method represents the ligand sphere surrounding a metal centre, and determines the amount of the sphere that is occupied by the ligand in question (Figure 1-6). The data required to build such a model can be conveniently obtained by x-ray crystallography. Commonly, coinage metals are used for this method, as their linear geometry is ideal for comparison of the ligands. A very important and attractive feature of this method is that it can be performed on any metal complex with any ligand, making comparisons between different ligand

classes facile. Furthermore, calculations can be preforming using SambVca (Salerno molecular buried volume calculation), a user-friendly tool that is available on-line.

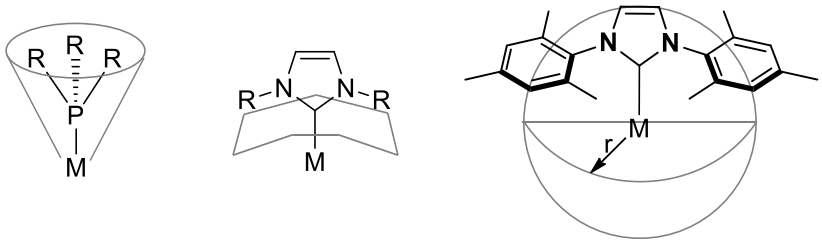


Figure 1-6: Comparisons of the steric environments surrounding phosphines and NHCs

Most known NHCs have been analyzed using this method. As many crystal structures of metal–NHC complexes have been reported, an exhaustive study was released comparing the %V_{Bur} values of many common NHCs on different metal centres (Table 1-1).[61] As expected, NHCs featuring small alkyl wingtip groups exhibit small %V_{Bur} values whereas larger aromatic substituents causes a fairly dramatic increase in this value. Interestingly, when the unsaturated NHCs IMes and IPr were compared to their saturated congeners SIMes or SIPr, a small but noticeable increase in steric parameters was observed.

In all cases, a noticeable decrease in steric parameters was observed in comparing [(NHC)AuCl] complexes to more substituted metal complexes such as [(NHC)Ir$(CO)_2$Cl] or [(NHC)Ni$(CO)_3$]. This is understandable as the NHC must now compete with more ligands in the metal coordination sphere relative to the linear gold complexes. Rotations of the N substituents will result in different conformations adopted by the ligand, resulting in deviations in the %V_{Bur} values obtained.

Table 1-1: Comparison of steric parameters for various NHCs. (r= 2.0 Å for all complexes)

NHC	%V_{Bur} [(NHC)AuCl]	%V_{Bur} [(NHC)Ir(CO)$_2$Cl]	%V_{Bur} [(NHC)Ni(CO)$_3$]
IDM	26.3	-	25.8
IiPr	27.4	-	-
ICy	27.4	27.6	-
IMes	36.5	33.8	34.0
SIMes	36.9	35.0	34.4
IPr	44.5	34.5	38.1
SIPr	47.0	37.7	39.0
IPr*	55.1	-	-
PPh_3	34.8	-	-
$PtBu_3$	43.9	41.7	-

As the steric parameters of the ligand are dependent on the nature of the metal complex itself, this points to a limitation of this method. While comparisons of the %V_{Bur} values appear to be legitimate and thus are particularly attractive for comparing steric parameters of ligands of the same complex structure, trends observed with one metal complex may not be necessarily universal. Different conformations of the NHC may be adopted in different complexes, which will be impacted by the number and nature of the auxiliary ligands present. Thus, this simplified method may not be truly reflective of the true nature of the ligand as it only provides a snapshot of a metal complex, and the flexibility or rigidity of the ligand is not taken into account.

To address this static nature, Cavallo and coworkers adopted the percent buried volume method to model the steric parameters during rotations of the N substituents in a dynamic manner.[62] By monitoring the %V_{Bur} at different rotations of the N-substituents and plotting the results on a 2D contour map, a more realistic steric map could be provided. This method has recently become popular as gives a more accurate depiction of the ligand

coordination to the metal which would more likely resemble the ligands' behaviour during catalysis.[63]

Possibly the most exciting property of NHC metal complexes is their remarkably high stability in comparison to complexes of phosphines, which gives numerous advantages including the ability to stabilize highly reactive metal complexes.[64] This can be described chemically by the high bond dissociation energy (BDE) of these ligands to metals. The BDE can be measured experimentally by performing calorimetric studies on reactions involving the metallation of NHCs, as long as these reactions are quantitative and produce no byproducts. For example, $[Cp^*RuCl]_4$ can be reacted with 4 equivalents of a free carbene to cleanly generate [Cp*Ru(NHC)Cl], and the enthalpy of the overall reaction can be measured. The results of these studies indicated that NHCs tend to bind more tightly than even the most basic phosphines (Table 1-2).[65]

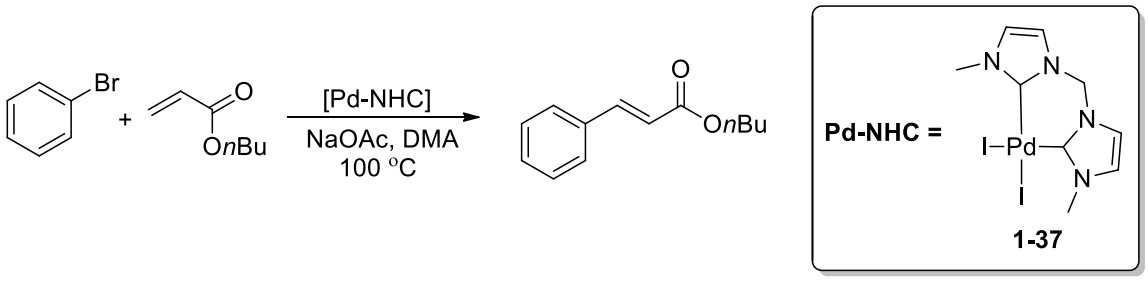
Table 1-2: Relative bond dissociation enthalpies for several standard NHCs and PCy_3 in kcal/mol.[57, 65]

NHC	BDE for $[LNi(CO)_2]$	BDE for [(L)RuCp*Cl]
ICy	46.3	21.2
SIMes	47.2	16.8
IMes	46.5	15.6
IPr	45.4	11.1
SIPr	46.1	12.1
PCy_3	-	10.5
$PtBu_3$	34.3	-

1.7 Important Catalytic Advances with NHCs

While the first examples of NHC metal complexes were reported in 1968,[36-37] the field initially appeared to predominantly be interested in the fundamental co-ordination chemistry of these ligands. It was not until 1995 that Herrmann reported the first example

of the use of Pd-NHC complex **1-37** in catalysis (Scheme 1-8).[66] This initial report demonstrated the potential of NHCs in homogenous catalysis, as very high turnover numbers were described without the requirement for excess ligand. In particular, the stability of the Pd-NHC complexes was highlighted as they were reported to undergo minimal decomposition under harsh oxidative conditions for multiple days. This factor could be observed experimentally by kinetic measurements of the reaction. After an initial induction period, the catalyst remained active even at high temperatures, and TOF numbers as high as 15000 h^{-1} could be obtained using unactivated bromoarenes. These turnover frequencies were much higher than the reported values of more classical phosphines at the time.

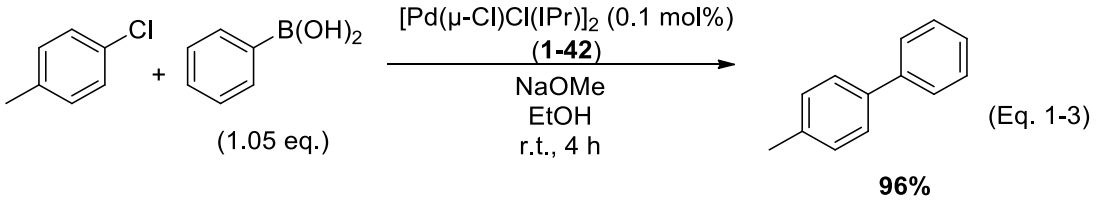


Scheme 1-8: Hermann's reported Pd-NHC catalysts for the Mizoroki-Heck reaction[66]

Since this initial report, there have been many reports of NHCs in catalysis.[9] Although these ligands are often compared to phosphines, in catalysis this comparison is often unfair and can be misleading. The properties of NHC complexes described above clearly demonstrate the unique character of these ligands and highlight the differences between them and phosphines, indicating that they are not interchangeable. Instead, they can offer distinct and complementary advantages over phosphines for catalysis as demonstrated in the following examples.

1.7.1 Pd-NHC Cross Coupling

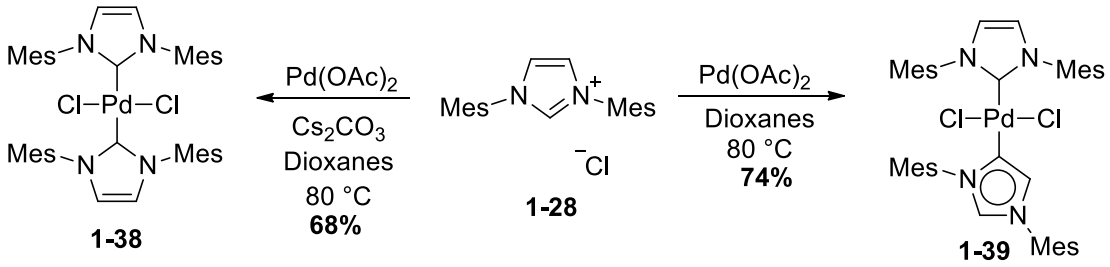
One of the most rapid fields of growth in the last twenty years is the investigation of Pd-NHC complexes in cross coupling.[67] The strong sigma donation, combined with the large, but flexible, steric bulk of the NHC provides Pd complexes that are particularly well suited for cross coupling. As a result of these properties, Pd-NHC complexes have been some of the most active catalysts in C-C and C-heteroatom cross coupling reactions reported in the literature.[68] In particular, the use of Pd-NHC complexes allows for the routine use of typically non-reactive aryl chlorides as substrates, as well as the synthesis of difficult cross coupling products, such as heavily substituted biaryl moieties.[68-69] For example, Cazin and coworkers reported the Suzuki-Miyaura coupling of aryl chlorides using a dimeric Pd-NHC complex (**1-42**) at very low (0.1 mol%) loading which occurs at room temperature (Eq. 1-3).[70] Amazingly, this reaction could even be performed under ambient air, albeit with lower yield (69%).



(Eq. 1-3)

Early investigations into Pd-NHC catalysts for cross coupling involved forming the catalyst *in situ* from a palladium source such as $Pd(OAc)_2$ and an imidazolium salt.[71] Although these conditions are convenient since both the palladium source and the imidazolium salt are air and moisture stable, careful analysis of the reaction mixture by Lebel and coworkers demonstrated that a mixture of palladium complexes are actually being formed under these conditions (Scheme 1-9).[72] This important observation points to

uncertainty in the nature of the metal complex being formed under these conditions. This has substantial ramifications for catalyst optimization as it is remarkably difficult to screen for catalytic activity when the nature of the catalytically active species is obscured. As a result, the chemical community has instead largely moved to investigating well-defined Pd-NHC complexes.[73]



Scheme 1-9: Lebel's synthesis of expected and abnormal Pd-NHC complexes[72]

A wide variety of well-defined palladium catalysts have been described in the literature which are active in cross coupling reactions, and there have been tremendous efforts to understand and predict catalytic activity. Studies have demonstrated that the active catalyst in most cross coupling reactions is a Pd^0 complex bound to one NHC ligand.[74] It is therefore no surprise that the majority of complexes reported are monoligated with an NHC, and vary with regard to ancillary ligands.[73] While few Pd^0 complexes have been reported, their relative instability has pushed researchers to instead investigate well-defined, bench-stable NHC-Pd^{II} complexes which can readily undergo reduction to form active NHC-Pd^0 complexes under the reaction conditions (Figure 1-7).

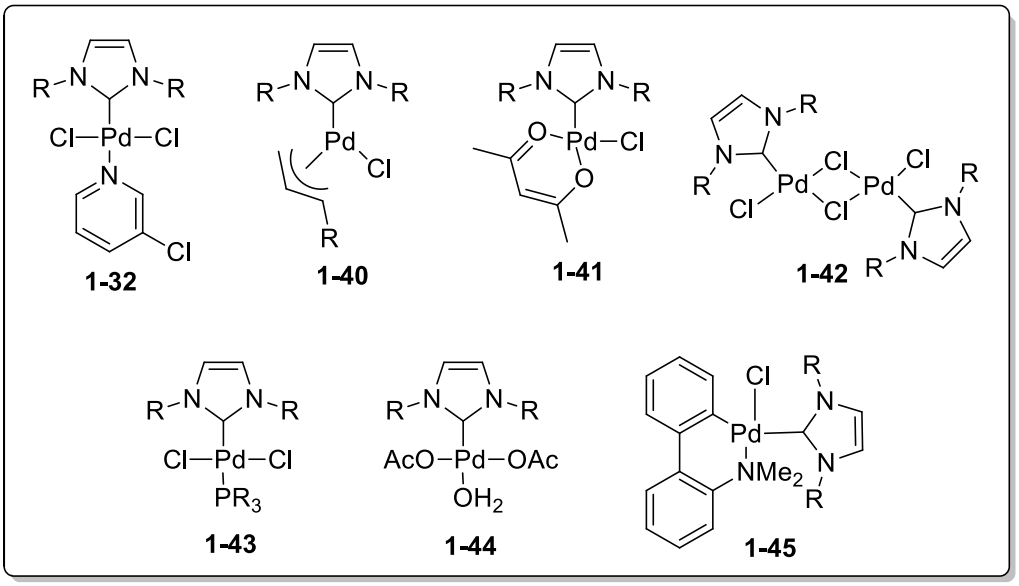


Figure 1-7: Selected examples of Pd^{II}-NHC precatalysts

A simplified mechanism for cross coupling is displayed in Figure 1-8. In particular, the PEPPSI family of precatalysts (**1-32**) has been demonstrated to be indiscriminately effective in most known cross coupling reactions with aryl chlorides, ranging from Negishi,[75] Kumada,[76] and Suzuki-Miyaura[42] coupling reactions as well as Buchwald-Hartwig aminations.[77] Further, Nolan demonstrated that [Pd(NHC)(acac)Cl] complexes (**1-41**) are reactive in the α-arylation of a variety of carbonyl containing compounds with aryl chlorides.[48, 78] Finally, in an interesting report, Fagnou demonstrated the reactivity of [Pd(NHC)$(OAc)_2OH_2$] (**1-44**) in intramolecular C-H arylation reactions.[79]

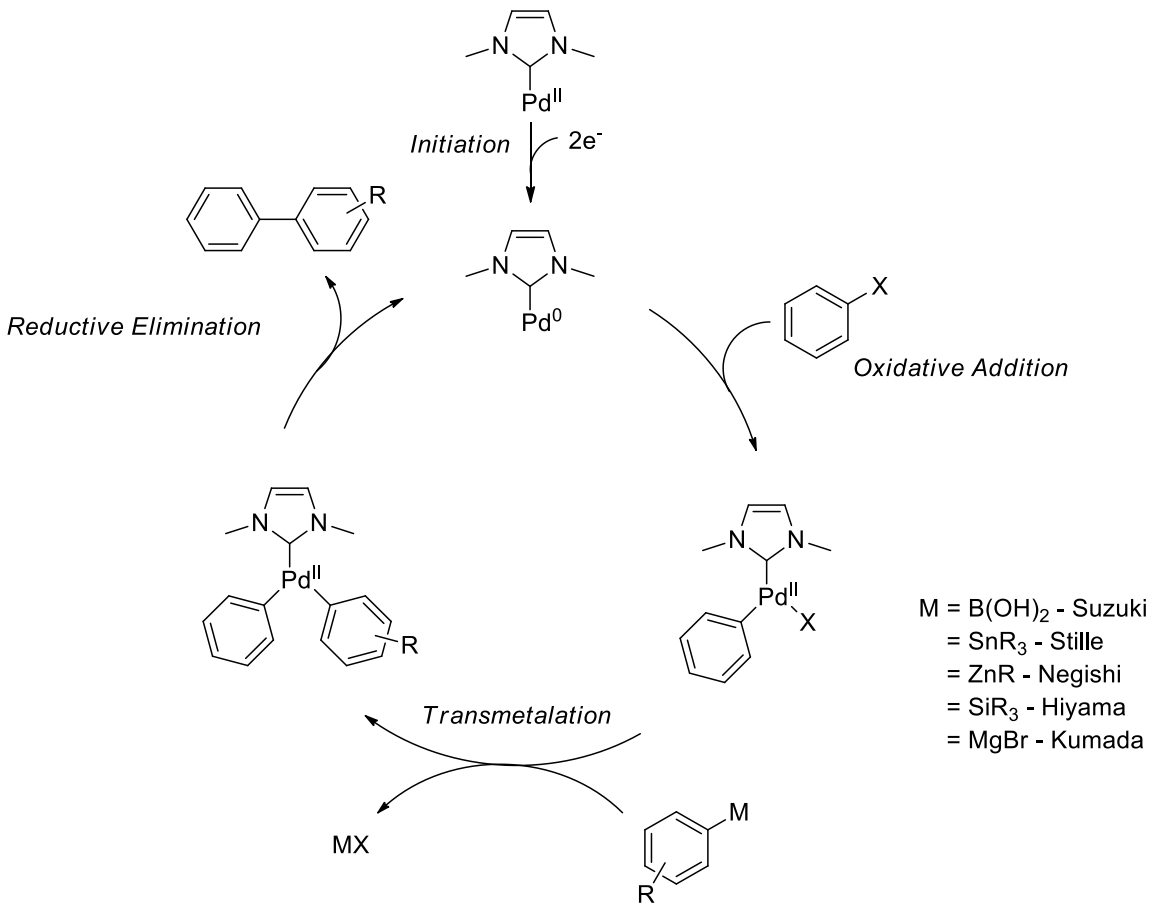


Figure 1-8: General mechanism for cross coupling with Pd-NHC complexes

Direct comparisons of Pd^{II}-NHC complexes are typically difficult, if not impossible to make, as their reduction and loss of spectator ligands are typically specific for each type of complex and catalysis in question.[80] In particular, when comparing the performance of different catalyst precursors, reaction conditions must be identical, as procedures which make the use of strong bases such as KOtBu cannot be compared to those that use of weak bases such as Cs_2CO_3 since the base can be directly relevant to reduction of palladium. This is an important distinction to make, as it is likely that one precatalyst structure will likely not be truly universal for all forms of cross coupling.

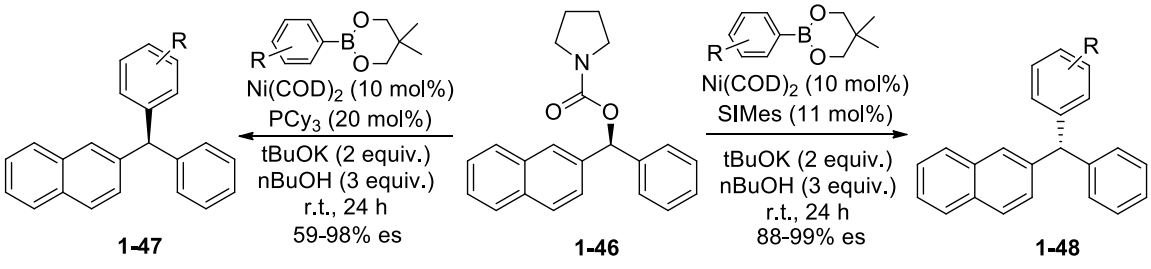
Current work in the field is predominantly centered on the fine tuning of NHC ligands to improve catalytic performance,[81] or extending the known transformations that Pd-NHC complexes are capable of affecting.[82] It has been observed that there is a substantial steric effect of the carbene on the catalytic activity of the catalyst. Ligands with larger wingtip groups which are flexible and non-restricted generally result in higher catalytic activity than those with smaller substituents.[69, 83] In addition, recent efforts for the modulation on the electronic properties have also been demonstrated.[81, 84]

1.7.2 Ni-NHC Catalyzed Cross Coupling Reactions

While palladium catalysts have undoubtedly dominated the cross coupling literature, the use of nickel catalysts can offer several advantages. Notably, the decreased cost of nickel relative to palladium has been a major impetus for the development of these catalysts.[85] In general however, Ni-NHC complexes have been reported to be substantially less reactive than their Pd congeners.[86] However, a particularly exciting feature of nickel catalysts in general are their increased activity towards a variety of typically less reactive electrophiles in cross coupling. While palladium-derived catalysts have been described for a wide variety of cross coupling reactions of aryl halides (*vide supra*), the activation of other electrophiles has lagged in comparison to nickel catalysts.[85a] Nickel phosphine complexes, which are typically generated *in situ*, are particularly effective in the activation of oxygen-derived electrophiles such as carbamates,[87] sulfamates,[88] and even anisoles.[89] Importantly, activity towards sp^3-hybridized electrophiles has also been reported, which gives access to enantiospecific transformations.[90]

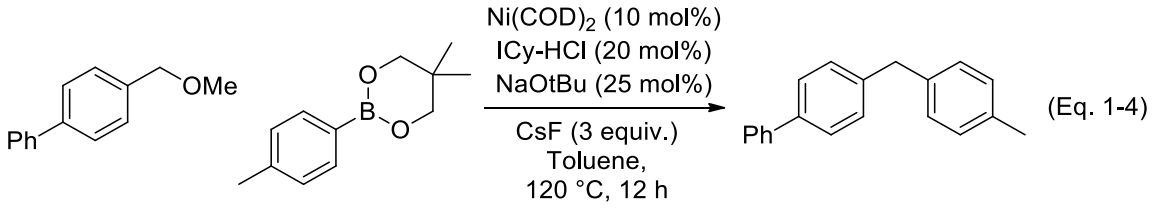
While nickel phosphine complexes have been quite successful in cross coupling reactions with these substrates, Ni-NHCs complexes have also been examined in an attempt to find longer lived and more active catalysts.[91] There have recently been examples of highly reactive Ni-NHC complexes for the Suzuki-Miyaura cross coupling reaction which are commonly formed *in situ* from the carbene ligand or precursor and $Ni(COD)_2$.[92] Ni^{II} precursors such as $[NiCl_2(dme)]$ and SIPr-HCl have also been demonstrated to be effective in amination reactions in the presence of a reducing agent.[93] As such, the development of highly active and well-defined Ni-NHC complexes is currently an active area of interest.[94]

Electrophilic coupling partners that are sp^3-hybridized [95] are also effective substrates with Ni-NHC catalysts. An interesting report on the cross coupling of enantioenriched (93% ee) benzylic carbamate **1-46** was reported by Jarvo and coworkers,[95b] with high selectivity observed for either **1-47**, or **1-48** depending on whether a phosphine or an NHC was used respectively (Scheme 1-10). To explain the difference in outcome, the authors proposed that the carbamate coordinates to the nickel centre and directs the oxidative addition in the presence of PCy_3. This coordination may not be observed when SIMes is instead coordinated to the nickel centre, and oxidative addition occurs in a manner more consistent with an S_N2 mechanism.[96]



Scheme 1-10: Jarvo's nickel catalyzed enantiodivergent cross coupling of benzylic ethers[95b]

A very similar process was recently reported by Chatani and coworkers (Eq. 1-4).[95a] Benzylic methyl ethers were reported to undergo Suzuki-Miyaura-like cross coupling with phenyl boronic esters in the presence of an *in situ* generated Ni NHC complex. The high reactivity observed with NHC-ligated Ni complexes was notable, since phosphine complexes were completely unsuccessful. Although this report focused on the coupling of primary benzylic methyl ethers, one example of a secondary benzylic methyl ether was also reported giving rise to a triarylmethane derivative in moderate yield.



(Eq. 1-4)

While the use of Ni-NHC catalysts in cross coupling is an active, and growing field, these results are exciting as they leave open the possibility of future coupling reactions which have the potential for the synthesis of enantioenriched versions of these important products.

1.7.3 Ru-NHC Olefin Metathesis

One of the fields most highly affected by the development of NHCs is undoubtedly the ruthenium catalyzed olefin metathesis.[97] Many important metathesis transformations have been developed such as ring closing metathesis (RCM) and ring opening metathesis polymerization (ROMP), which are of high importance to the synthetic community. Initially these transformations utilized early transition metal alkylidenes complexes such

as **1-40**, which were highly active.[98] These complexes however displayed low functional group tolerance, and were highly reactive to both air and moisture. These limitations sparked researchers to actively investigate the development catalysts of improved stability, while maintaining high reactivity.

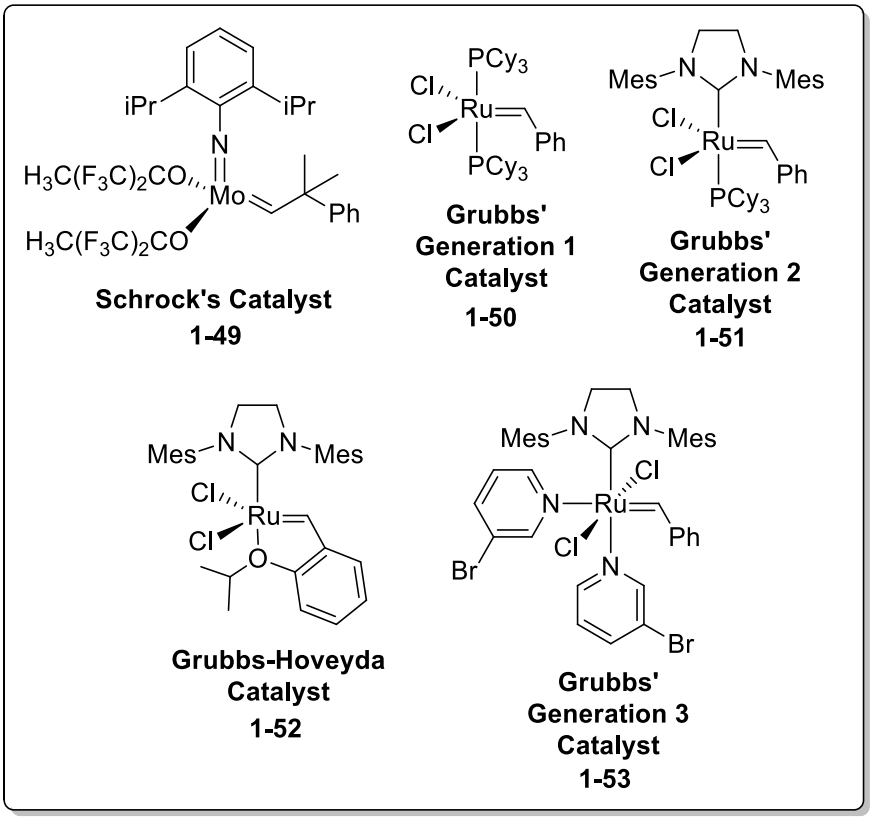
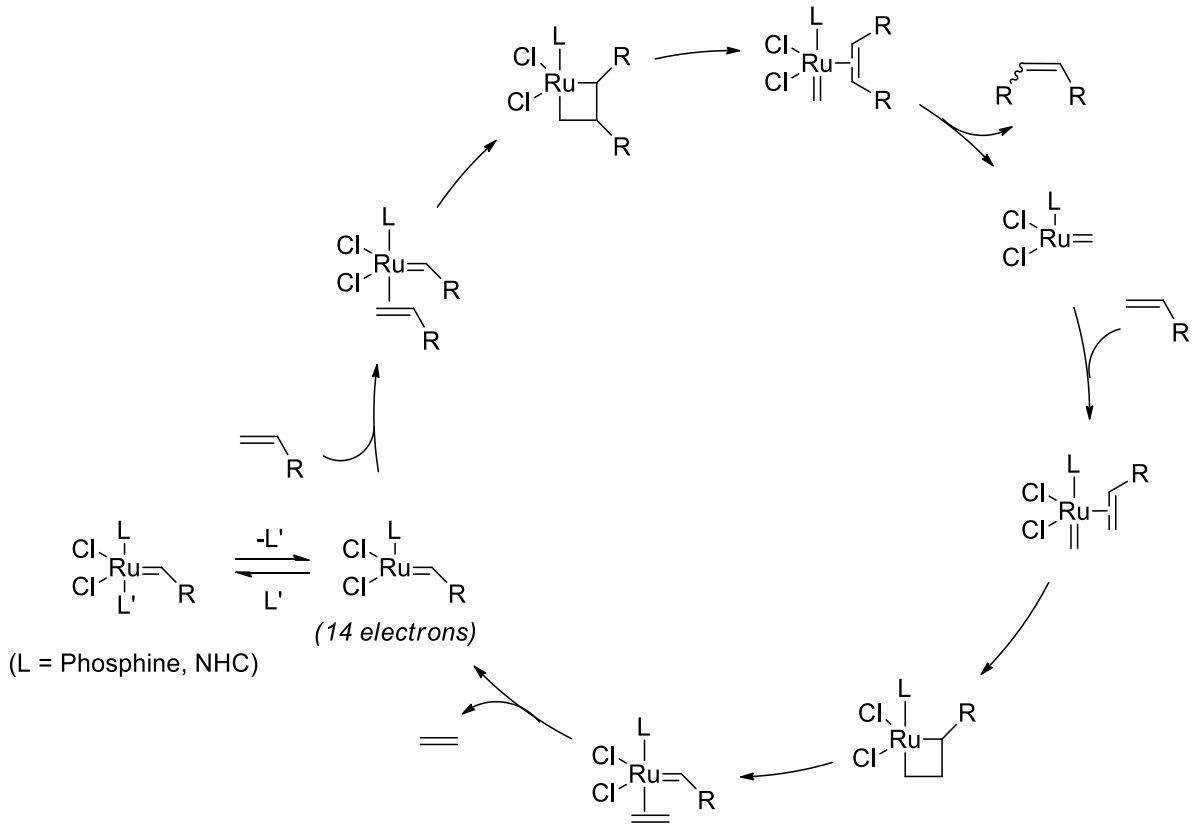


Figure 1-9: Selected olefin metathesis catalysts

The development of ruthenium catalysts marked an important stage (Figure 1-9), as these catalysts had increased stability under aerobic conditions, which makes them substantially more user friendly, and substrate compatible. For example, phosphine-derived Grubbs' 1st generation catalyst (**1-50**) can be conveniently synthesized, and displays substantially higher stability and substrate tolerance while maintaining high reactivity that is more characteristic of early transition metal complexes.[99]



Scheme 1-11: Generalized mechanism for Ru-NHC catalyzed olefin metathesis

Although Grubbs' 1st generation catalyst displayed many significant advantages, it too suffered from stability issues as well as decreased rates of reaction, relative to the parent Molybdenum catalysts. Mechanistic studies indicated that loss of one of the neutral phosphines results in the catalytically active 14 electron complex (Scheme 1-11).[100] As a result, spectator ligands which could stabilize this intermediate would in turn be expect to result in higher activities. It is in this regard that Grubbs' 2nd generation catalyst (**1-52**) was synthesized, which takes advantage of a single SIMes NHC ligand. This complex shows a dramatic increase in turnover number relative to the 1st generation (**1-50**).[101] The higher basicity of the NHC relative to the phosphine results in faster initiation by promoting dissociation of the phosphine to generate the catalytically active species. Since the original

report of the Grubbs' generation 2 catalyst, many research groups have actively been investigating alternative throw-away ligands which display a higher lability,[102] including the Grubbs' third generation catalyst (**1-53**). Employing two highly labile 3-bromopyridine ligands, **1-53** has substantially higher catalytic activity.[103]

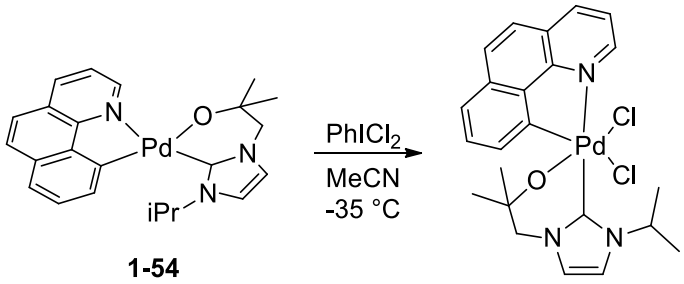
Current work in the field revolves around fine-tuning of the NHC[104] ligand to maximize efficiency, or tuning selectivity as well as the development of latent catalysts which only initiate under highly selective conditions.[105]

1.7.4 Oxidation Catalysis with Pd-NHC complexes

The high stability of NHC transition metal complexes under oxidative conditions relative to phosphines (*vide supra*) has particular implications for oxidation catalysis.[10] Transition metal-catalyzed selective oxidation is an important but challenging topic, and therefore has warranted intense research.[106] One of the significant challenges is the low oxidative stability of common ligands such as phosphines. In contrast, while free NHCs can display sensitivity to molecular oxygen,[107] their complexes tend to display remarkable oxidative stabilities which will be highlighted below.

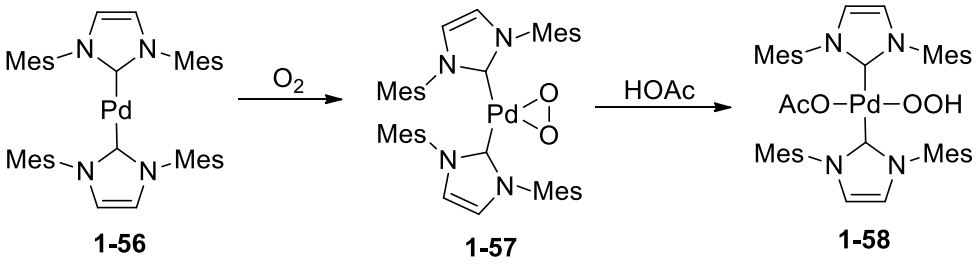
Several high oxidation state metal NHC complexes have been reported, which feature beneficial stabilization by NHC ligands. For example, Sanford and Arnold described the synthesis of Pd^{IV} complex **1.55** utilizing a chelating alkoxy-functionalized NHC ligand (Eq. 1-5).[108] Although Pd^{IV} complexes have been commonly proposed as intermediates in various C-H functionalization reactions,[109] isolated high oxidation state palladium complexes have been predominantly limited to those bearing sp^2 N-donors and carboxylates as ligands, due to the harsh conditions required for oxidation to Pd^{IV}.[110] The

isolation of complex **1-55** highlights the oxidative stability of NHC-ligated complexes, and indicates the significant potential of these ligands with high oxidation state metals. Importantly, complex **1-55** displayed catalytic activity in the C-H halogenation of pyridine derivatives.



1-54 **1-55** (Eq. 1-5)

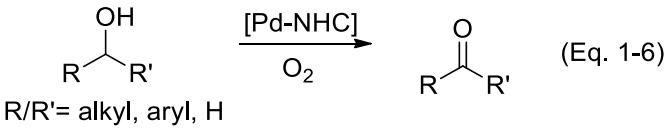
The reactivity of Pd-NHC complex **1-56** towards molecular oxygen can further illustrate the stability of the bound NHC (Scheme 1-12).[111] Treatment of **1-56** with dioxygen results in the formation of peroxo complex **1-57**. Interestingly, treatment of this complex with HOAc resulted in the formation of hydroperoxo complex **1-58**, which is the first structurally characterized dioxygen-derived palladium hydroperoxide complex.[112] It is important to note that while palladium peroxo complexes have been prepared before, the facile oxidation of phosphines severely limited the stability of these complexes, clearly demonstrating significant utility of NHCs in oxidation catalysis. Importantly, the direct reactivity of complex **1-56** with molecular O_2 suggests great promise for oxidation catalysis with this greenest of oxidants.[113]



1-56 **1-57** **1-58**

Scheme 1-12: Reactivity of Pd-NHC complexes with molecular oxygen

Figure 1-10 shows Pd-NHC complexes that have been described as active catalysts in the aerobic oxidation of alcohols (Eq. 1-6).[114] While dimeric complexes **1-42** were effective in the oxidation of secondary alcohols, they required the presence of a base such as sparteine for effective turn over.[115] In contrast, complex **1-44** displayed high reactivity in the oxidation of primary and secondary alcohols to aldehydes or ketones respectively under very mild conditions, in the absence of base, and using O_2 as the terminal oxidant.[116]



The mechanisms of these oxidations were proposed to involve NHC-Pd(O_2) intermediates, and addition of small amounts of HOAc was found to be crucial at lower catalyst loadings. This is likely associated with the regeneration of the Pd catalyst, via a Pd-hydroperoxide intermediate (Scheme 1-12). The high activity observed with complex **1-44** is likely related to the presence of a single NHC ligand bound to the Pd centre, while the water molecule can easily dissociate from the Pd centre, and the two carboxylates acting

as internal bases in the reaction. Importantly, the high catalyst turnover is indicative of the NHC ligand remaining bound to the Pd centre, despite the harsh oxidative conditions.

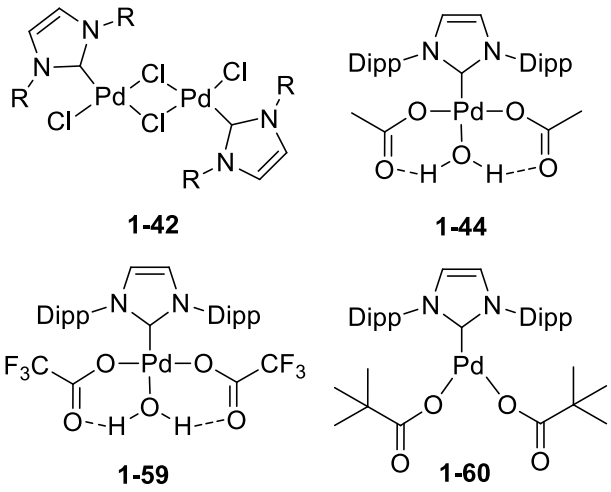
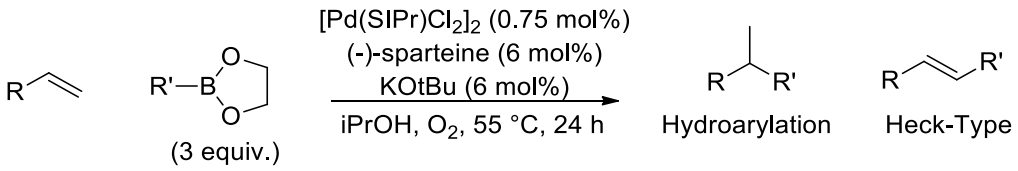


Figure 1-10: Pd-NHC catalysts for oxidation of alcohols

Pd-NHC complexes have also demonstrated high activity in Wacker-type processes, which require oxidative conditions. In particular, Pd-NHC trifluoroacetic acid complex **1-59** displays high reactivity in intramolecular oxidative cyclizations of alkenes to form both oxygen and nitrogen heterocycles,[117] and is active in the oxidation of styrene derivatives.[118] In addition, Sigman and coworkers have investigated Pd-NHC complexes in the coupling reactions of alkenes with organometallic reagents under oxidative conditions.[119] These processes can often be run with molecular oxygen as the terminal oxidant, taking advantage of the reactivity of Pd-NHC complexes towards O_2. For example, alkenes can be effectively hydroarylated with phenyl boronic esters utilizing a Pd-NHC/sparteine catalytic system (Scheme 1-13). High yields, and very high selectivities (>30:1) can be obtained over the undesired Heck-type product.



Scheme 1-13: Hydroarylation of boronic esters and alkenes with Pd-NHC catalysis under oxidative conditions

The proposed mechanism is displayed in Figure 1-11, and involves the generation of a Pd^{II}-H (**B**), which forms upon oxidation of the isopropanol solvent. Insertion of **B** into the alkene gives palladium alkyl species **C**, which can then undergo transmetallation with the boronic ester to form **D**. Reductive elimination then generates the product. The resulting Pd^0 complex **E** can then undergo oxidation with O_2 to regenerate its active form **A**. Similar processes have also been developed for oxidative Heck sequences,[120] or instead utilizing alkyl organozinc reagents to affect overall hydroalkylation.[121] Protocols have also been developed for 1,1 and 1,2 diarylations with organostannane reagents.[119c, 122]

1.8 Conclusions

The pioneering work on the synthesis and isolation of stable carbenes has developed into the routine use of carbenes, more specifically NHCs, as ligands in transition metal catalysis and organocatalysts. NHCs have matured into entities that are now routinely synthesized and formed into transition metal complexes under well understood conditions. The electronic and steric parameters of these ligands are well understood, and methods are in place that permit one to quantify and compare properties in different NHC complexes. These investigations have demonstrated NHCs to display several unique features relative to the more commonly observed phosphines. Several important catalytic examples of

transition metal NHC complexes have been reported, which utilize these beneficial properties, demonstrating that they are also highly versatile. NHCs are continually being modified and refined for various applications, as they continue to develop as ligands.

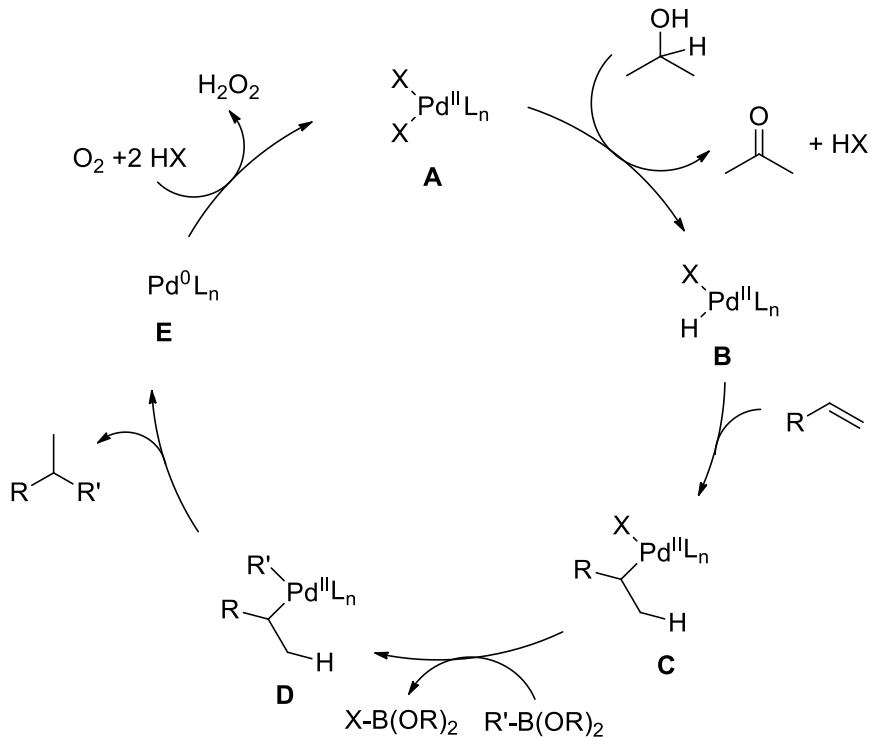


Figure 1-11: The proposed mechanism for the hydroarylation with Pd-NHC complexes under oxidative conditions

1.9 Research Objectives

As described in this chapter, NHCs are highly exciting ligands for transition metal catalysis. As such, our group has been interested in investigating the synthesis and coordination chemistry of NHC ligands with transition metals for catalytic applications. At the outset of this work, our goal was to study the interactions of transition metal NHC complexes with small molecules, in order to determine what factors influence structure and bonding. Chapter 2 describes our investigations into the coordination of O_2 to rhodium

NHC complexes. Our group has previously reported the synthesis of Rh-NHC dioxygen complexes, which featured coordination of O_2 in the uncommon singlet state. In order to determine what influence the nature of the NHC as well as the auxiliary ligands present had on the O_2 binding, several Rh-NHC complexes were synthesized and reacted with O_2. In order to accomplish this, we investigated the synthesis of highly reactive dimeric rhodium NHC complexes which could be used as precursors for heteroleptic rhodium NHC complexes. Chapter 3 will describe the use of dimeric Rh-NHC olefin complexes as catalysts in C-H activation reactions. Stoichiometric reactions reveal that these catalysts display high reactivity towards C-H bonds of phenyl pyridines, which is then exploited for C-H borylation reactions.

Chapter 4 describes the study of mesoionic carbenes derived from 1,2,3 triazoles, and investigations into their use as ligands for transition metals. The properties of these ligands offer exciting possibilities for catalysis, such as their ease of tunability. Our efforts to use Pd complexes of these ligands in the Mizoroki-Heck reaction of aryl halides with acrylates, as well as attempts to synthesize pincer complexes derived from these ligands is reported.

Finally, chapter 5 describes our investigations into the cross coupling of benzylic sulfones. The use of these substrates as electrophiles in cross coupling has not previously been investigated. Our efforts to utilize these reagents in Suzuki-Miyaura cross coupling reactions is reported. Pd-NHC catalysts were investigated for the formation of triaryl methane derivatives under relatively mild conditions.

1.10 References

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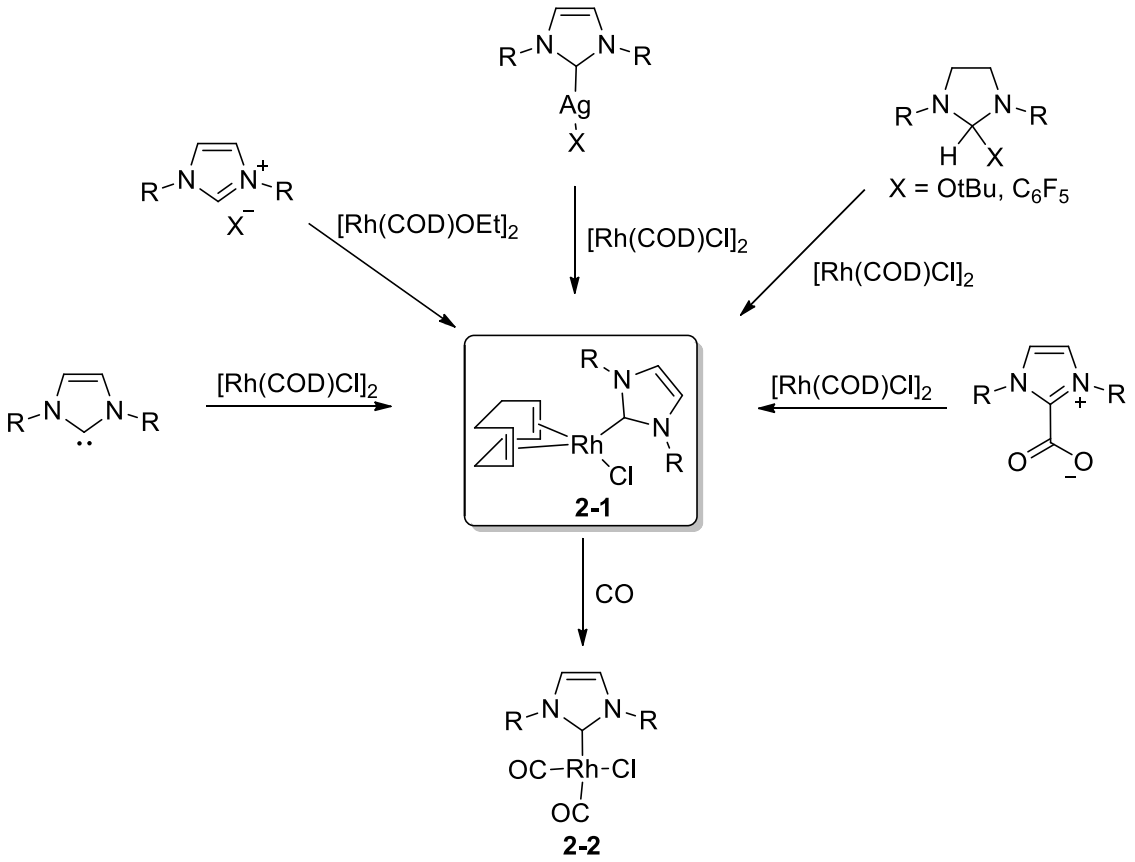
Chapter 2 Development of Highly Unsaturated Rhodium N-Heterocyclic Carbene Complexes, and Their Reactivity

2.1 Introduction

2.1.1 Rhodium NHC complexes

NHC complexes of rhodium are highly represented in the literature.[1] In particular, likely due to their facile synthesis, complexes of general formula [(NHC)Rh(COD)Cl] (**2-1**) are a very common occurrence (Figure 2-1). Generally these species exhibit exceptional stability to both air and moisture, and can often be purified by column chromatography. Further, upon treatment with CO, the COD can be displaced, to form complexes of general structure [(NHC)Rh$(CO)_2$Cl] (**2-2)**, which are convenient for the measurement of donor strengths via IR spectroscopy (Section 1-6).[2] It is no surprise therefore, that complexes of this general formula are commonly synthesized with novel NHC ligands, in order to probe their coordination chemistry and to determine electronic factors.[3] Indeed, an incredible library of complexes of general structure **2-1** has been synthesized varying in both steric and electronic parameters, and even featuring chelating donor species.[4]

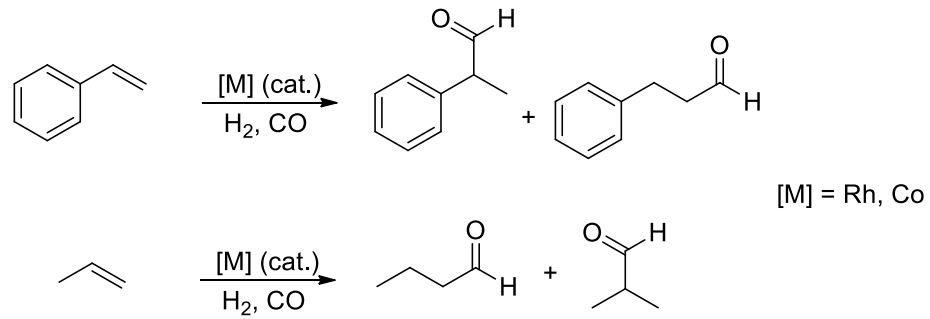
In addition, although rhodium NHC complexes do not enjoy the catalytic fame that either palladium[5] or ruthenium[6] NHC complexes do, Rh-NHC complexes have been investigated as catalysts for reactions such as hydrogenation,[7] and hydroformylation of alkenes,[8] and hydrosilylation of ketones[9] to C-C bond forming reactions.[10]



Scheme 2-1: Synthesis of [(NHC)Rh(COD)Cl] by commonly reported routes[9a, 11]

2.1.2 Previous Work in the Crudden Group:

Our group has been interested in the development of Rh-NHC complexes as catalysts for the hydroformylation and hydrogenation of alkenes.[1b] Hydroformylation is currently the largest industrial process involving homogeneous catalysis, giving rise to high value aldehyde and alcohol products from relatively inexpensive and abundant starting materials (Scheme 2-2).[12] Most commonly, rhodium catalysts ligated with phosphines or phosphites are utilized, which tend to give high selectivities for the desired linear products in the case of aliphatic alkenes and branched products with vinyl arenes.[13]

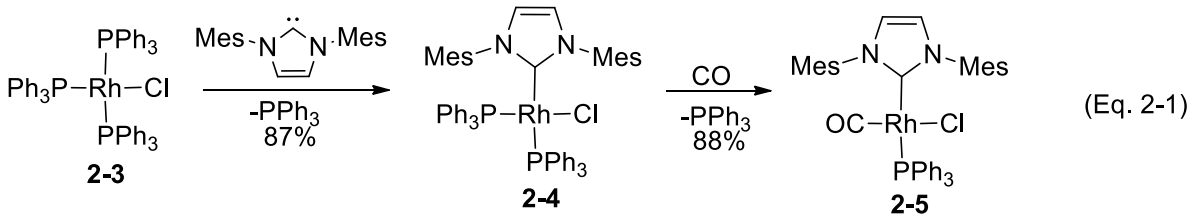


Scheme 2-2: Generalized hydroformylation

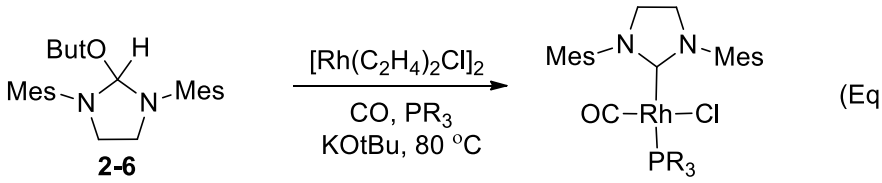
However there are many drawbacks associated with common catalysts, chiefly related to their decomposition to heterogeneous rhodium and the requirement for very high ligand loadings to affect highly linear selective hydroformylations.[14] In this regard, our group became interested in pursuing the use of Rh-NHCs in hydroformylation.[15] It was hypothesized that the high BDE of the Rh–carbon bond would result in stable rhodium species, which may overcome some of these problems.[16]

In 2000, our group published the synthesis of **2-4** by the treatment of Wilkinson's catalyst (**2-3**) with free IMes (Eq. 2-1).[15] This complex was active in the hydroformylation of styrene derivatives with a high selectivity for branched products. While **2-4** showed instability towards O_2, treatment of **2-4** with CO resulted in complex **2-5** which was substantially more stable and could be handled under air, and even purified by column chromatography. $^{31}P\{^1H\}$ NMR spectroscopy and X-ray crystallography indicated that the phosphine was oriented trans to the NHC, likely for steric reasons. Importantly, although **2-5** exhibited lower catalytic activity, addition of PPh_3 to the reaction mixture resulted in comparable activity and selectivity to **2-4**, which is higher than the analogous $[ClRh(CO)(PPh_3)_2]$.

Variants of **2-5** which instead featured saturated NHCs were synthesized by the treatment of an alkoxide NHC adduct (**2-6**) with $[Rh(C_2H_4)_2Cl]_2$ in the presence of added phosphine under an atmosphere of CO (Eq. 2-1).[11f] A variety of phosphines could be employed, giving **2-7** in moderate to good yields. In all cases, the phosphine was situated trans to the NHC.



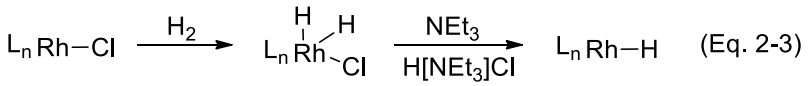
(Eq. 2-1)



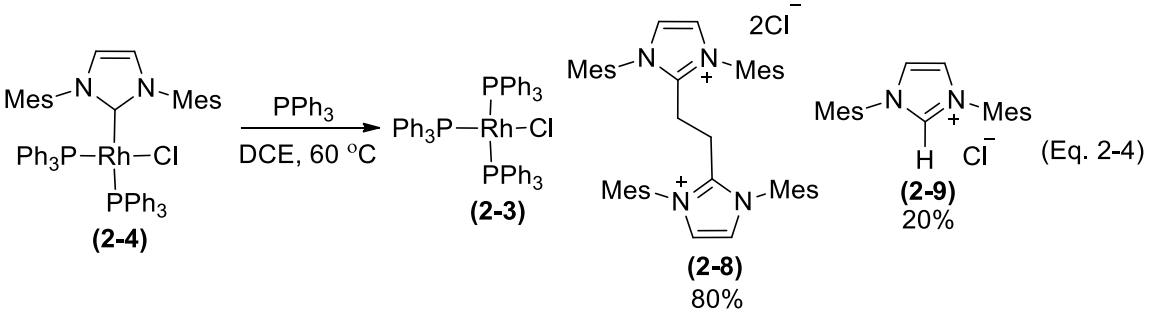
(Eq. 2-2)

2-7a; R= PPh_3, 83%
2-7b; R= $P(OPh)_3$, 77%
2-7c; R= $P(p\text{-}OMePh)_3$, 64%
2-7d; R= $P(p\text{-}FPh)_3$, 63%
2-7e; R= $P(furyl)_3$, 31%
2-7f; R= PCy_3, 29%
2-7g; R= $P(o\text{-}Tol)_3$, 31%

Complexes **2-7a-g** were all active in the hydroformylation of styrene upon addition of additional PR_3 to the reaction mixture, giving high branched to linear product ratios.[17] In general, SIMes complexes exhibited higher TOFs than the analogous IMes complexes. Addition of NEt_3 to the reaction mixture resulted in dramatic increases in TOF, without erosion of selectivity. It was hypothesized that NEt_3 was involved in the activation of the catalyst by assisting in reductive elimination of HX from the rhodium center to form the catalytically active Rh-H species (Eq. 2-3).

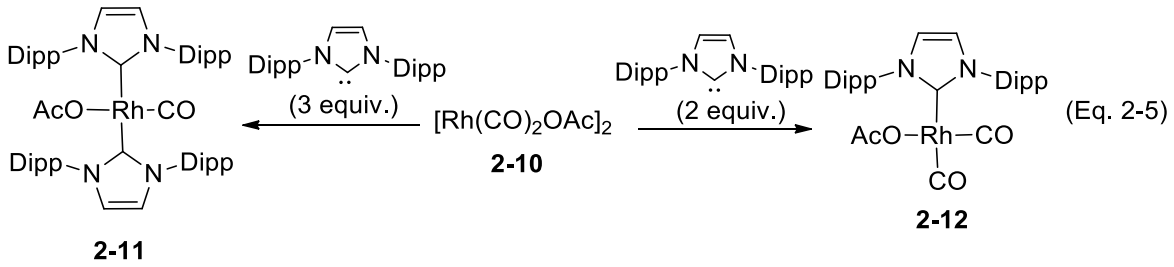


Interestingly, upon exposure of bis-PR_3 complex **2-4** to dichloroethane (DCE) at 60 °C, the $^{31}P\{^1H\}$ NMR spectroscopy indicated the formation of Wilkinson's catalyst, along with the formation of **2-8** and IMes-HCl.[18] Compound **2-8** is likely formed by the nucleophilic attack of the free carbene on the solvent, indicating the relatively facile cleavage of the NHC from the metal complex. The lability of the NHC is in stark contrast to a wide body of literature which considers the M-NHC bond to be inert.[19] In contrast, carbonyl complex **2-5** displayed no apparent reactivity with dichloroethane under comparable conditions. As a result, carbonyl-containing complexes were further investigated in hydroformylation reactions.



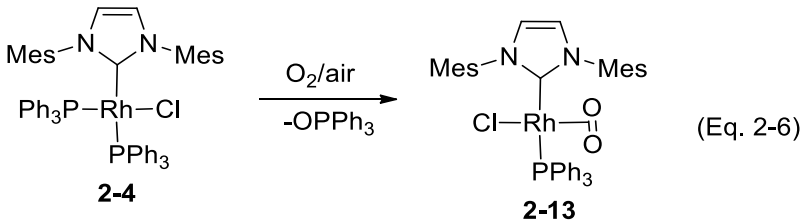
Further developments in our group led to air stable rhodium NHC carboxylate complexes **2-11** and **2-12** by treatment of $[Rh(CO)_2(OAc)]_2$ with 2 and 3 equivalents of the free carbene respectively.[20] While **2-11** was completely inactive in the hydroformylation of styrene, **2-12** displayed very high TOFs and TONs in the presence of PPh_3. NEt_3 was not necessary for turnover, which may be associated with the presence of the carboxylate ligand, which was facilitating reductive elimination of HOAc from the rhodium to initiate catalysis. Importantly, the use of **2-12** as a catalyst occurs without concomitant

isomerization of internal olefins, which is a common problem in other Rh-NHC systems.[8e,21]



(Eq. 2-5)

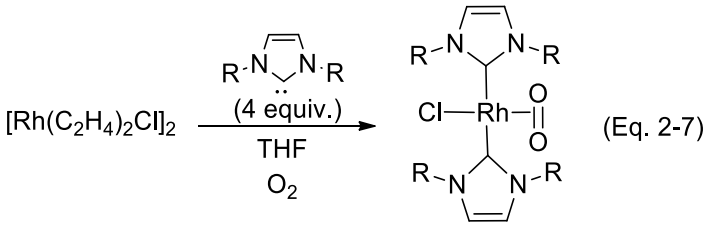
As indicated previously, complex **2-4** displayed substantial sensitivity to aerobic conditions.[11f] Treatment of a solution of **2-4** with O_2 resulted in a dramatic colour change from yellow to green, from which previous Ph.D. student Daryl Allen was able to isolate single crystals of complex **2-13**.[22] The crystal structure clearly displayed the coordination of O_2 in complex **2-13**. Interestingly, complex **2-13** represents a very rare example of a formally square planar Rh-O_2 complex, and the O_2 bond length was also quite short in comparison to most other complexes (vide infra) (precise determination of bond length was not possible due to issues with positional disorder). Unfortunately, full characterization of **2-13** was inhibited by its further decomposition upon oxidation of the phosphine.



(Eq. 2-6)

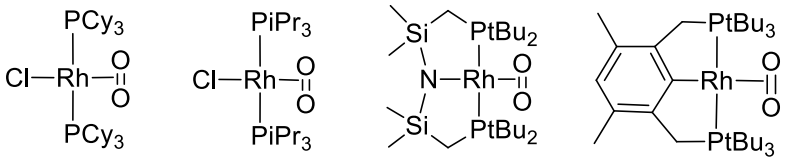
In order to overcome the sensitivity of **2-13** towards phosphine oxidation, previous Ph.D. student Jeremy Praetorius instead synthesized all NHC variants of **2-13** (Eq. 2-7). It was hypothesized that **2-14** and **2-15** would not undergo the same decomposition reactions due the increased oxidative stability of these ligands. Complexes **2-14** and **2-15** were

synthesized by the treatment of $[Rh(C_2H_4)_2Cl]_2$ with 4 equivalents of free carbene, followed by exposure to O_2 (Eq. 2-7).[22] These species displayed substantially higher stability under aerobic conditions, allowing for their full characterization. Similarly to **2-13**, single crystals of complexes **2-14** and **2-15** were also characterized as square planar complexes which displayed short O-O bond lengths. This is in contrast to many Rh^{III}-peroxo complexes which display bond lengths ~1.4.1.5 Å.



2-14; R= Mes, O-O = 1.267(13) Å
2-15; R= Dipp, O-O = 1.315(3) Å

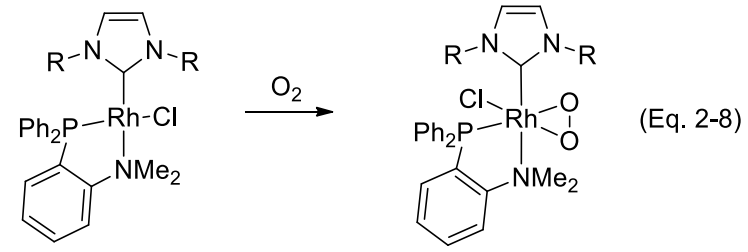
Along with collaborator Dr. Pierre Kennepohl, complexes **2-14** and **2-15** were extensively characterized by X-ray crystallography, IR and Raman spectroscopy, as well as L-edge XAS and DFT analysis. The combined results indicated that **2-14** and **2-15** can be best characterized as a Rh^{I} complex, bound to singlet oxygen.[22] This would imply that the coordination of O_2 had occurred without oxidation of the rhodium complex. Such a coordination model had not been proposed before for rhodium complexes. Surveying known Rh-O_2 complexes, a few examples had been previously reported which also feature short O-O bonds, and it was hypothesized that these may have been previously unrecognized examples.[23] All of these species utilize sterically bulky strong field ligands which may be crucial for favouring this coordination mode (Chart 2-1).



2-16 **2-17** **2-18** **2-19**

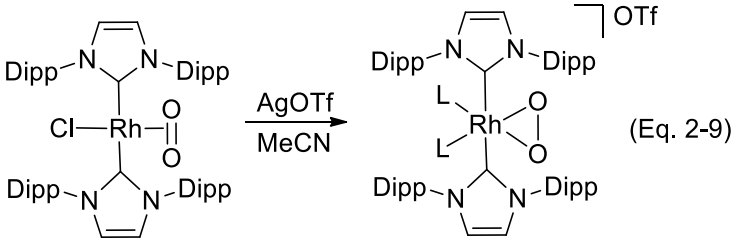
Chart 2-1: Rh-O_2 complexes displaying short O-O bond lengths[23]

In contrast however, at around the same time as the report from our group, James and coworkers reported the synthesis and isolation of other Rh-NHC complexes bound to O_2 which displayed substantially longer O-O bond lengths (Eq. 2-8).[24] For example, complexes **2-20** and **2-21** which also features a more flexible P-N donor ligand appear to be octahedral in geometry and have O-O bond lengths of ~1.45 Å, which is more typical of a metal peroxo.[18] The increased O-O bond lengths in **2-22** and **2-23** are likely related to the higher coordination number of complexes **2-20** and **2-21** which would permit the reduction of the O_2 to form octahedral [$Rh^{III}\{O_2^{2-}\}$] type complexes.[25] Postdoctoral Fellow in our group Judy Cipot-Wechsler further demonstrated the importance of coordination number on the nature of O_2 binding with the formation of complex **2-24** upon treatment of **2-15** with AgOTf in acetonitrile (Eq. 2-9) (*vide intra*).[25c] Similar results were later reported by Oro and coworkers with pyridine ligands.[25b]



2-20; R = Mes
2-21; R = Dipp

2-22; R = Mes, O-O = 1.450(2) Å
2-23; R = Dipp, O-O = 1.450(3) Å



2-15

L = MeCN
2-24, O-O = 1.428(3) Å

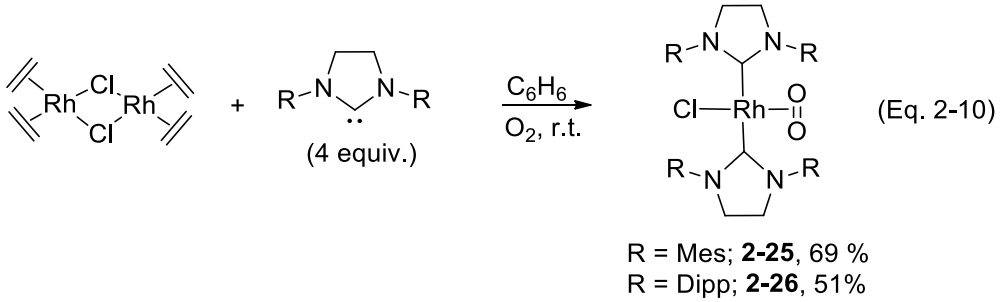
These differing results inspired our group to further explore the reactivity of other Rh-NHC complexes towards O_2, and determine what factors affect the binding modes of O_2. The outcome of these investigations may in turn be relevant for oxidation catalysis.[26]

2.2 Results and Discussion

2.2.1 Investigations into Rhodium NHC Dioxygen Complexes

To further explore this unique coordination mode and investigate the factors that affect the nature of O_2 binding, we examined NHCs that differed in steric and electronic parameters. We began by synthesizing complexes that instead featured saturated NHCs. In a similar synthetic strategy, $[Rh(C_2H_4)_2Cl]_2$ was reacted with 4 equivalents of free SIMes or SIPr at room temperature in C_6H_6, then exposed to molecular oxygen resulting in **2-25** and **2-26** in 51% and 69% yield respectively after purification by column chromatography using neutral alumina as a stationary phase. Complexes **2-25** and **2-26** were isolated as

light blue powders and were characterized by ^{1}H and ^{13}C NMR spectroscopy, as well as HRMS and elemental analysis.



Single crystals of **2-25** and **2-26** were obtained by the slow diffusion of hexanes into concentrated THF solutions (Figure 2-1). Similarly to the previously described complexes, the O-O bond length of **2-26** was measured to be 1.392(11) Å. Similar effects were observed with **2-25**, which gave an O-O bond length of 1.372(16) Å. As X-ray crystallography is not always definitive, especially in the case of Rh square planar complexes which tend to display positional disorder between the Cl and the O_2 ligand, causing problems accurately determining the O-O bond length,[25b, 27] the IR spectra of both complexes were also obtained, and compared to their $^{18}O_2$ labeled isotopomers to aid in the assignment of appropriate signals. In both cases, the O-O stretching frequencies appeared in the expected range for singlet O_2 complexes (Table 2-1).

Table 2-1: O-O bond lengths in Rh-NHC complexes

Complex	O-O Bond length (Å)	ν(O-O) (cm^{-1})
2-14	1.267(13)	1020
2-15	1.315(3)	1010
2-25	1.392(11)	1056
2-26	1.372(16)	1053

These results imply that coordination of singlet oxygen is general for bis(NHC) complexes (Table 2-1). To further investigate the generality of this binding mode, we became interested in pursuing the synthesis of heteroleptic Rh NHC complexes and studying their reactivity with O_2. In order to further probe Rh-NHC complexes with other ancillary ligands, a straightforward and reliable route for their synthesis was required.

2.2.2 Dimeric Rhodium NHC Complexes as Precursors for Heteroleptic Complexes

Inspired by related work with palladium,[28] we hypothesized that dimeric rhodium NHC complexes could be precursors to the desired heteroleptic species (Scheme 2-3). Complexes of general structure **2-27** would provide access to a wide variety of complexes of novel structures, which could then be probed for their activation of O_2.

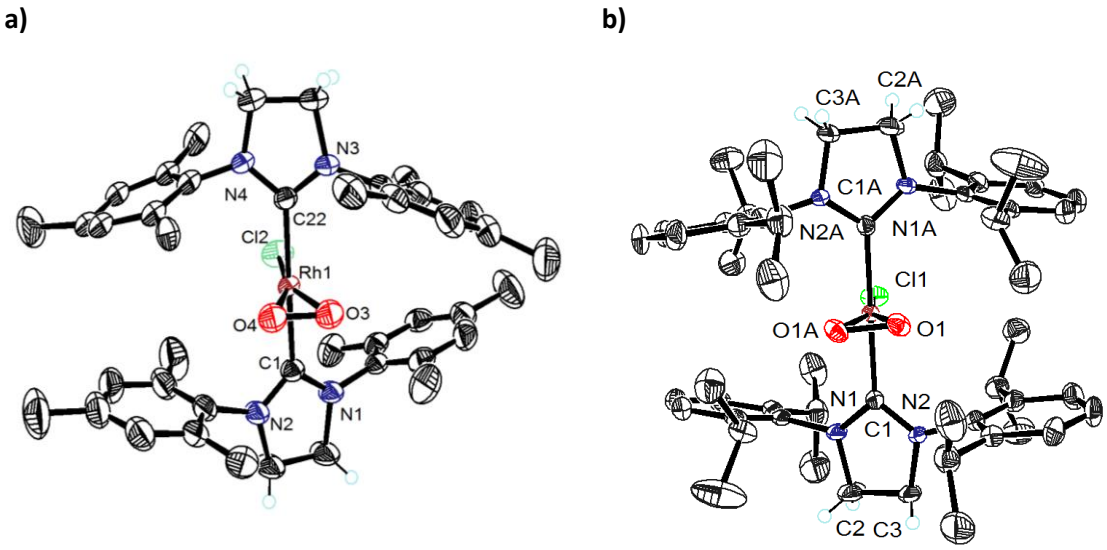
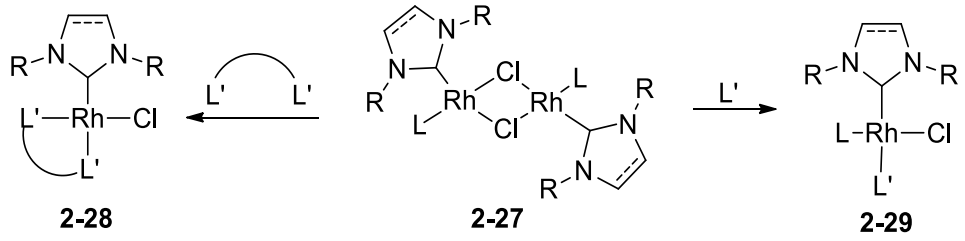
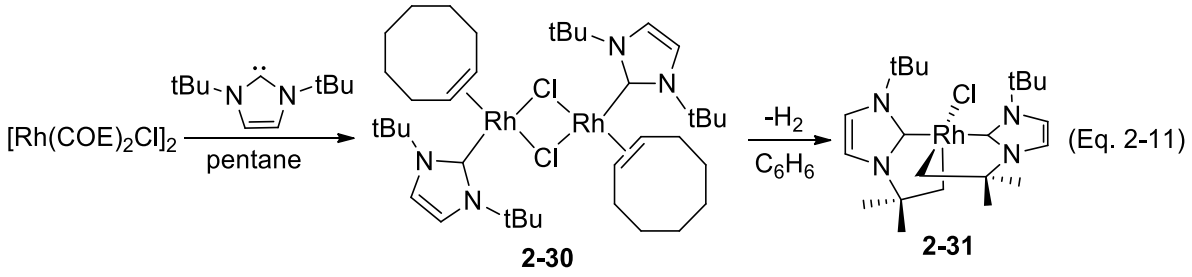


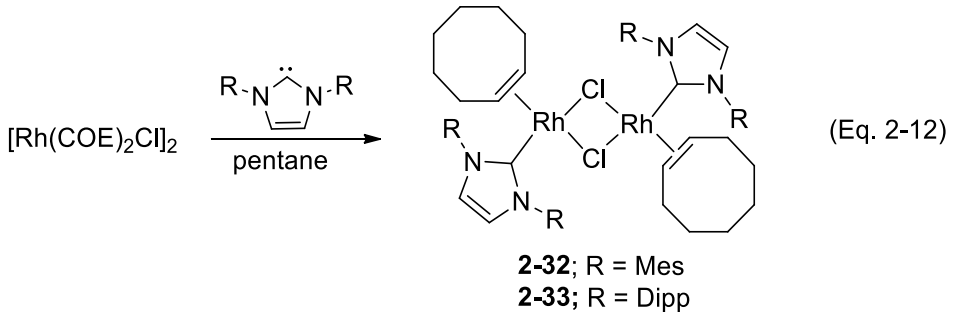
Figure 2-1: Crystallographically determined structures of (a) **2-25** and (b) **2-26**, displaying thermal ellipsoids drawn at the 50 % confidence level. Hydrogen atoms (except for the SIPr and SIMes backbone hydrogens) are omitted for clarity. Selected interatomic distances [Å] and angles [°]: For **2-25**: Rh(1)–O(3), 2.090(5); Rh(1)–C(1), 2.049(3); Rh(1)–C(22), 2.058(3), Rh(1)–Cl(1), 2.185(3); O(3)–O(4), 1.372(16); N(1)–C(1), 1.335(4); N(2)–C(1), 1.339(4); C(2)–C(3), 1.521(5); O(3)–Rh(1)–C(1), 88.40(17); O(3)–Rh(1)–C(22), 92.06(17); C(1)–Rh(1)–C(22), 179.15(13); O(3)–Rh(1)–Cl(1), 88.40(17); C(1)–Rh(1)–Cl(1), 87.32(11); C(22)–Rh(1)–Cl(1), 93.34(11). For **2-26**: Rh(1)–N(3), 1.889(6); Rh(1)–C(1), 2.0581(16); Rh(1)–Cl(1), 2.2892(9); N(3)–N(4), 1.110(10); N(1)–C(1), 1.352(2); N(2)–C(1), 1.348(2); C(2)–C(3), 1.481(3); N(3)–Rh(1)–C(1), 91.23(5); N(3)–Rh(1)–Cl(1), 180.000(1); C(1)–Rh–C(1A), 177.53(10); C(1)–Rh(1)–Cl(1), 88.77(5); C(1A)–Rh(1)–Cl(1), 88.77(5), N(1)–C(1)–N(2), 106.49(14).



Scheme 2-3: Predicted Reactivity of dimeric NHC complexes of rhodium

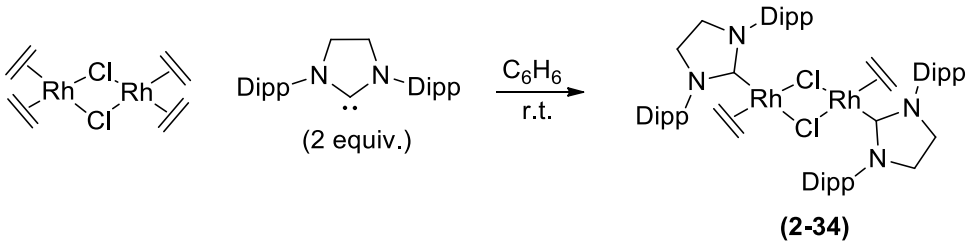
Dimeric complex **2-30** had been previously reported by Nolan, however it was reported to be remarkably unstable, decomposing rapidly to complex **2-31** upon introduction of any solvent more polar than pentane (Eq. 2-11).[29] Similarly, Herrmann had also reported dimeric Rh-NHC carbonyl complexes, which were also reported to be unstable.[30] James[24] had also reported dimeric Rh-NHC complexes bound to COE, using NHCs with less steric bulk than Nolan (Eq. 2-12). As a result, **2-32** and **2-33** were found to be relatively stable and effective precursors for various other complexes. Unfortunately however, no X-ray crystal structure had been reported for these species, which may be associated with the highly fluxional COE ligand.





We hypothesized that ethylene would be a more appropriate ancillary ligand due to its lability and volatility. Accordingly, the reaction of $[Rh(C_2H_4)_2Cl]_2$ with 2 equivalents of free SIPr in C_6H_6 at room temperature resulted in the formation of complex **2-34** along with the loss of one molecule of C_2H_4 (Eq. 2-13).[31] The presence of the ethylene was confirmed by NMR spectroscopy, with broad resonances at 2.58 and 2.27 ppm in the ^1H

NMR spectroscopy, as well as the characteristic resonance at 46.7 ppm ($^{1}J_{Rh\text{-}C}$ = 17 Hz) in the $^{13}C\{^{1}H\}$ NMR spectra. The coordination of the NHC was also confirmed as the $^{13}C\{^{1}H\}$ NMR spectrum displayed a resonance at 205.9 ppm $^{1}J_{Rh\text{-}C}$ = 58 Hz. HRMS gave a m/z of 1137 (M+Na), which was consistent with the proposed structure. X-ray quality crystals were grown from the slow diffusion of hexanes into a concentrated THF solution (Figure 2-2). The crystal structure of **2-34** clearly confirms its dimeric structure, and the coordination of both an NHC and an olefin that was predicted by NMR data.



(Eq. 2-13)

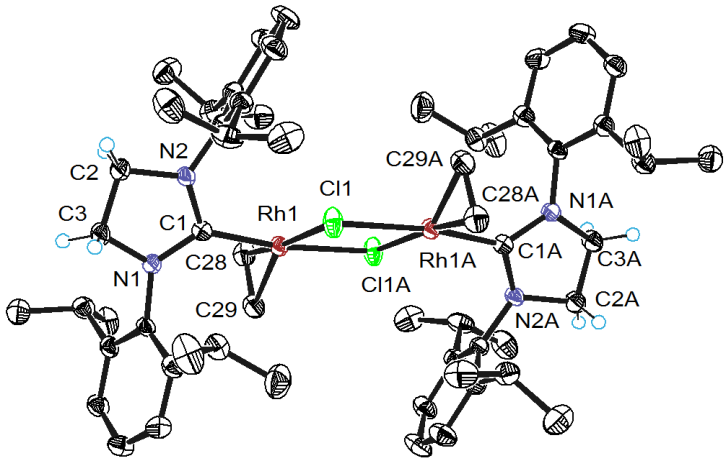
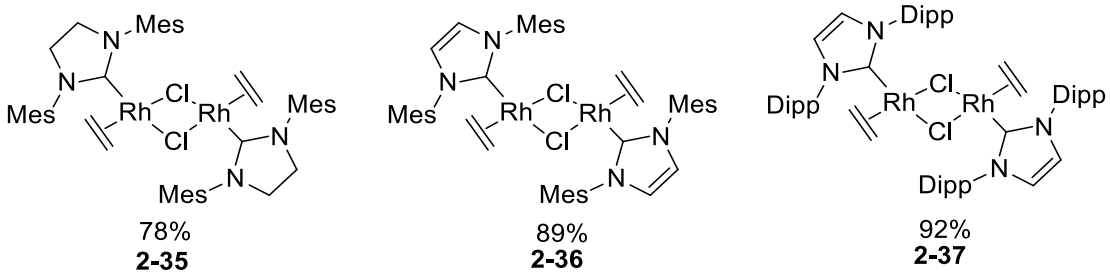


Figure 2-2: Crystallographically determined structure of **2-34** displaying thermal ellipsoids drawn at the 50% confidence level. Hydrogen atoms removed for clarity (except for the SIPr backbone hydrogens). Selected interatomic distances [Å] and angles [°]: Rh(1)–C(1), 1.937(2); Rh(1)–C(28), 2.108(3); Rh(1)–C(29), 2.093(3); C(28)–C(29), 1.383(4); Rh(1)–Cl(1), 2.3969(7); Rh(1)–Cl(1A), 2.4425(7); N(1)–C(1), 1.362(3); N(2)–C(1), 1.368(3); C(2)–C(3), 1.511(3); C(1)–Rh(1)–C(28), 90.94(10); C(1)–Rh(1)–C(29), 90.36(10); C(1)–Rh(1)–Cl(1), 94.70(7); C(1)–Rh(1)–Cl(1A), 172.50(7); C(28)–Rh(1)–Cl(1), 169.69(8); C(29)–Rh(1)–Cl(1), 148.30(8); C(1)–Rh(1)–Cl(1), 94.70(7); C(28)–Rh(1)–Cl(1A), 89.87(8); C(29)–Rh(1)–Cl(1A) 87.89(8), N(1)–C(1)–N(2), 105.62(19).

Other commonly used NHCs displayed similar reactivity (Scheme 2-4). Using the same procedure, complexes **2-35** to **2-37** were synthesized in high yield. In all cases, complexes **2-34** to **2-37** were stable enough to be isolated in the absence of either H_2O or O_2. Decomposition to elemental rhodium was observed however after ten days, when complexes **2-34** to **2-37** were stored in solution. Generally the NHCs were oriented anti to each other, likely due to steric constraints, in solution however, SIMes-containing **2-35** appeared as a mixture of syn and anti-isomers as observed by NMR spectroscopy. The $^{13}C\{^1H\}$ NMR spectra of complexes **2-35** to **2-37** featured many similarities to **2-34** (Table 2-2). The chemical shift of the carbene was dependant on the saturation of the NHC, with saturated SIPr and SIMes >204 ppm, and unsaturated <180ppm. X-ray crystallography confirmed the identities of **2-35** and **2-37** (Figure 2-3).



Scheme 2-4: Dimeric Rh-NHC complexes bound to different NHCs. Isolated yields.

Table 2-2: Characteristic features in the $^{13}C\{^1H\}$ NMR spectra of complexes **2-34** to **2-37**

	NHC_{NCN}-Rh		**(η^2-C_2H_4)**	
Complex	**δ(ppm)**	**$^1J_{Rh\text{-}C}$ (Hz)**	**δ(ppm)**	**$^1J_{Rh\text{-}C}$ (Hz)**
2-34	205.89	58.0	46.7	16.7
2-35	207.02 (204.02)	58.5 (55.9)	45.9	16.1 (16.8)
2-36	176.03	61.8	43.3	16.5
2-37	179.05	62.5	43.7	16.5

When the much larger ItBu ligand was used, significant decomposition was instead observed (Scheme 2-5). While the formation of **2-38** appeared to be rapid and occur in quantitative yield when conducted in pentane, the increased steric bulk of ItBu relative to the other NHCs resulted in rapid decomposition, as indicated by the precipitation of elemental rhodium from the reaction mixture. The initial formation of **2-38** was confirmed by ^{1}H and ^{13}C NMR spectroscopy, however the decomposition made characterization difficult.

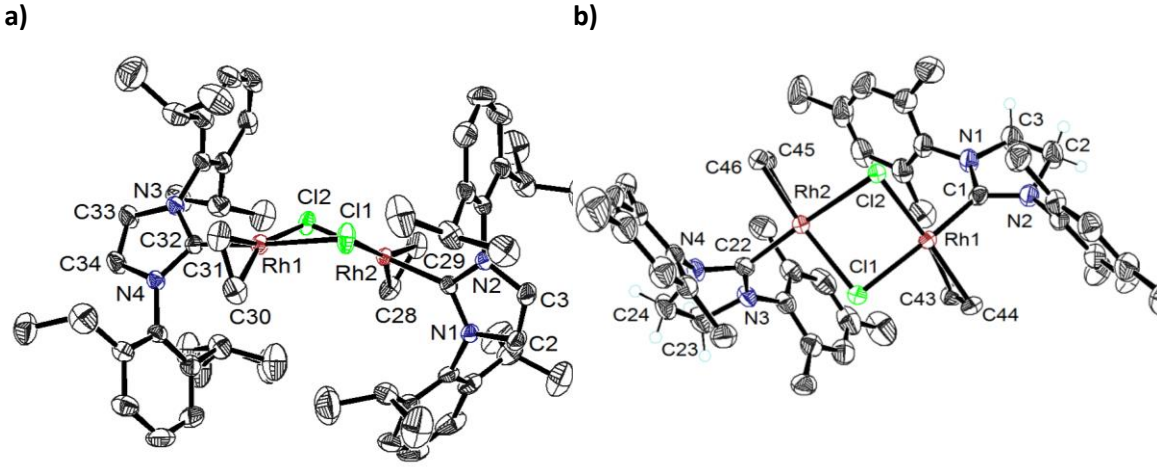
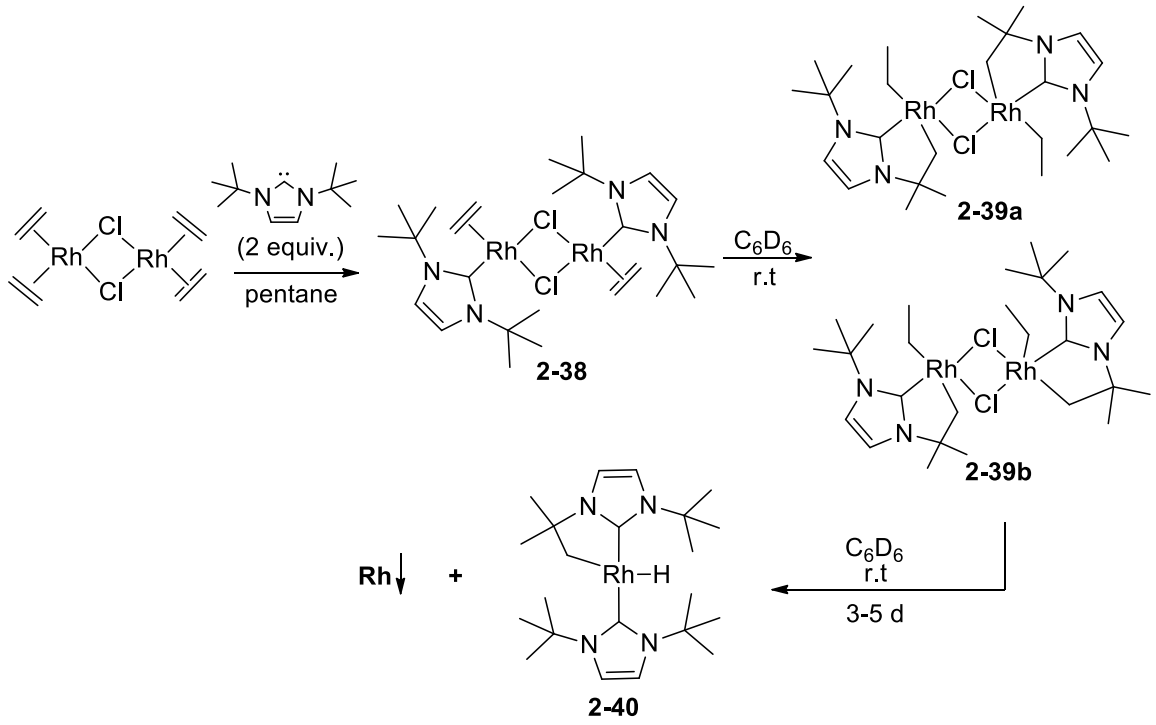


Figure 2-3: Crystallographically determined structure of (a) **2-35** and (b) **2-37** displaying thermal ellipsoids drawn at the 50% confidence level. Hydrogen atoms removed for clarity (except for the SIMes backbone hydrogens). Selected interatomic distances [Å] and angles [°] are: For **2-35**: Rh(2)–Cl(1), 2.3826(5); Rh(2)–C(1), 1.9681(17); Rh(2)–C(28), 2.0985(19); Rh(2)–C(29), 2.0986(19); C(28)–C(29), 1.389(3); Rh(2)–Cl(2), 2.4259(4); N(1)–C(1), 1.372(2); N(2)–C(1), 1.378(2); C(2)–C(3), 1.337(3); C(1)–Rh(2)–C(28), 98.53(7); C(1)–Rh(2)–C(29), 93.13(8); C(1)–Rh(2)–Cl(1), 93.43(5); C(1)–Rh(2)–Cl(2), 176.15(5); C(28)–Rh(2)–Cl(1), 155.99(6); C(29)–Rh(2)–Cl(1), 160.11(7); C(1)–Rh(2)–Cl(1), 93.43(5); C(28)–Rh(2)–Cl(2), 85.03(6); C(29)–Rh(2)–Cl(2) 90.57(6), N(1)–C(1)–N(2), 102.30(14). For **2-37**: Rh(1)–C(1), 1.943(3); Rh(1)–Cl(1), 2.4486(8); Rh(1)–C(43), 2.092(3); Rh(1)–C(44), 2.098(3); C(43)–C(44), 1.399(5); Rh(1)–Cl(2), 2.3900(8); N(1)–C(1), 1.352(4); N(2)–C(1), 1.368(4); C(2)–C(3), 1.513(5); C(1)–Rh(1)–C(44), 96.72(14); C(1)–Rh(1)–C(43), 89.74(14); C(1)–Rh(1)–Cl(1), 176.24(10); C(1)–Rh(1)–Cl(2), 95.17(9); C(43)–Rh(1)–Cl(1), 90.91(11); C(44)–Rh(1)–Cl(1), 86.10(10); C(1)–Rh(1)–Cl(1), 176.24(10); C(43)–Rh(1)–Cl(2), 163.05(11); C(44)–Rh(1)–Cl(2) 154.83(11), N(1)–C(1)–N(2), 105.9(3).

Fortunately, single crystals of a mixture of **2-39a** and **2-39b** suitable for X-ray crystallography were obtained from a concentrated C_6D_6 solution, which confirmed the original formulation of **2-38** as shown above. The increased steric bulk of the ItBu group induced the cyclometallation of the wingtip groups resulting in a mixture of **2-39a** and **2-39b** in a 23:77 ratio. Complexes **2-39a** and **2-39b** further decomposed to bis(NHC) complex **2-40**, which was previously reported by Nolan and coworkers.[29]



Scheme 2-5: Reactivity of rhodium ItBu dimeric complexes

a) **b)**

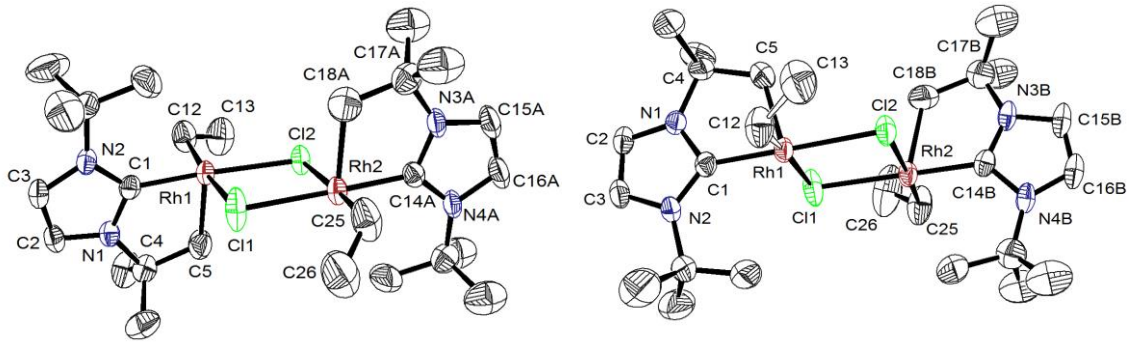
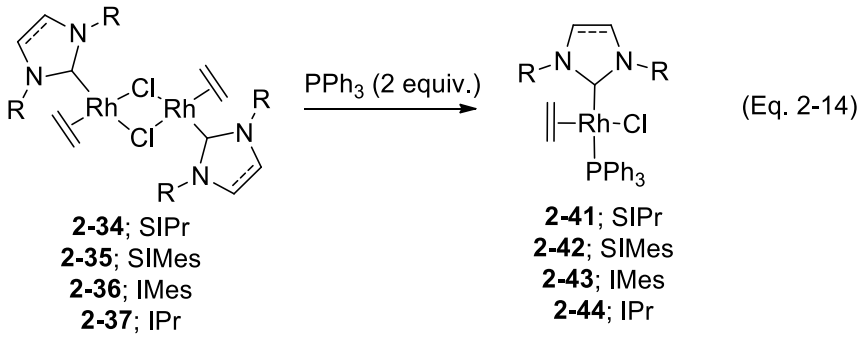


Figure 2-4: Crystallographically determined structure of (a) **2-39a** and (b) **2-39b** displaying thermal ellipsoids drawn at the 50% confidence level. Hydrogen atoms removed for clarity. Selected interatomic distances [Å] and angles [°]:Rh(1)–C(1), 1.928(2); Rh(1)–Cl(1), 2.5446(7); Rh(1)–Cl(2), 2.4585(6); Rh(1)–C(12), 2.051(3); Rh(1)–C(5), 2.013(3); C(4)–C(5), 1.551(4); Rh(1)–Cl(2), 2.4585(6); N(1)–C(1), 1.357(3); N(2)–C(1), 1.377(3); C(2)–C(3), 1.336(4); C(12)–C(13), 1.469(5); C(25)–C(26), 1.408(5); Rh(2)–Cl(2), 2.5447(7); Rh(2)–Cl(1), 2.4483(7); Rh(2)–C(14A), 1.935(1); Rh(2)–C(14B), 1.977(3); Rh(2)–C(18A), 2.102(5); Rh(2)–C(18B), 2.180(12); Rh(2)–C(25), 2.045(3);C(1)–Rh(1)–C(12), 88.94(11); C(1)–Rh(1)–C(5), 80.90(11); C(5)–Rh(1)–C(12), 93.57(16); C(1)–Rh(1)–Cl(1), 92.33(7); C(1)–Rh(1)–Cl(2), 176.01(7); C(5)–Rh(1)–Cl(2), 97.49(9); C(12)–Rh(1)–Cl(1), 171.42(11); C(12)–Rh(1)–Cl(2), 94.81(9); N(1)–C(1)–N(2), 105.4(2).

With straightforward routes to **2-34** to **2-37** in hand, we were interested in exploring their reactivity with other ancillary ligands. The treatment of **2-34** with 2 equivalents of free IPr resulted in a mixture of products. By $^{13}C\{^{1}H\}$ NMR spectroscopy, three compounds were observed, which were interpreted as resulting from of NHC scrambling. Similar behaviour was also observed by James and coworkers.[7b] Due to the mixture of products obtained, we chose to investigate other classes of ligands instead. In light of our groups' previous studies with phosphine complexes, we were particularly interested in the reactivity of **2-34** to **2-37** towards PPh_3 (Eq. 2-17).[32] Complexes **2-34** to **2-37** react with 2 equivalents of PPh_3 to cleanly form tetraheteroleptic complexes **2-41** to **2-44** in high yield, as determined by ^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectroscopy.



(Eq. 2-14)

In all cases, the $^{13}C\{^{1}H\}$ NMR spectra of **2-41** to **2-44** contain a characteristic resonance at ~41 ppm, $^{1}J_{Rh\text{-}C}$ = 15 Hz, confirming the presence of the ethylene ligand. The large $^{2}J_{PC}$ coupling values in the $^{31}P\{^{1}H\}$ NMR spectra (132-146 Hz) indicated that the phosphine ligands lie trans to the carbene, likely for steric reasons. Complexes which exhibit a cis relationship display much smaller $^{2}J_{PC}$ values ($^{2}J_{PC}$ = 10-20 Hz).[33] During the preparation of our manuscript, complex **2-44** was also reported by Oro and Castarlenas by a different route.[34] Although no crystal structure was reported, the solution characterization data matched our data.

Single crystals of **2-42** were obtained by the slow diffusion of hexanes into a concentrated THF solution, which further confirmed the trans configuration (Figure 2-5). The C-C bond in the ethylene ligand is appreciably elongated to 1.408(9) Å, in comparison to free ethylene (1.3391(13) Å), likely an indication of considerable backbonding from the electron rich metal center.

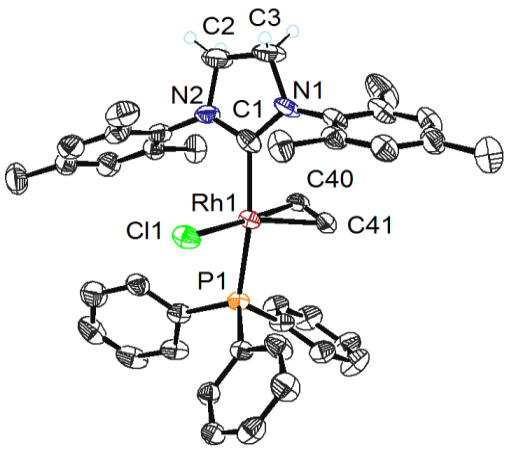
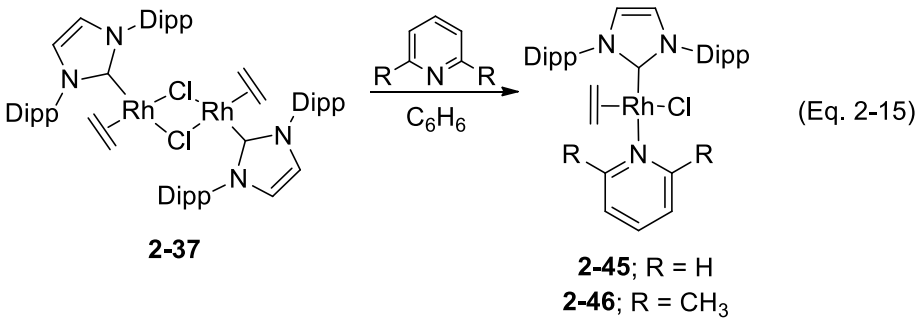


Figure 2-5: Crystallographically determined structure of **2-42** displaying thermal ellipsoids drawn at the 50% confidence level. Hydrogen atoms removed for clarity (except for the SIMes backbone hydrogens). Selected interatomic distances (Å) and angles [°]: Rh(1)–C(40), 2.128(6); Rh(1)–C(41), 2.099(5); Rh(1)–C(1), 2.071(6); Rh(1)–Cl(1), 2.3918(14); C(40)–C(41), 1.408(9); N(1)–C(1), 1.352(2) 1.353(7); N(2)–C(1), 1.342(7); C(2)–C(3), 1.523(9); C(40)–Rh(1)–C(1), 85.5(2); C(41)–Rh(1)–C(1), 95.4(2); C(1)–Rh(1)–P(1), 169.62(16); C(1)–Rh(1)–Cl(1), 93.06(15); P(1)–Rh(1)–Cl(1), 93.06(15), N(1)–C(1)–N(2), 108.0(5).

With a straightforward and high yielding synthetic route to complexes **2-41** to **2-44** in hand, we wished to investigate their reactivity with O_2. Unfortunately, in all cases, treatment with O_2 resulted in an intractable mixture of products as judged by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy. This was further plagued by the presence of the oxidizable phosphine ligand, as triphenyl phosphine oxide was observed by $^{31}P\{^{1}H\}$ NMR spectroscopy. This inspired us to instead investigate the coordination of ligands that are less sensitive to oxidation.

Treatment of **2-37** with 2 equivalents of pyridine resulted in pyridine adduct **2-45** quantitatively as confirmed by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy. The $^{13}C\{^{1}H\}$ NMR spectra clearly showed the presence of the ethylene ligand, as a doublet at 41.6 ppm, ($^{1}J_{Rh\text{-}C}$ = 16.7 Hz). The ^{1}H NMR spectrum of complex **2-45** displayed incredibly broad resonances for both the pyridine and the ethylene protons, which sharpened at -50 °C,

indicating substantial fluxionality. Unfortunately, all of our efforts to obtain single crystals suitable for X-ray diffraction of **2-45** were met with failure. During the preparation of our manuscript, **2-45** was also reported by Castarlenas and Oro, who described similar issues in its isolation.[35]



As a result, we attempted the synthesis of 2,6-lutidine complex **2-46** which we expected to not suffer from the same fluxionality. The increased steric parameters of the lutidine required extended reaction times, and an excess (10 equivalents) of lutidine. After stirring for 14 days at room temperature in THF, **2-46** was observed in 70 % yield, as determined by ^{1}H and ^{13}C NMR spectroscopy. Despite the incomplete conversion, single crystals of **2-46** were obtained confirming its structure (Figure 2-6).

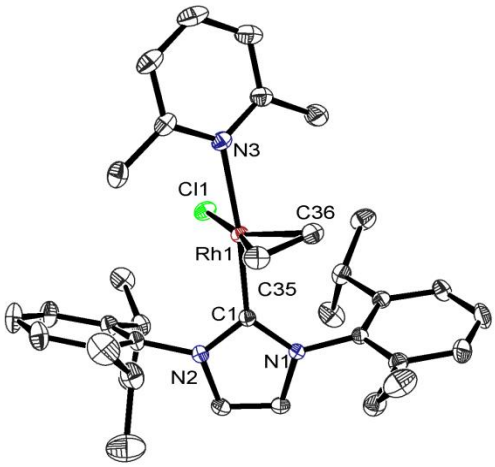
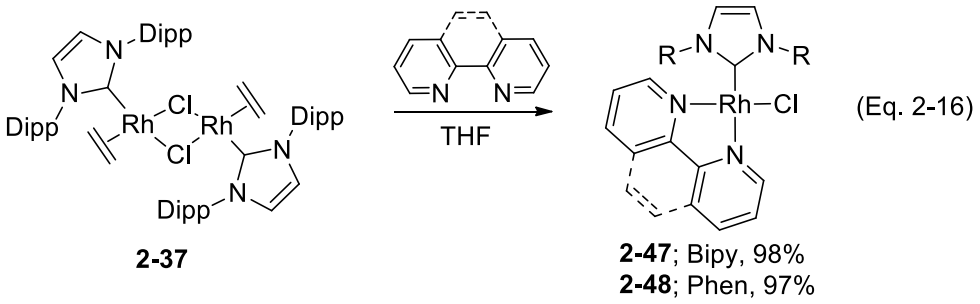


Figure 2-6: Crystallographically determined structure of **2-46** displaying thermal ellipsoids drawn at the 50% confidence level. Hydrogen atoms removed for clarity. Selected interatomic distances [Å] and angles [°]: Rh(1)–N(3), 2.1365(13); Rh(1)–C(36), 2.0984(16); Rh(1)–C(35), 2.1101(17); Rh(1)–C(1), 1.9722(15); Rh(1)–Cl(1), 2.3685(4); N(1)–C(1), 1.3705(19); N(2)–C(1), 1.3783(18);

C(35)–C(36), 1.382(3); N(3)–Rh(1)–Cl(1), 86.21(4); N(3)–Rh(1)–C(1), 174.06(5); C(1)–Rh(1)–C(35), 91.63(7); C(1)–Rh(1)–C(36) 97.94(6), C(35)–Rh(1)–Cl(1), 170.22(5), C(36)–Rh(1)–Cl(1), 150.75(5), C(1)–Rh(1)–Cl(1), 89.78(4); N(1)–C(1)–N(2), 102.76(12).

We further investigated the coordination of chelating pyridine-derived donors. The reaction of **2-37** with bipy or 1,10 phenanthroline resulted in the immediate formation of intensely coloured solutions (Eq. 2-19).[36] The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were consistent with the proposed structures. The ^{1}H NMR spectra of both **2-47** and **2-48** were consistent with non-symmetric environments. Single crystals suitable for X-ray crystallography were obtained of both complexes **2-47** and **2-48**, which clearly demonstrated the coordination of the chelating ligands, along with the displacement of ethylene (Figure 2-7).



2-37

2-47; Bipy, 98%
2-48; Phen, 97%

a) **b)**

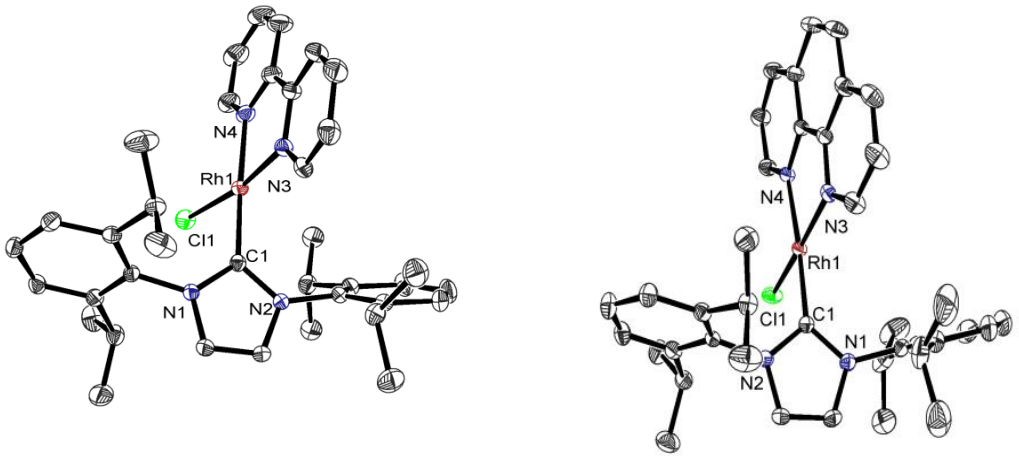
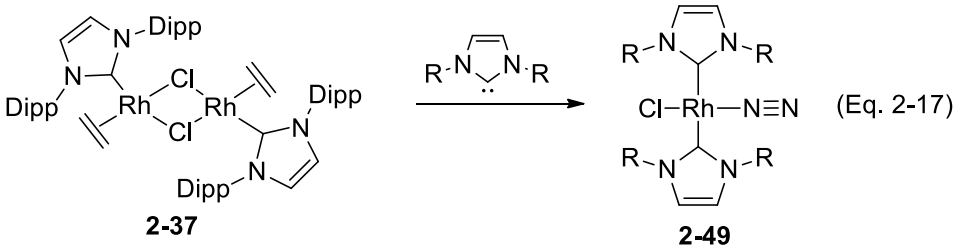
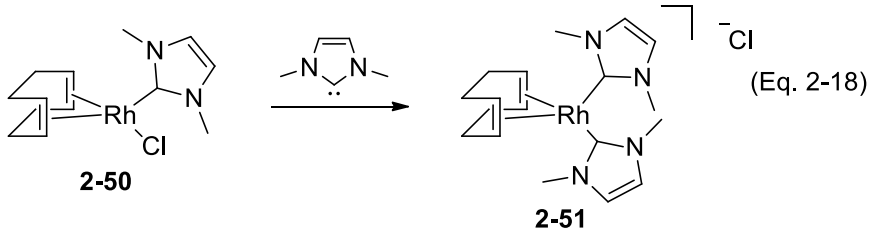


Figure 2-7: Crystallographically determined structures of (a) **2-47** and (b) **2-48**, displaying thermal ellipsoids drawn at the 50% confidence level. Hydrogens and solvent molecules (C_6H_6) are omitted for clarity. Selected interatomic distances [Å] and angles [°]: For **2-47**: Rh(1)–N(3), 1.990(2); Rh(1)–N(4), 2.063(2); Rh(1)–C(1), 1.986(2); Rh(1)–Cl(1), 2.3530(6); N(1)–C(1), 1.375(3); N(2)–C(1), 1.378(3); N(3)–Rh(1)–Cl(1), 170.68(6); N(3)–Rh(1)–C(1), 98.48(9); C(1)–Rh(1)–N(4), 177.19(9); N(4)–Rh(1)–Cl(1), 92.65(7), C(1)–Rh(1)–Cl(1), 89.46(7); N(1)–C(1)–N(2), 102.48(18). For **2-48**: Rh(1)–N(3), 2.0085(16); Rh(1)–N(4), 2.0729(16); Rh(1)–C(1), 1.9896(19); Rh(1)–Cl(1), 2.3480(5); N(1)–C(1), 1.382(2); N(2)–C(1), 1.378(3); N(3)–Rh(1)–Cl(1), 168.91(5); N(3)–Rh(1)–C(1), 101.92(7); C(1)–Rh(1)–N(4), 176.04(7); N(4)–Rh(1)–Cl(1), 89.94(5), C(1)–Rh(1)–Cl(1), 88.28(5); N(1)–C(1)–N(2), 102.19(16).

The formation of complexes **2-47** and **2-48** illustrates the high level of unsaturation in complex **2-37**. In contrast, the reaction of [Rh(COD)(IPr)Cl] under the same reaction conditions did not result in any formation of **2-47**, and instead gave the full return of starting materials. This is likely associated with the decreased lability of the cyclooctadiene ligand. The difference in reactivity can further be seen in the reaction of **2-37** with free carbenes. While **2-37** results in bis(NHC) complex **2-49**, displaying a trans arrangement of the NHCs,[32, 37] Herrmann has previously reported that reaction of COD complex **2-50** with an additional equivalent of an NHC instead results in bis(NHC) complex **2-51**, where the two NHCs are situated cis to each other.[11c] While IMe is substantially smaller, nonetheless the difference in reactivity indicates the lower lability of the COD ligand relative to the ethylene.

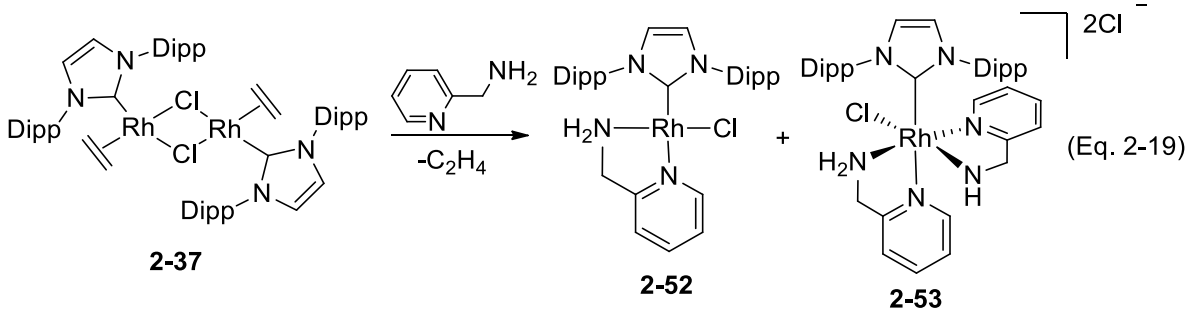


2-37 **2-49**



2-50 **2-51**

Other chelating donors such as 2-picolylamine were also investigated by Dr. Olena Zenkina under similar conditions. Unfortunately, 2-picolylamine was far less well behaved in comparison to bipyridine or 1,10-phenanthroline. Treatment of **2-37** with 2 equivalents of 2-picolylamine resulted in a complicated mixture of compounds by ^{1}H NMR spectroscopy (Eq. 2-19). The slow evaporation of a C_6H_6 solution of the reaction mixture resulted in red single crystals of complex **2-52** and blue crystals of cationic Rh^{III} **2-53**, which could be separated physically. The X-ray structures of these complexes are displayed in Figure 2-8. Significant amounts of rhodium black were formed during the reaction. Unfortunately, complexes **2-52** and **2-53** could only be isolated in small quantities preventing their full analyses, or further investigation.



2-37 **2-52** **2-53**

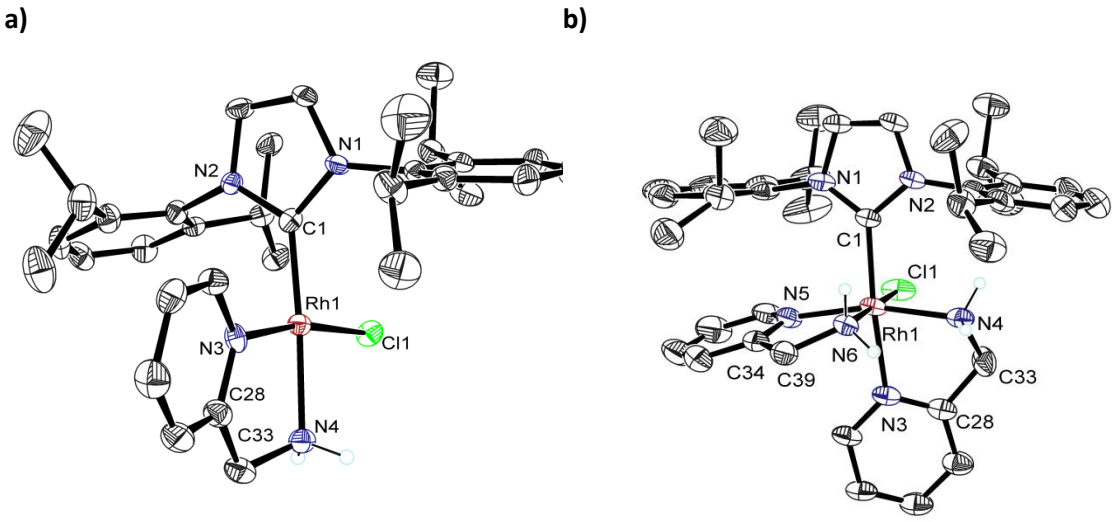
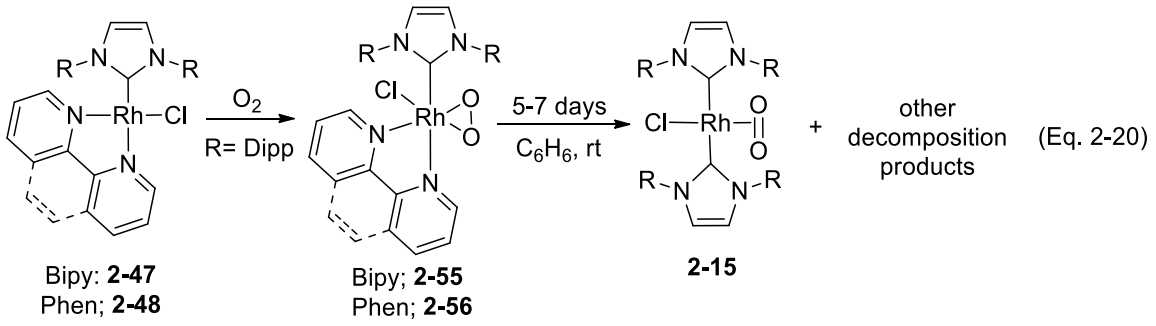


Figure 2-8: Crystallographically determined structures of (a) **2-52** and (b) **2-53**, displaying thermal ellipsoids drawn at the 50% confidence level. Hydrogens (except NH_2 hydrogens) are omitted for clarity. Selected interatomic distances [Å] and angles [°]: For **2-52**: Rh(1)–N(3), 1.947(6); Rh(1)–N(4), 2.130(5); Rh(1)–C(1), 2.035(5); Rh(1)–Cl(1), 1.957(6); N(1)–C(1), 1.396(7); N(2)–C(1), 1.408(7); C(33)–N(4), 1.472(7); C(33)–C(28), 1.512(8); N(3)–Rh(1)–Cl(1), 169.02(15); N(3)–Rh(1)–C(1), 94.4(2); N(4)–Rh(1)–C(1), 175.1(2); N(4)–Rh(1)–Cl(1), 88.46(14); Rh(1)–N(4)–C(33), 109.7(4); C(1)–Rh(1)–Cl(1), 96.39(17); N(1)–C(1)–N(2), 102.8(5). For **2-53**: Rh(1)–N(3), 2.133(4); Rh(1)–N(5), 2.028(5); Rh(1)–N(4), 2.063(5); Rh(1)–N(6), 2.060(4); Rh(1)–C(1), 2.061(5); Rh(1)–Cl(1), 2.3460(15); N(1)–C(1), 1.377(7); N(2)–C(1), 1.392(6); C(33)–N(4), 1.466(7); C(39)–N(6), 1.495(7); C(33)–C(28), 1.504(8); C(34)–C(39), 1.474(8); N(3)–Rh(1)–Cl(1), 87.81(13); N(5)–Rh(1)–Cl(1), 96.19(15); N(3)–Rh(1)–C(1), 174.4(2); N(5)–Rh(1)–C(1), 95.4(2); N(4)–Rh(1)–C(1), 98.6(2); N(6)–Rh(1)–C(1), 93.04(18); N(4)–Rh(1)–Cl(1), 98.6(2); N(6)–Rh(1)–Cl(1), 177.74(12); Rh(1)–N(4)–C(33), 110.1(4); Rh(1)–N(6)–C(39), 110.6(3); C(1)–Rh(1)–Cl(1), 88.26(14); N(1)–C(1)–N(2), 102.7(4).

With synthetic procedures for compounds **2-45** to **2-48** in hand, we investigated their reactivity towards O_2. Exposure of pyridine complex **2-45** to O_2 resulted in a rapid colour change of yellow to green, and finally deep red. Unfortunately, all attempts to identify the products of this transformation were unsuccessful. In contrast however, upon exposure of C_6H_6 solutions of bipy and phen complexes **2-47** and **2-48** to O_2, the intensely coloured solutions underwent dramatic colour changes to light yellow within seconds at room temperature.

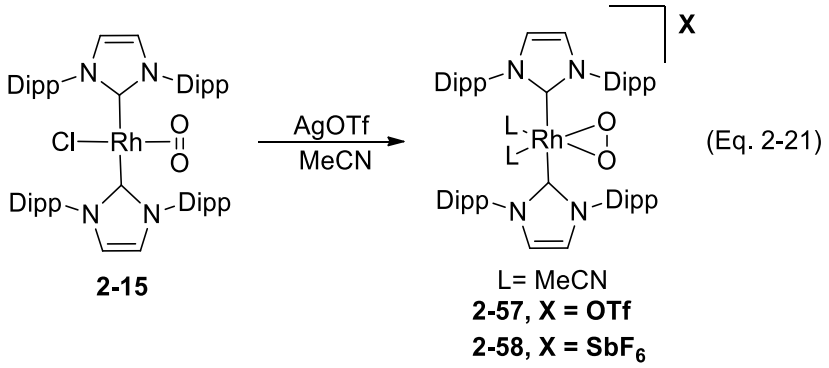
The complete conversion of **2-47** and **2-48** to new species could be observed by ^{1}H and ^{13}C NMR spectroscopy. The $^{13}C\{^{1}H\}$ NMR spectra of these compounds display substantial upfield chemical shifting of the carbene resonances, likely indicating oxidation to Rh^{III}. As such, we proposed the structures **2-58** and **2-59**. To further confirm their identities, we synthesized $^{18}O_2$ labeled complexes and measured their IR spectra and compared them to those of non-labeled complexes. In both cases, the IR spectra were nearly identical, except for the red shifting of a single band at 882 cm^{-1} and 883 cm^{-1} in **2-58** and **2-59** respectively by 50 nm, which is the amount expected by a simple harmonic oscillator approximation. These results clearly confirm the formation of a Rh-O_2 complex. The wavelengths of the bands likely indicate the formation of a Rh^{III} peroxo species, as these species typically give stretching frequencies in the range of 800-930 cm^{-1}.[38] In contrast, superoxo, or singlet oxygen species would be expected to give stretching frequencies in the range of 1050-1200 cm^{-1}.[39] All attempts to grow single crystals of **2-58** and **2-59** were unsuccessful. DFT analysis performed on model complexes of **2-47** demonstrated that the HOMO was largely metal based, and the intense colours observed were likely due to MLCT charge transfer. The loss of colour upon exposure to O_2 is consistent with oxidation of the metal center which would directly affect MLCT.

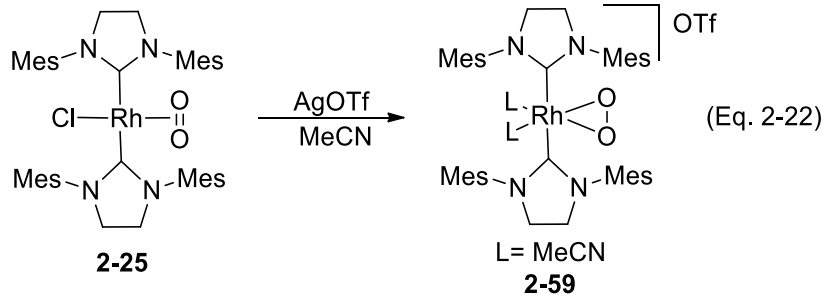


Complexes **2-55** and **2-56** are not stable in solution for prolonged periods of time. After several days at room temperature, complex **2-15** appeared as a major decomposition product, along with other unidentifiable species. The formation of **2-15** is rather remarkable, as it suggests the facile cleavage of a metal NHC bond under incredibly mild conditions. This result adds to the body of literature detailing the mild cleavage of NHCs from metal centers.[18, 40] The driving force for this reaction may be the formation of the thermodynamically stable **2-15**.

The above results appear to suggest that, as expected, the binding of O_2 in the singlet state is highly dependent on the nature of the ligands about the metal center. In order to further investigate the nature of O_2 coordination, our group hypothesized varying the nature of the anionic ligand trans to the oxygen in bis(NHC) complexes may have a dramatic effect on the coordination mode of O_2. In particular, previous group member Dr. Judy Cipot-Wechsler investigated the formation of cationic Rh-O_2 complexes by treatment of **2-15** with AgOTf in MeCN at room temperature (Eq. 2-21).[25c] This resulted in the formation of acetonitrile complex **2-57** in low yield. Higher yields were obtained using $AgSbF_6$ resulting in **2-58**. Interestingly, a dramatic colour change from deep blue to beige accompanied this transformation, which may be indicative of the oxidation to Rh^{III}. In accordance with this, the $^{13}C\{^1H\}$ NMR spectrum of **2-57** displayed substantial upfield shifting of the carbene resonance. Single crystals of **2-57** suitable for X-ray diffraction were obtained which demonstrated a lengthening of the O-O bond length to 1.428(3) Å and the presence of two coordinated acetonitrile ligands in an overall octahedral geometry. This bond length is more consistent with a traditional peroxo ligand, confirming the oxidation of the rhodium center to Rh^{III}. SIMes bound complex **2-25** reacted with AgOTf in MeCN

resulting in **2-59** in 48% yield. We demonstrated that similar effects were also observed in complex **2-59**, as the O-O bond length was increased to 1.439(8) Å, indicating this phenomenon was general (Eq. 2-22).





The formation of Rh^{III} peroxo complexes was further corroborated by IR spectroscopy using labeled $^{18}O_2$. The IR spectra of $^{16}O_2$-**2-57** and $^{18}O_2$-**2-57** were identical except for a 50 nm red shift of a band at 910 cm^{-1} to 860 cm^{-1}. This band is in good agreement with predicted values for peroxo compounds. In comparison to the parent Rh^{I}-O_2 complex, this is a dramatic shift from 1020 cm^{-1}. Similar results were obtained using the SIMes variant **2-59**, which displayed a band at 856 cm^{-1}, in comparison to Rh^{I} complex **2-25** at 1056 cm^{-1}. These results are in good agreement with the complexes previously reported by James, which are presented in Table 2-3.

Table 2-3: Comparison of different Rh peroxo complexes

Complex	O-O Bond length (Å)	ν(O-O) (cm^{-1})
$[Rh(IPr)_2(MeCN)_2(O_2)][BF_4]$ (**2-57**)	1.428(3)	910
$[Rh(SIMes)_2(MeCN)_2(O_2)][BF_4]$ (**2-59**)	1.439(8)	856
$[Rh(IMes)Cl(PPh_2C_6H_4NMe_2)(O_2)]$ (**2-22**)[24]	1.450(2)	870
$[Rh(IPr)Cl(PPh_2C_6H_4NMe_2)(O_2)]$ (**2-23**)[24]	1.450(3)	871

To further confirm the characterization of **2-57** and **2-59** as Rh^{III} peroxide complexes, our collaborator Pierre Kennepohl analyzed the L_3-edge XAS spectra of **2-57**. A drastically different electronic structure than **2-14** was observed, and instead **2-57** had a spectra more characteristic of a Rh^{III}-peroxo complex. DFT analysis was further utilized to investigate geometry optimizations on complexes of general structure $[(X)Rh(NHC)(O_2)]$ to investigate the effect of the X ligand on the coordination of the O_2. While halide ligands were found to favour symmetrical η^2-$^1O_2$ complexes (case **A**, Figure 2-8), π-accepting ligands such as MeCN instead resulted in asymmetric binding with the MeCN oriented trans to one of the two oxygen atoms (case **B**, Figure 2-8). This does not occur with an increase in O-O bond lengthening. The same effect was observed for anionic π-accepting ligands such as cyanide.

The coordination of a second equivalent of MeCN results in the formation of octahedral complex (case **C**, Figure 2-9). This occurs along with elongation of the O-O bond, resulting in a Rh^{III} peroxide species. The addition of a second σ- bonding interaction increases the energy of the metal 4d orbitals, enabling greater charge transfer to the O_2 ligand. Similar results were reported by Caulton, in a DFT study that indicated increasing an extra ligand resulted in the greater reducing power of metal complex, and in turn increasing the O-O bond lengths.[23a] Unfortunately however, all efforts to experimentally verify this effect by observing the intermediate case have so far been unsuccessful.

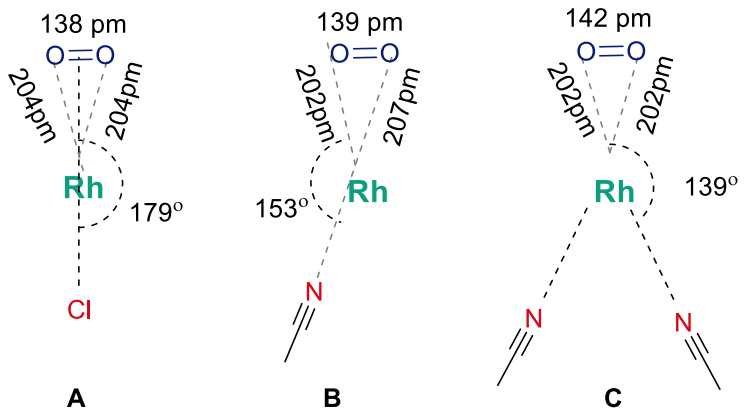
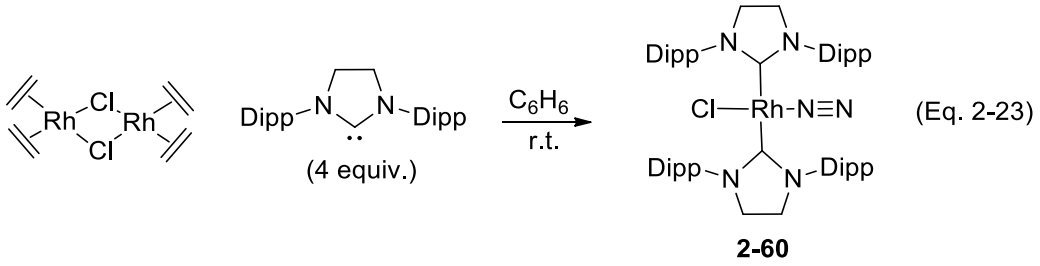


Figure 2-9: Geometries of calculated for Rh-NHC complexes bound to O_2 featuring different ancillary ligands.[25c]

2.2.3 Crystal to Crystal Transformations with Rhodium NHC Complexes

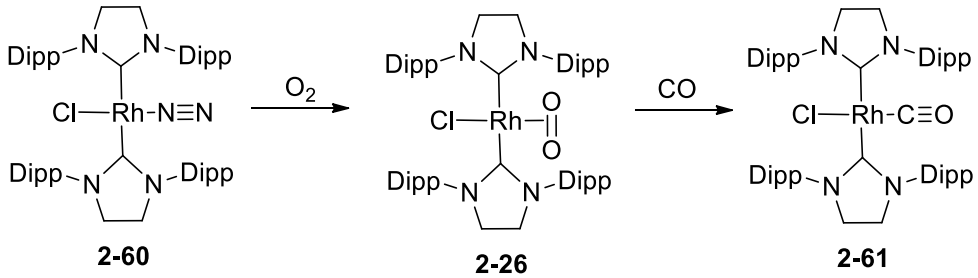
In an effort to further explore the small molecule activation of Rh-NHC complexes, our group had previously demonstrated that in the absence of molecular oxygen, rhodium bis(NHC) complexes readily activate dinitrogen from the glovebox atmosphere.[37] The labile N_2 ligand can then be readily exchanged with other small molecules such as O_2, H_2 or CO. This reactivity appears to be general for all NHCs tested. For example, dinitrogen complex **2-60** is formed when $[Rh(C_2H_4)_2Cl]_2$ is reacted with 4 equivalents of free SIPr at room temperature under nitrogen (Eq. 2-23).[31] The coordination of N_2 could be observed by IR spectroscopy, via a characteristic resonance ν(N-N) at 2107 cm^{-1}. Single crystals of **2-60** suitable for X-ray diffraction were obtained by the slow diffusion of hexanes into a saturated THF solution. The bound N_2 displays end-on coordination to the rhodium and the N-N bond length was determined to be 1.118(19)-1.110(10) Å (ranging from different independent measured structures), which is slightly elongated from free dinitrogen (1.0975 Å).[41]



(Eq. 2-23)

2-60

Exposure of a THF solution of **2-60** to molecular oxygen, or the atmosphere resulted in a drastic colour change from yellow to greenish-blue. After purification by column chromatography using neutral alumina as a stationary phase, complex **2-26** was isolated in 51% yield. ^{1}H and ^{13}C NMR spectra obtained matched our previously reported data.[31] Single crystals were obtained by slow diffusion of hexanes into a concentrated THF solution. Finally, the exposure of a THF solution of **2-26** to an atmosphere of CO once again resulted in a drastic colour change from blue to brown. The coordination of CO in complex **2-61** was confirmed by IR spectroscopy which displayed a characteristic resonance at 1945 cm^{-1}. Complex **2-61** was further characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy which confirmed the proposed structure. The X-ray crystal structures of **2-61**, **2-26** and **2-61** are displayed in Figure 2-9.



(Eq. 2-24)

2-60 **2-26** **2-61**

Although all of the transformations described above occurred in solution, we also observed that yellow powders of **2-60** would turn blue upon exposure to O_2 indicating the formation of **2-26**. Similar results were observed when powders of O_2 complex **2-26** were

exposed to an atmosphere of CO which resulted in **2-61**. Even in the solid state, these transformations appeared to take place cleanly, and could conveniently be monitored by IR spectroscopy. These results inspired postdoctoral fellow Dr. Olena Zenkina to hypothesize that single crystals of these complexes may be capable of undergoing these same transformations, without disruption of the crystal lattice.[42]

Single crystal-to-single crystal transformations of organometallic complexes are incredibly rare,[43] as most organometallic transformations generally occur with significant structural rearrangements which would likely break crystallinity. Despite these difficulties, just prior to our investigations, Brookhart had recently reported single crystal-to-single crystal transformations of Ir pincer complexes with small molecules.[43b] Iridium pincer complex **2-62** was reported to readily undergo the activation and exchange of several small molecules (Scheme 2-6). As complexes **2-62** to **2-67** were crystallized along with disordered toluene molecules, it was proposed that this provided channels for the gaseous small molecules to enter the crystal and interact with the iridium center.

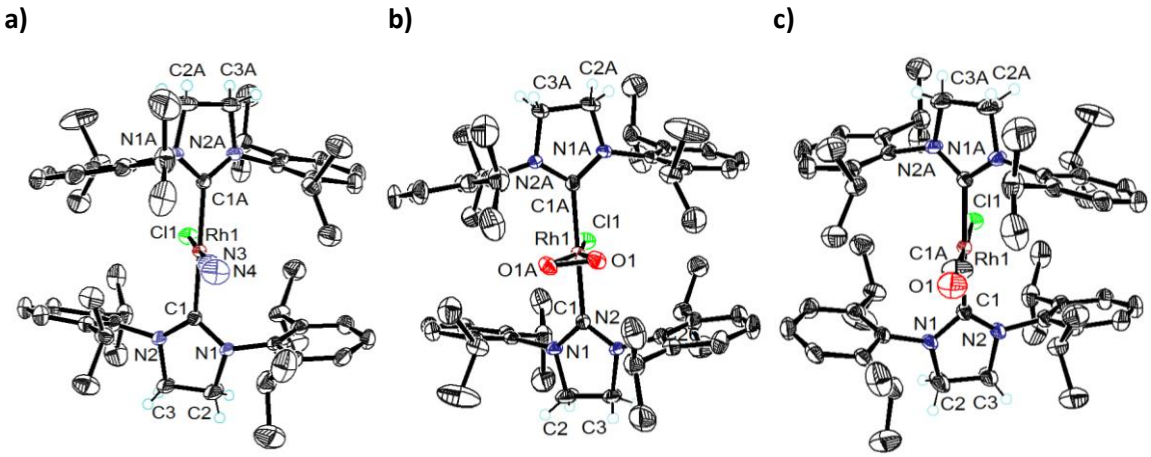
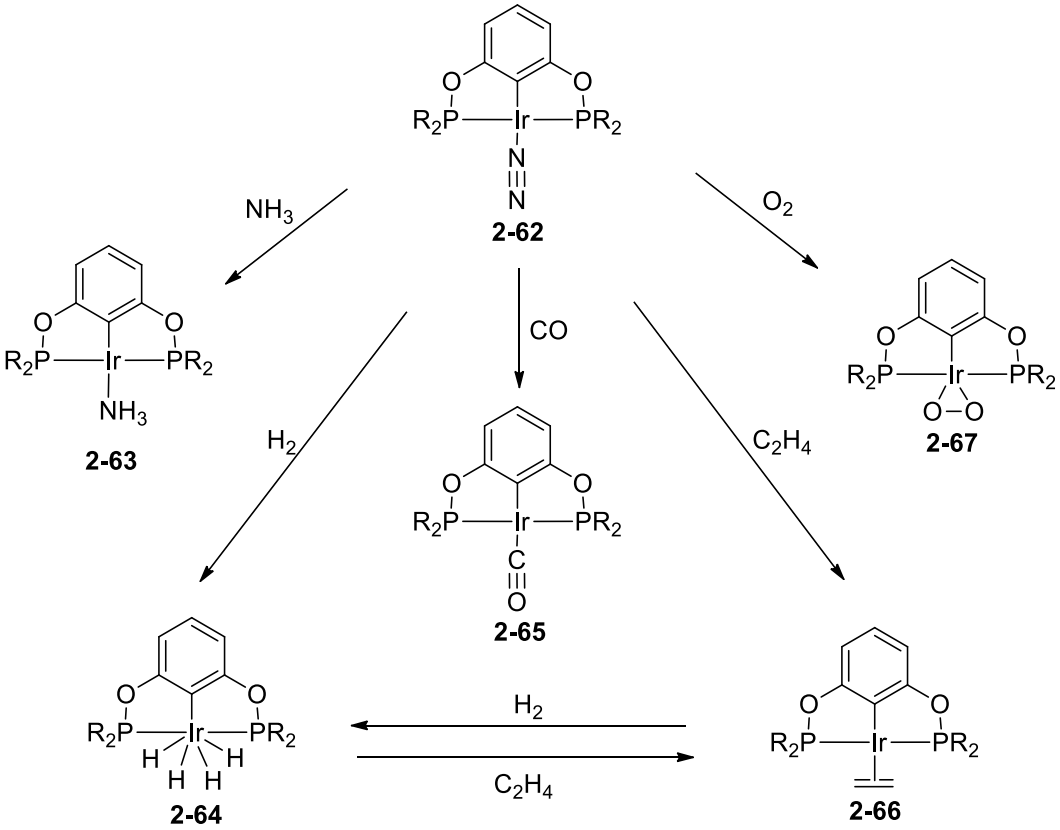


Figure 2-10: Crystallographically determined structure of (a) **2-60**, (b) **2-26**, and (c) **2-61** displaying thermal ellipsoids drawn at the 50% confidence level. Hydrogen atoms removed for clarity (except for the SIPr backbone hydrogens). Selected interatomic distances (Å) and angles [°]: For **2-60**: Rh(1)–N(3), 1.889(6); Rh(1)–C(1), 2.0581(16); Rh(1)–Cl(1), 2.2892(9); N(3)–N(4), 1.110(10); N(1)–C(1), 1.352(2); N(2)–C(1), 1.348(2); C(2)–C(3), 1.481(3); N(3)–Rh(1)–C(1), 91.23(5); N(3)–Rh(1) Cl(1), 180.000(1); C(1)–Rh–C(1A), 177.53(10); C(1)–Rh(1)–Cl(1), 88.77(5); C(1A)–Rh(1)–Cl(1), 88.77(5), N(1)–C(1)–N(2), 106.49(14). For **2-26**: Rh(1)–O(1), 1.980(4); Rh(1)–C(1), 2.068(3); Rh(1)–Cl(1), 2.3092(10); O(1)–O(1A), 1.392(11); N(1)–C(1), 1.345(4); N(2)–C(1), 1.345(3); C(2)–C(3), 1.496(5); O(1)–Rh(1)–C(1), 90.24(16); O(1)–Rh(1)–C(1A), 87.96(15); C(1)–Rh–C(1A), 178.08(16); O(1)–Rh(1)–Cl(1), 159.42; C(1)–Rh(1)–Cl(1), 90.96(8); C(1A)–Rh(1)–Cl(1), 90.96(8). For **2-61**: Rh(1)-C(1A), 1.818(13); Rh(1)-C(1), 2.057(2); Rh(1)-Cl(1), 2.240(3); C(1A)-O(1), 1.17(3); C(1A)-Rh(1)-C(1), 90.78(6); C(1A)-Rh(1)-Cl(1), 180.000(3); C(1)-Rh(1)-Cl(1), 89.22(6).



Scheme 2-6: Single crystal-to-single crystal transformations reported by Brookhart[43b]

To test this hypothesis, single crystals of **2-60** were exposed to an atmosphere of O_2 at room temperature. To avoid the crystals cracking from dryness, they were left as a heterogeneous suspension in hexanes. After 15 days, noticeable changes in colour were

observed, yielding single crystals suitable for X-ray diffraction analysis, which confirmed the formation of **2-26**. We further exposed crystals obtained from this transformation to an atmosphere of CO. Once again, a noticeable colour change was observed after 7 days, yielding single crystals of **2-61**. X-ray diffraction analysis was performed, confirming the second transformation had in fact taken place. To our knowledge, this was the first report of two sequential back-to-back-to-back single crystal-to-single crystal transformations. This is an important distinction, as the crystals used in the second transformation were derived from the original batch of N_2 complex **2-60**.

Figure 2-11 depicts photographs of the same crystal undergoing the two sequential transformations described above. The vibrant colour changes between the different crystals can clearly be observed. In addition, several of the characteristic features such as the smooth edges, and the defined layers of yellow crystal of **2-60** appear to be maintained throughout.

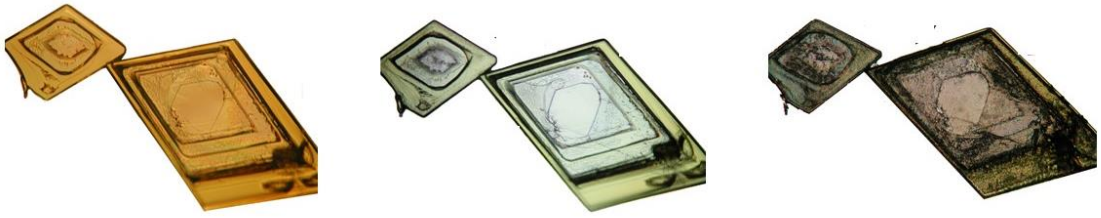


Figure 2-11: Pictures of crystals of **2-60** (left), **2-26** (middle), and **2-61** (right), which were followed during the transformation.[31]

Selected crystal lattice parameters are displayed in Table 2-4. In all cases observed, crystals of complexes **2-60**, **2-26** and **2-61** are orthorhombic, and crystallize in the P2(1)2(1)2 space group, with nearly identical unit cells. This would indicate that the ligand structure, chiefly the NHCs, dominate the configuration in which the complex crystallizes. As a result, minimal rearrangement has to occur within the crystal during the reactions.

Very similar results were observed in Brookhart's report, as all of the complexes in question crystallize in the same crystal system and space group, with nearly identical crystal lattice parameters.[43b] A further similarity to Brookhart's can be pointed out, as complexes **2-60**, **2-26**, and **2-61** all crystallize along with a molecule of n-hexane, which likely provides pores within the crystal for the exchange of gases.

Table 2-4: Crystal lattice parameters of **2-60**, **2-26**, and **2-61**

	2-60	**2-26**	**2-61**
Crystal System	Orthorhombic	Orthorhombic	Orthorhombic
Space Group	P2(1)2(1)2	P2(1)2(1)2	P2(1)2(1)2
a (Å)	13.0231(2)	13.0050(3)	13.0289(7)
b (Å)	20.5961(16)	20.6119(5)	20.6010(11)
c (Å)	10.6446(2)	10.6400(3)	10.6609(6)
V (Å^3)	2855.15(8)	2852.13(12)	2861.5(3)

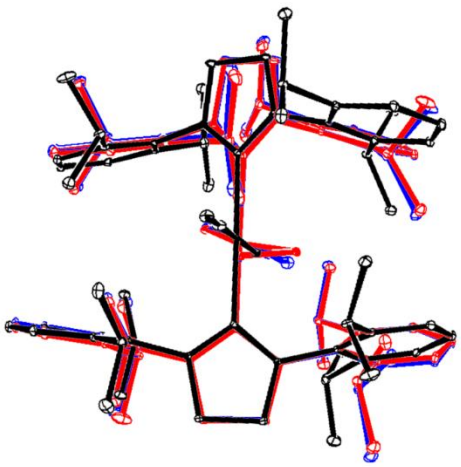


Figure 2-12: Overlaid ball and stick structures of **2-60** (blue), **2-26** (red), and **2-61** (black).

In order to probe the mechanism of this transformation, single crystals of **2-60** were exposed to an atmosphere of argon for 13 days which resulted in no apparent loss of N_2. In comparison, exposure to O_2 under comparable conditions resulted in the clean formation

of **2-26** as indicated above. These results may indicate that the exchange of the ligands does not occur by a dissociative route, which is consistent with the proposal by Brookhart.[43b]

2.3 Conclusions

The reactivity of several Rh-NHC complexes towards oxygen and other small molecules has been investigated. We have demonstrated that the nature of the auxiliary ligands plays a large factor in determining the coordination mode of the O_2 in either the singlet or triplet state. While neutral bis(NHC) complexes featuring a chloride ligand appear to be square planar Rh^I bound to singlet oxygen, cationic complexes which instead feature two acetonitrile ligands are octahedral Rh^{III} peroxo complexes.

In order to study heteroleptic Rh complexes, dimeric Rh-NHC ethylene complexes were synthesized and were demonstrated to be useful as precursors for a wide variety of other Rh-NHC complexes of various structures. While heteroleptic Rh NHC phosphine complexes largely decompose upon exposure to oxygen, complexes instead featuring bipyridine-derived ligands appear to also form Rh^{III} peroxo complexes.

Rh bis(NHC) complexes readily undergo the exchange of small molecules N_2, O_2 and CO both in solution and in solid state. Single crystals were capable of undergoing ligand exchange reactions without disruption of the crystal lattice. To our knowledge, we demonstrated the first example of two back to back single crystal-to-single crystal transformations.

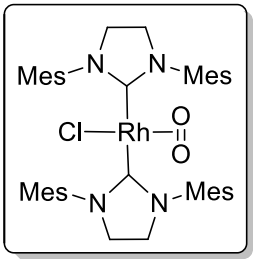
Finally, we have demonstrated the surprising lability of NHCs in several Rh complexes. These results are in contrast with the wide body of literature which report this ligands to be highly inert. The factors underlying the lability in these complexes are not

currently clear, and will require detailed investigations. The complexes we have reported may demonstrate catalytic activity, and we are pursuing their further development.

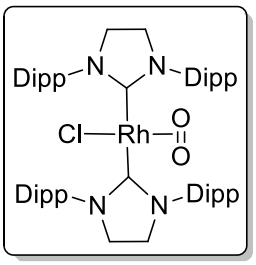
2.4 Experimental

General considerations: All manipulations were carried out under an atmosphere of dry argon in oven dried glassware, or under a nitrogen atmosphere in a glovebox (M. Braun) with oxygen and water levels ≤2 ppm. All solvents were distilled from either Na/Benzophenone (THF, Et_2O, toluene, benzene), or CaH_2 (CH_2Cl_2, NEt_3) and degassed via three cycles of freeze-pump-thaw and stored over 4 Å molecular sieves prior to use. Transition metal precursors $[Rh(COD)_2Cl]_2$,[44] $[Rh(C_2H_4)_2Cl]_2$[45] and $[Rh(IPr)(COE)Cl]_2$[24] were synthesized by previously reported procedures from $RhCl_3•3H_2O$. The free carbenes IPr,[46] SIPr,[47] IMes,[48] and SIMes[47] were prepared from their corresponding imidazolium[46, 49] or imidazolinium[47] hydrochloride salts according to previously reported literature procedures.[48] $RhCl_3·3H_2O$ was generously donated by Johnson-Matthey. All other reagents were purchased from commercial suppliers and used without further purification. ^1H NMR spectra were recorded on a Bruker Avance 400 or 500 MHz spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using residual protonated solvent as an internal standard (CD_3CN, 1.94 ppm, C_6D_6, 7.15 ppm; $CDCl_3$, 7.26 ppm). ^{13}C NMR spectra were recorded at 100 or 125 MHz. Chemical shifts are reported as above using the solvent as an internal standard (CD_3CN, 118.26 ppm, C_6D_6, 128.0 ppm; $CDCl_3$, 77.16). Assignments of the ^1H and $^{13}C\{^1H\}$ NMR spectra were made using ^1H-^1H gs-COSY, ^1H-^{13}C-HSQC and ^1H-^{13}C-

HMBC NMR experiments. X-ray data collection was performed on a Bruker SMART APEX II X-ray diffractometer.



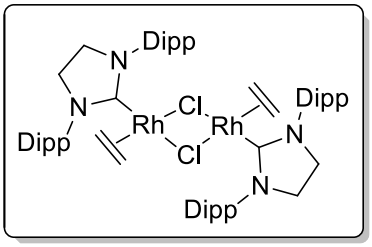
Synthesis of [Rh(SIMes)$_2$(O$_2$)Cl] (2-25): In a nitrogen-filled glove box, a solution of SIMes (79.0 mg, 0.258 mmol) in 20 mL of THF was added dropwise to a stirring solution of [Rh(C_2H_4)Cl_2]$_2$ (25.0 mg, 0.064 mmol) in 10 mL of THF in a round bottomed flask. The reaction mixture was stirred for 12 hours at room temperature. The solution was then removed from the glovebox and allowed to stir under ambient air for an additional 48 hours. After 4 hours, the solution turned noticeably green. The volatiles were then removed *in vacuo*, and the resulting green residue was purified by column chromatography with neutral alumina, eluting with benzene, to obtain pure complex **2-25** as a blue powder (70.4 mg, 0.088 mmol) in 69 % yield. X-ray quality crystals of complex **2-25** were obtained by the slow diffusion of hexanes into a concentrated THF solution. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 6.87 (s, Ar*H*, 4H), 6.79 (s, Ar*H*, 4H), 3.85 (m, br, 8H, NCH_2), 2.44 (s, 12H, CH_3), 1.92 (m, 12H, CH_3), 1.83 (m, 12H, CH_3). **^{13}C{^{1}H} NMR** (125.6 MHz, $CDCl_3$): δ = 207.6 (d, $^1J_{Rh\text{-}C}$ = 35.0 Hz, *C*-carbene), 138.1, 136.8, 136.7, 136.4, 128.8, 128.7, 51.3 (N-*C*H_2), 21.3, 19.0, 18.0. **HRMS** (ESI-TOF, m/z) calculated for $C_{42}H_{52}ClN_4Rh$ (M-O_2): 751.2476, found: (M-O_2) 751.3355.



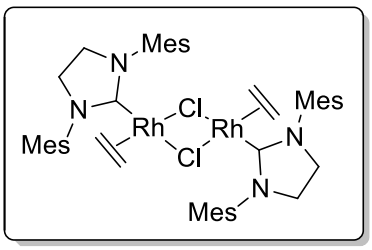
Synthesis of [Rh(SIPr)$_2$(O$_2$)Cl] (2-26): Procedure A (from [Rh(C$_2$H$_4$)$_2$Cl]$_2$: In a nitrogen filled glove box, a solution of SIPr (100.7 mg, 0.258 mmol) in 20 mL of THF and added dropwise to a stirring solution of [Rh(C$_2$H$_4$)Cl$_2$]$_2$ (25.0 mg, 0.06 mmol) in 10 mL of THF. The reaction mixture was stirred for 12 hours at room temperature. The solution was then removed from the glovebox and allowed to stir under ambient air for an additional 48 hours. After 4 hours the solution turned noticeably green. The volatiles were then removed *in vacuo*, and the resulting green residue was purified by column chromatography with neutral alumina, eluting with benzene, to obtain pure complex **2-26** as a blue powder with 51 % (62.1 mg, 0.07 mmol) yield.

Procedure B (from **2-60**): A 50 mL round bottom flask was charged with complex **2-60** (35.0 mg, 0.04 mmol), and 10 mL of THF. The flask was firmly closed with a rubber septum, and exposed to an atmosphere of O_2 in a balloon. An immediate colour change from yellow to green-blue was observed. All volatiles were removed *in vacuo* and the residue was purified by column chromatography using neutral alumina as a stationary phase eluting with benzene resulting in a blue powder (25 mg, 0.02 mmol) in 65 % yield. X-ray quality crystals of complex **2-26** were obtained by the slow diffusion of hexanes into a concentrated THF solution. **^{1}H NMR** (400 MHz, 1,1,2,2-tetrachloroethane d_2, 253K): δ = 7.25 (t, 4H, $J_{H\text{-}H}$ = 7.7 Hz, Ar*H*), 7.05 (d, 4H, $J_{H\text{-}H}$ = 7.5 Hz, Ar*H*), 6.99 (d, 4H, $J_{H\text{-}H}$ = 7.5 Hz, Ar*H*), 3.78-3.69 (m, 8H, N-CH_2), 3.24 (br, 4H, C*H*), 1.12 (d, 12H, $J_{H\text{-}H}$ = 6.4 Hz, CH_3) 1.02 (d, 12H, $J_{H\text{-}H}$ = 6.4 Hz, CH_3), 0.93-0.88 (m, 24H, CH_3). **^{13}C{^{1}H} NMR** (125.6 MHz, 1,1,2,2-dichloroethane d_2) : δ = 207.3 (d, $^1J_{Rh\text{-}C}$ = 36.5.0 Hz, *C*-carbene), 148.4, 137.9, 128.5, 124.1, 54.5 (N-CH_2), 28.5, 26.8. **HRMS** (ESI-TOF, m/z): Calculated for

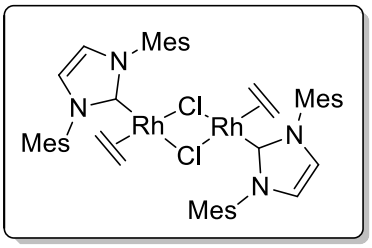
$C_{54}H_{76}ClN_4Rh$ (M-O_2): 918.4813, found: 918.4973. **(EA)** Anal. Calcd for $RhC_{54}H_{76}N_4O_2Cl \cdot 0.95H_2O$: Calc for C 69.38, H 8.71, N 5.42; found C 68.78, H 8.83, N 4.98.



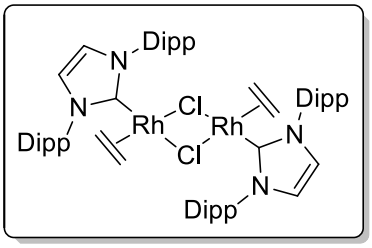
Synthesis of [Rh(SIPr)(C_2H_4)Cl]$_2$ (2-34): In a nitrogen-filled glovebox, a solution of free SIPr (100.8 mg, 0.254 mmol) in 20 mL of benzene was added dropwise to a stirring solution of [Rh(C_2H_4)$_2$Cl]$_2$ (50.0 mg, 0.13 mmol) in a round bottomed flask in 10 mL of benzene at room temperature. The solution was stirred for 12 hours at room temperature. The reaction mixture was filtered through a plug of Celite^{TM} and all volatiles were removed *in vacuo*, affording complex **2-34** as a yellow powder (124.4 mg, 0.11 mmol) in 87 % yield. X-ray quality crystals were obtained by slow the diffusion of hexane into a concentrated THF solution of the product at -20°C. **^{1}H NMR** (500 MHz, CD_2Cl_2, 203K): δ = 7.43 (t, 4H, J_{H-H} = 7.6 Hz, Ar*H*), 7.37-7.1 (d, 4H, J_{H-H} = 7.2Hz, Ar*H*), 3.73 (d, 4H, NCH_2), 3.47-2.97 (m, br, 4H, η^2-CH_2=CH_2), 2.58-2.27 (m, br, 4H, η^2-CH_2=CH_2), 2.05 (d, 4H, NCH_2), 1.49 (m, 8H, C*H*), 1.12 (m, 48H, CH_3). **^{13}C{^{1}H} NMR** (125.6 MHz, CD_2Cl_2): δ = 205.89 (d, $^1J_{Rh-C}$= 58.0 Hz, *C*-carbene), 147.7, 138.1, 129.1, 126.7, 124.9, 111.3, 60.1 (br, N*C*H$_2$), 46.7 (d, η^2- *C*H$_2$=*C*H$_2$, $^1J_{Rh-C}$= 16.7 Hz), 29.1, 26.5, 24.5. **LRMS** (ESI-TOF, m/z): calculated for $C_{58}H_{84}N_4Rh_2Cl_2Na$ (M+Na$^+$): 1137.39, found: (M+Na$^+$) =1137.24. **(EA)** Anal. Calcd for $C_{58}H_{84}N_4Cl_2Rh$: C 62.53, H 7.60, N 5.03; found C 62.53, H 7.65, N 4.78.



Synthesis of [Rh(SIMes)(C_2H_4)Cl]$_2$ (2-35): In a nitrogen-filled glovebox, free SIMes carbene (63.0 mg, 0.206 mmol) was dissolved in 15 mL of benzene and added dropwise to a stirred solution of [Rh(C_2H_4)$_2$Cl]$_2$ (40.0 mg, 0.10 mmol) in a round bottomed flask in 8 mL of benzene and 8 mL of THF at room temperature, and the solution was stirred for 16 hours. After this time, the reaction mixture was filtered through a plug of Celite^{TM}, and all volatiles were removed *in vacuo*, affording spectroscopically pure complex **2-35** as a yellow powder in (76.0 mg, 0.08 mmol) 78 % overall yield. X-ray quality crystals were obtained by the slow diffusion of hexanes into a concentrated THF solution of the product at −20 °C. Two isomers were observed in solution. **2-35a**: **^{1}H NMR** (CD_2Cl_2, 600 MHz, 273K): δ = 7.07 (s, 4H, $J_{H\text{-}H}$ = 7.5 Hz, Ar*H*), 6.92 (br, 4H, Ar*H*), 3.75 (d, 4H, NCH_2), 3.68 (d, 4H, NCH_2), 2.56 (br, 4H, η^2-CH_2=CH_2), 2.43 (br, 4H, η^2-CH_2=CH_2), 2.43 (12H, CH_3), 2.38 (12H, CH_3), 2.20 (12H, CH_3). **^{13}C{^{1}H} NMR** (CD_2Cl_2, 150.9 MHz): δ = 207.02 (d, $^1J_{Rh\text{-}C}$ = 58.5 Hz, *C*-carbene), 137.84, 137.55, 137.96, 129.64, 129.40, 129.13, 51.62 (N-*C*H$_2$), 45.93 (d, η^2-*C*H$_2$=*C*H$_2$, $^1J_{Rh\text{-}C}$ = 16.1 Hz), 20.94, 19.63, 18.64. **2-35b**: **^{1}H NMR** (CD_2Cl_2, 600 MHz, 273K): δ = 6.95 (s, 4H, Ar*H*), 6.77 (br, 4H, Ar*H*), 3.59 (d, 4H, NCH_2), 3.51 (d, 4H, NCH_2), 2.34 (12H, CH_3), 2.32 (12H, CH_3), 2.22 (br, 4H, η^2-CH_2=CH_2), 2.07 (br, 4H, η^2-CH_2=CH_2), 2.17 (12H, CH_3). **^{13}C{^{1}H} NMR** (CD_2Cl_2, 150.9 MHz): δ 204.0 (d, $^1J_{Rh\text{-}C}$ = 55.9 Hz, *C*-carbene), 138.6, 138.0, 135.9, 129.6, 129.3, 128.7, 51.5 (N-*C*H$_2$), 45.1 (d, η^2-*C*H$_2$=*C*H$_2$, $^1J_{Rh\text{-}C}$ = 16.8 Hz), 20.9, 19.4, 18.4. **(EA)** Anal. Calcd for $C_{46}H_{60}N_4Cl_2Rh_2$: C 58.42, H 6.39, N 5.92. Found: C 58.41, H 6.24, N 6.14.

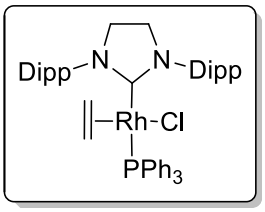


Synthesis of [Rh(IMes)(C_2H_4)Cl]$_2$ (2-36): In a nitrogen-filled glovebox, a solution of free IMes (100.8 mg, 0.207 mmol) in 10 mL of benzene was added dropwise to a stirring solution of [Rh(C_2H_4)$_2$Cl]$_2$ (40.0 mg, 0.10 mmol) in a round bottom flask in 10 mL of benzene at room temperature, and the solution was stirred for 4 hours. After this time, the solution was then filtered through Celite^{TM}, and all volatiles were removed *in vacuo*, affording complex **2-36** as a light yellow powder (85.0 mg, 0.09 mmol) in 89 % overall yield. **^{1}H NMR** (CD_2Cl_2, 600 MHz, 273 K): δ = 7.00 (br, 8H, Ar*H*), 6.69 (br, 4H, C*H*=C*H*), 2.40 (m, 24H, CH_3), 2.25 (d, 4H, η^2-CH_2=CH_2), 2.14 (d, 4H, η^2-CH_2=CH_2), 2.20 (m, 12H, CH_3). **^{13}C{^{1}H} NMR** (CD_2Cl_2, 150.9 MHz): δ = 176.0 (d, $^1J_{Rh\text{-}C}$ = 61.8 Hz, *C*-carbene), 138.0, 136.9, 128.5, 123.3 (*C*H=*C*H), 43.3 (d, η^2-*C*H$_2$=*C*H$_2$, $^1J_{Rh\text{-}C}$ = 16.5 Hz), 21.0, 19.5, 18.6. **(EA)** Anal. Calcd for $C_{46}H_{56}N_4Rh_2Cl_2$·0.9 H_2O: C 57.68, H 6.08, N 5.85. Found: C 58.06, H 6.39, N 5.46.



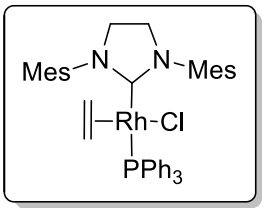
Synthesis of [Rh(IPr)(C_2H_4)Cl]$_2$ (2-37): In a nitrogen-filled glovebox, a solution of IPr (100.0 mg, 0.257 mmol) was dissolved in 20 mL of benzene and added dropwise to a stirred solution of [Rh(C_2H_4)$_2$Cl]$_2$ (50.0 mg, 0.13 mmol) in a round bottom flask in 15 mL of benzene at room temperature, and the solution was stirred for 12 hours. After this time, the solution was filtered through a plug of Celite^{TM}, and all volatiles were removed *in vacuo*, affording complex **2-37** as a dark yellow powder (131.2 mg, 0.12 mmol) in 92 % yield. X-ray quality dark orange crystals were obtained by the slow diffusion of hexanes into a concentrated solution of the product in a mixture of

THF−CH_2Cl_2 (10:1) at room temperature. **^{1}H NMR** (CD_2Cl_2, 400 MHz, 293 K): δ = 7.49 (t, 4H, J_{H-H} = 7.6 Hz, Ar*H*), 7.33 (br, 8H, Ar*H*), 6.80 (s, 4H, C*H*=C*H*), 2.92 (septet, 8H, J_{H-H} = 7.6 Hz, C*H*), 2.23 (br, 4H, η^2-CH_2=CH_2), 1.96 (br, 4H, η^2-CH_2=CH_2), 1.38 (d, 24H, J_{H-H} = 6.6 Hz, CH_3), 1.02 (d, 24H, J_{H-H} = 5.9 Hz, CH_3). **^{13}C{^{1}H} NMR** (CD_2Cl_2, 125.6 MHz): δ = 179.0 (d, $^1J_{Rh-C}$ = 62.5 Hz, *C*-carbene), 147.0, 137.6, 129.8, 128.7, 124.9, 124.2, 43.7 (d, η^2-*C*H$_2$=*C*H$_2$, $^1J_{Rh-C}$ = 16.6 Hz), 29.2, 26.4, 23.4. **HRMS** (ESI-TOF, m/z): calculated for $C_{58}H_{80}N_4Rh_2Cl_2$ 1108.3870, found 1108.3822. **(EA)** Anal. Calcd for $C_{58}H_{80}N_4Rh_2Cl_2 \cdot 1.85\ H_2O$: C 60.93, H 7.38, N 4.90. Found: C 61.14, H 7.17, N 4.68.

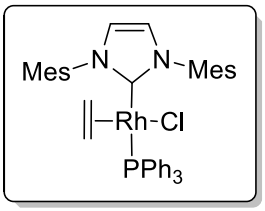


Synthesis of [Rh(PPh$_3$)(SIPr)(C$_2$H$_4$)Cl] (2-41): A solution of PPh_3 (21 mg, 0.08 mmol) in 5 mL of C_6H_6 was added dropwise to 5 mL C_6H_6 solution of complex **2-34** (44.0 mg, 0.04 mmol) in a 4 dram vial. The resulting orange solution was stirred for 24 hours at room temperature, and the volatiles were removed *in vacuo*. The yellow residue was then triturated with cold hexanes and collected by filtration in 81 % overall yield (61.8 mg, 0.06 mmol). **^{1}H NMR** (CD_2Cl_2, 600 MHz): δ = 7.47 (t, 2H, J_{H-H} = 7.7 Hz, Ar*H*), 7.36 (br, 4H, Ar*H*), 7.28 (br, 9H, Ar*H*), 7.25 (t, 6H, J_{H-H} = 6.8 Hz, Ar*H*), 3.96 (br, 2H, NCH_2), 3.89 (br, 2H, NCH_2), 3.82 (septet, 2H, J_{H-H} = 6.6 Hz, C*H*), 3.48 (septet, 2H, J_{H-H} = 6.7 Hz, C*H*), 1.68 (br, 4H, η^2-CH_2=CH_2), 1.52 (d, 6H, J_{H-H} = 6.08 Hz, CH_3), 1.38 (d, 6H, J_{H-H} = 6.6 Hz, CH_3), 1.28 (d, 6H, J_{H-H} = 6.5 Hz, CH_3), 1.22 (d, 6H, J_{H-H} = 6.80 Hz, CH_3). **^{13}C{^{1}H} NMR** (100.6 MHz, C_6D_6): δ = 215.7 (dd, $^1J_{Rh-C}$ = 44.6 Hz, $^2J_{P-C}$ = 132.9 Hz, *C*-carbene), 149.4, 147.0, 135.7 (d, $^2J_{P-C}$ = 10.7 Hz), 134.1, 133.7, 129.1, 127.6 (d, $^3J_{PC}$ = 8.8), 125.3, 123.9, 54.4, 54.3, 41.4 (d, η^2-*C*H$_2$=*C*H$_2$, $^1J_{Rh-C}$ = 15.4 Hz), 30.6, 29.4, 27.1, 26.9, 24.9, 23.9. **^{31}P{^{1}H} NMR**

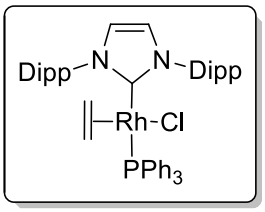
(C_6D_6, 161.9 MHz, 293 K): δ = 37.8 (d, $^1J_{Rh\text{-}P}$ = 111.6 Hz). **HRMS** (ESI-TOF, m/z) calculated for $C_{47}H_{57}N_2PRhCl$: 818.3003, found 818.2978. **(EA)** Anal. Calcd for $C_{47}H_{57}N_2RhCl{\cdot}1.1H_2O$: C 67.27, H 7.11, N 3.34. Found: C 67.04, H 7.03, N 3.64.



Synthesis of [Rh(PPh$_3$)(SIMes)(C$_2$H$_4$)Cl] (2-42): In a nitrogen-filled glovebox, a solution of PPh_3 (21 mg, 0.080 mmol) in 5 mL of C_6H_6 was added dropwise 20 mL vial was charged with complex **2-35** (38.0 mg, 0.04 mmol) dissolved in C_6H_6 (5 mL). The resulting yellow-orange solution was stirred for 24 hours at room temperature, and the volatiles were removed *in vacuo*. The yellow residue was then triturated with cold hexanes and collected by filtration (48.0 mg, 0.06 mmol) in 82 % yield. **^{1}H NMR** (400 MHz, C_6D_6): δ = 7.72 (t, 5H, $J_{H\text{-}H}$ = 8.0 Hz, Ar*H*), 7.25 (br, 2H, Ar*H*), 7.10-7.07 (m, 9H, Ar*H*), 6.96 (br, 3H, Ar*H*), 3.74-3.68 (m, 2H, C*H*$_2$=C*H*$_2$), 3.35 (m, 4H, NC*H*$_2$), 3.16-3.10 (m, 2H, C*H*$_2$=C*H*$_2$), 2.96 (s, 3H, C*H*$_3$), 2.55 (s, 3H, C*H*$_3$), 2.44 (s, 3H, C*H*$_3$), 2.30 (s, 3H, C*H*$_3$), 2.17 (s, 3H, C*H*$_3$), 2.04 (s, 3H, C*H*$_3$). **^{13}C{^{1}H} NMR** (125.6 MHz, C_6D_6): δ = 214.9 (dd, $^1J_{Rh\text{-}C}$ = 45.2 Hz, $^2J_{P\text{-}C}$ = 133.9 Hz, *C*-carbene), 163.9, 139.2, 137.5, 135.1, 135.9 (d, $^2J_{P\text{-}C}$ = 10.9 Hz), 134.5, 134.2, 130.5, 130.2, 129.1, 129.1 (d, $^2J_{P\text{-}C}$ = 8.9 Hz), 51.7 (s, N-*C*H$_2$), 51.4 (s, N-*C*H$_2$), 41.5 (d, η^2-*C*H$_2$=*C*H$_2$, $^1J_{Rh\text{-}C}$ = 15.32 Hz), 21.3 (s, *C*H$_3$), 20.8 (s, *C*H$_3$), 19.0 (s, *C*H$_3$)**. ^{31}P{^{1}H} NMR** (C_6D_6, 161.95 MHz, 293 K): δ = 39.1 (d, $^1J_{Rh\text{-}P}$ = 111.5 Hz). **(EA)** Anal. Calcd for $C_{41}H_{45}N_2PRhCl$: C 66.99, H 6.17, N 3.81. Found: C 66.38, H 6.29, N 3.94.

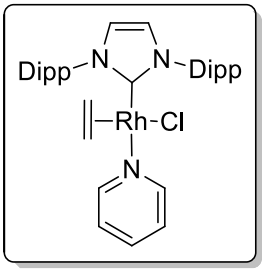


Synthesis of [Rh(PPh$_3$)(IMes)(C$_2$H$_4$)Cl] (2-43): In a nitrogen-filled glovebox, a solution of PPh_3 (21 mg, 0.080 mmol) in 5 mL of C_6H_6 was added dropwise to a 20 mL vial charged with complex **2-36** (37.7 mg, 0.04 mmol) dissolved in C_6H_6 (5 mL). The resulting orange solution was stirred for 24 hours, and the volatiles were removed *in vacuo*. The residue was then triturated with cold hexanes and collected by filtration as a yellow powder (50.1 mg, 0.07 mmol) in 85 % yield. **^{1}H NMR** (400 MHz, C_6D_6): δ = 7.78 (t, 6H, $J_{H\text{-}H}$ = 8.0 Hz, Ar*H*), 7.12-7.10 (m, 9H, $J_{H\text{-}H}$ = 7.5 Hz, Ar*H*), 7.03 (d, 2H, Ar*H*), 6.96 (br, 2H, Ar*H*), 6.30 (s, 2H, C*H*=C*H*), 2.81 (br, 6H, CH_3), 2.50 (br, 4H, CH_2=CH_2), 2.31 (br, 12H, CH_3). **^{13}C{^{1}H} NMR** (100.6 MHz, C_6D_6): δ = 187.57 (d, $^1J_{Rh\text{-}C}$ = 47.5 Hz, $^2J_{P\text{-}C}$ = 141.9 Hz, *C*-carbene), 138.6, 138.4, 135.9 (d, $^2J_{P\text{-}C}$ = 11.0 Hz), 135.2, 134.6, 134.3, 130.2, 129.3, 128.7, 127.7 (d, $^2J_{P\text{-}C}$ = 9.0 Hz), 41.4 (d, η^2-*C*H$_2$=*C*H$_2$, $^1J_{Rh\text{-}C}$ = 15.3 Hz), 21.3 (s, *C*H$_3$), 20.6 (s, *C*H$_3$), 18.9 (s, *C*H$_3$). **^{31}P{^{1}H} NMR** (C_6D_6, 161.95 MHz, 293 K): δ = 40.5 (d, $^1J_{Rh\text{-}P}$ = 116.3 Hz). **HRMS** (ESI-TOF, m/z): calculated for $C_{41}H_{43}N_2PRhCl$: 732.1907, found 732.2189. **(EA)** Anal. Calcd for $C_{41}H_{43}N_2PRhCl$: C 67.17, H 5.91, N 3.82. Found: C 67.34, H 6.01, N 3.67.



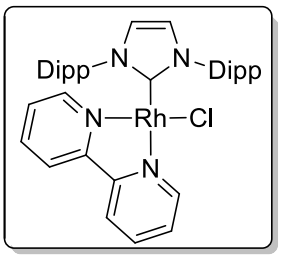
Synthesis of [Rh(PPh$_3$)(IPr)(C$_2$H$_4$)Cl] (2-44): In a nitrogen-filled glovebox, a solution of PPh_3 (21 mg, 0.080 mmol) in 5 mL of C_6H_6 was then added dropwise to a solution of complex **2-37** (44.0 mg, 0.04 mmol) in 5 mL of C_6H_6 in a 20 mL vial. The resulting orange solution was stirred for 24 hours, and the volatiles were removed *in vacuo*. The yellow residue was then triturated with cold hexanes and collected by filtration (57.1 mg, 0.07 mmol) in 87 % yield. **^{1}H NMR** (600 MHz, CH_2Cl_2): δ = 7.57 (t, 6H, $J_{H\text{-}H}$ = 7.7 Hz, Ar*H*), 7.37 (br d, 3H), 7.16

(m, 4H, Ar*H*), 7.01 (br, 8H), 6.61 (m, 2H, Ar*H*), 3.54 (septet, 2H, $J_{H\text{-}H}$ = 5.7 Hz, C*H*), 3.10 (septet, 2H, $J_{H\text{-}H}$ = 5.6 Hz, C*H*), 1.99 (br, 4H, CH_2=CH_2), 1.47 (d, 6H, $J_{H\text{-}H}$ = 5.2 Hz, CH_3), 1.33 (d, 6H, $J_{H\text{-}H}$ = 5.3 Hz, CH_3), 1.17 (d, 6H, $J_{H\text{-}H}$ = 5.5 Hz, CH_3), 1.07 (d, 6H, $J_{H\text{-}H}$ = 5.6 Hz, CH_3). **^{31}P{^{1}H} NMR** (C_6D_6, 161.95 MHz, 293 K): δ = 40.12 (d, $^1J_{Rh\text{-}P}$ = 116.9 Hz). **^{13}C{^{1}H} NMR** (100.6 MHz, C_6D_6): δ = 188.9 (dd, $^1J_{Rh\text{-}C}$ = 47.5 Hz, $^2J_{P\text{-}C}$ = 141.4 Hz, *C*-carbene), 148.6, 146.1, 137.5, 135.9 (d, $^2J_{P\text{-}C}$ = 10.8 Hz), 134.3, 133.9, 129.9, 129.2, 127.7 (d, $^3J_{PC}$ = 9.0 Hz), 124.8, 124.3, 123.5, 41.3 (d, η^2-CH_2=CH_2, $^1J_{Rh\text{-}C}$ = 15.3 Hz), 29.3, 29.0, 26.5, 26.4, 23.7, 23.1. **HRMS** (ESI-TOF, m/z): calculated for $C_{47}H_{55}N_2PRhCl$: 816.2847, found 816.3390. **(EA)** Anal. Calcd for $C_{47}H_{55}N_2PRhCl$: C 69.07, H 6.78, N 3.43. Found: C 69.18, H 7.01, N 3.13.



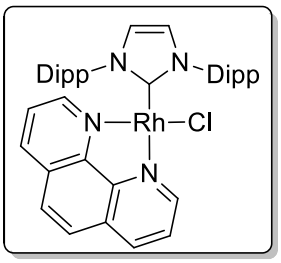
Synthesis of [Rh(IPr)(Pyr)(C_2H_4)Cl] (2-45): In a nitrogen-filled glovebox, a solution of pyridine (4.25 mg, 0.05 mmol) in 0.4 mL C_6H_6 was added dropwise to a solution of complex **2-37** (30.0 mg, 0.027 mmol) in 1.0 mL of C_6H_6 in a 20 mL vial. The resulting yellow solution was stirred for 6 days at room temperature. All the volatiles were removed *in vacuo* resulting in **2-45** as a yellow powder (39.9 mg, 0.53 mmol) in 99 % overall yield. **^{1}H NMR** (500 MHz, 223 K, CH_2Cl_2): δ 8.33 (d, 2H, $J_{H\text{-}H}$ = 4.8, Pyr*H*), 7.51 (t, 1H, $J_{H\text{-}H}$ = 7.5 Hz, Ar*H*), 7.48 (t, 2H, $J_{H\text{-}H}$ = 7.7 Hz, Ar*H*), 7.34 (m, 4H, $J_{H\text{-}H}$ = 8.8 Hz, Ar*H*), 7.07 (t, 2H, $J_{H\text{-}H}$ = 6.5 Hz, Ar*H*), 6.96 (br, 2H, C*H*=C*H*), 3.38 (septet, 2H, $J_{H\text{-}H}$ = 6.5 Hz, C*H*), 2.91 (septet, 2H, $J_{H\text{-}H}$ = 6.6 Hz, C*H*), 2.05 (d, 2H, $J_{H\text{-}H}$ = 11.8 Hz, η^2-CH_2=CH_2), 1.72 (d, 2H, $J_{H\text{-}H}$ = 11.7 Hz, η^2-CH_2=CH_2), 1.49 (d, 6H, $J_{H\text{-}H}$ = 6.4 Hz, CH_3), 1.44 (d, 6H, $J_{H\text{-}H}$ = 6.5 Hz, CH_3), 1.13 (d, 6H, $J_{H\text{-}H}$ = 6.5 Hz, CH_3), 1.05 (d, 6H, $J_{H\text{-}H}$ = 6.68 Hz, CH_3). **^{13}C{^{1}H} NMR**

(100.6 MHz, C_6D_6, 298 K): δ 183.7 (d, $^1J_{Rh\text{-}C}$ = 53.8 Hz, C-carbene), 151.7, 148.1, 145.5, 137.6, 134.6, 129.6, 124.1, (CH=CH), 123.1, 41.63 (d, η^2-CH_2=CH_2, $^1J_{RhC}$ = 16.7 Hz), 28.9 (s, CH), 26.2, 26.0, 24.0, 23.5. **HRMS** (ESI-TOF, m/z) Calculated for: $C_{34}H_{45}N_3Rh$ (M − Cl): 598.26, found: 597.86.



Synthesis of [Rh(IPr)(Bpy)Cl] (2-47): In a nitrogen-filled glovebox, a solution of 2,2′-bipyridine (bipy) (7.08 mg, 0.045 mmol) in 2 mL of THF was added dropwise to a stirring solution of **2-37** (25.0 mg, 0.02 mmol) in 3 mL of THF in a round bottomed flask. The reaction mixture immediately turned a deep dark green-blue colour. The resulting solution was stirred for 16 hours at room temperature. After this time, all volatiles were removed *in vacuo*. The residue was triturated with 3 mL cold (−20 °C) hexanes and an intensely coloured blue powder was collected by filtration in (28.9 mg, 0.04 mmol) 98 % yield. X-ray quality crystals were obtained by the slow evaporation from a concentrated benzene solution. **^{1}H NMR** (500 MHz, C_6D_6): δ = 10.61 (br, 1H, Pyr*H*), 9.05 (br, 1H, Pyr*H*), 7.56 (t, 1H, $J_{H\text{-}H}$ = 7.2 Hz, Ar*H*), 7.32 (d, 2H, $J_{H\text{-}H}$ = 6.2 Hz, Ar*H*), 7.27 (br, 2H, Ar*H*), 7.55–7.54 (two triplets, 2H, $J_{H\text{-}H}$ = 7.3 Hz, Ar*H*), 7.09 (br, 2H, Ar*H*), 6.92 (t, 1H, $J_{H\text{-}H}$ = 5.8 Hz, Ar*H*), 6.75 (d, 1H, $J_{H\text{-}H}$ = 6.7 Hz, Ar*H*), 6.64 (d, 2H, C*H*=C*H*), 6.61 (d, 1H, , $J_{H\text{-}H}$ = 5.5 Hz, Ar*H*), 3.90 (septet, 2H, $J_{H\text{-}H}$ = 5.7 Hz, C*H*), 3.82 (septet, 2H, $J_{H\text{-}H}$ = 5.6 Hz, C*H*), 1.90 (d, br, 6H), 1.52 (d, br, 6H), 1.33 (d, br, 6H) 1.15 (d, br, 6H). **^{13}C{^{1}H} NMR** (125.6 MHz, C_6D_6): δ = 195.42 (d, $^1J_{Rh\text{-}C}$ = 57.11 Hz, C-carbene), 157.6, 154.6, 151.2, 151.2, 150.2, 148.9, 144.8, 138.4, 133.4, 133.2, 129.5, 128.5, 126.2, 125.0, 124.6, 124.4,

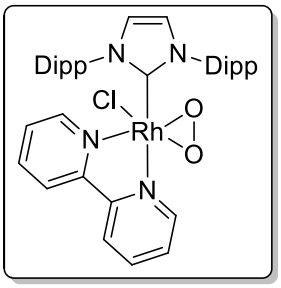
123.5, 122.9, 119.3, 29.5, 29.1, 26.6, 24.2, 23.0. **HRMS** (ESI-TOF, m/z) Calculated for [$C_{37}H_{44}ClN_4Rh$]: 682.2310, found: 682.2339.



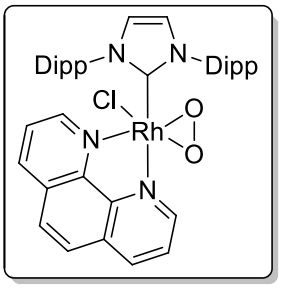
Synthesis of [Rh(IPr)(Phen)Cl] (2-49): In a nitrogen-filled glovebox, a solution of 1,10-phenanthroline (Phen) (8.1 mg, 0.045 mmol) in 3 mL of THF was added to a stirring solution of [$Rh(IPr)(C_2H_4)Cl]_2$ (25.0 mg, 0.02 mmol) in 3 mL of THF in a round bottomed flask. The reaction mixture immediately turned a deep dark violet colour. The resulting solution was stirred for 24 hours at room temperature. After this time, all volatiles were removed *in vacuo*. The residue was then triturated with 5 mL of cold (−20 °C) hexanes that resulted in an intensely coloured violet powder that was collected by filtration in (31.0 mg, 0.04 mmol) 97 % yield. X-ray quality crystals were obtained by slow solvent evaporation from a concentrated benzene solution of the product. **^{1}H NMR** (600 MHz, C_6D_6): δ =10.47 (d, 1H, $J_{H\text{-}H}$ = 4.9 Hz, Pyr*H*), 9.35 (d, 1H, $J_{H\text{-}H}$ = 4.9 Hz, Pyr*H*), 8.22 (d, 1H, $J_{H\text{-}H}$ = 7.8 Hz, Pyr*H*), 7.31 (d, 2H, $J_{H\text{-}H}$ = 7.3 Hz, Ar*H*), 7.21 (d, 1H, $J_{H\text{-}H}$ = 7.2 Hz, Ar*H*), 7.14 (t, 2H, $J_{H\text{-}H}$ = 7.7 Hz, Ar*H*), 7.12 (br, 2H, C*H*=C*H*), 7.03 (d, 2H, $J_{H\text{-}H}$ = 7.3 Hz, Ar*H*), 6.94 (d, 1H, $J_{H\text{-}H}$ = 8.6 Hz, Ar*H*), 6.84 (m, 1H, $J_{H\text{-}H}$ = 5.5 Hz, Ar*H*), 6.81 (d, 1H, $J_{H\text{-}H}$ = 8.5 Hz, Ar*H*), 6.68 (m, 1H, $J_{H\text{-}H}$ = 7.6 Hz, Ar*H*), 4.01 (septet, 2H, $J_{H\text{-}H}$ = 6.6 Hz, C*H*), 3.81 (septet, 2H, $J_{H\text{-}H}$ = 6.7 Hz, C*H*), 1.93 (d, 6H, $J_{H\text{-}H}$ = 6.5 Hz, CH_3), 1.30 (d, 6H, $J_{H\text{-}H}$ = 6.8 Hz, CH_3), 1.27 (d, 6H, $J_{H\text{-}H}$ = 6.8 Hz, CH_3), 1.02 (d, 6H, $J_{H\text{-}H}$ = 6.7 Hz, CH_3). **^{13}C{^{1}H} NMR** (125.6 MHz, C_6D_6): δ = 195.4 (d, $^1J_{Rh\text{-}C}$ = 57.3 Hz, C-carbene), 168.8, 150.8, 148.9, 147.6, 146.7, 144.9, 138.4, 131.4, 129.4, 126.7, 125.3, 124.9, 124.6, 123.4,

30.3, 29.5, 28.9, 26.8, 26.6, 24.1, 22.6. **HRMS** (ESI-TOF, m/z): Calculated for $C_{39}H_{44}ClN_4Rh$: 706.2310, found: 706.2289.

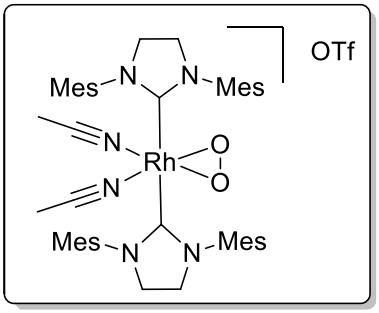
Synthesis of [Rh(IPr)(O_2)(bipy)Cl] (2-55)



A 10 mL round bottomed flask was charged with complex **2-47** (20 mg, 0.029 mmol) and 5 mL of C_6H_6 under an atmosphere of N_2 and firmly sealed with a septa. The solution was then exposed to a steady stream of O_2 for 30 seconds. An immediate colour change from dark green to bright yellow was observed. The solution was stirred at room temperature for 10 minutes. The reaction mixture was then filtered through Celite^{TM} and all volatiles removed *in vacuo*. **^{1}H NMR** (600 MHz, C_6D_6): δ = 8.95 (d, 1H, $J_{H\text{-}H}$ = 5.1 Hz, Pyr*H*), 8.82 (d, 1H, $J_{H\text{-}H}$ = 8.0 Hz, Pyr*H*), 8.70 (d, 1H, $J_{H\text{-}H}$ = 4.8 Hz, Ar*H*), 8.61 (d, 2H, $J_{H\text{-}H}$ = 6.5 Hz, Ar*H*), 7.46 (d, 1H, $J_{H\text{-}H}$ = 9.2 Hz, Ar*H*), 7.37 (br, 2H, Ar*H*), 7.29 (dd, 1H, $J_{H\text{-}H}$ = 7.6 Hz, 1.6 Hz, Pyr*H*), 7.19 (d, 1H, $J_{H\text{-}H}$ = 6.7 Hz, Ar*H*), 7.14 (d, 1H, $J_{H\text{-}H}$ = 7.6 Hz, Ar*H*), 7.08 (d, 1H, $J_{H\text{-}H}$ = 7.8 Hz, Ar*H*), 7.01 (d, 1H, $J_{H\text{-}H}$ = 7.8 Hz, Ar*H*), 6.76 (t, 1H, $J_{H\text{-}H}$ = 4.8 Hz, Ar*H*), 6.76 (m, 2H, $J_{H\text{-}H}$ = 4.8 Hz, Ar*H*), 6.68 (br, 2H, CH=CH), 6.65 (d, 1H, $J_{H\text{-}H}$ = 6.7 Hz, Ar*H*), 6.45 (d, 1H, $J_{H\text{-}H}$ = 6.1 Hz, Ar*H*), 3.73 (br, 2H, C*H*), 3.08 (septet, 2H, $J_{H\text{-}H}$ = 7.1 Hz, C*H*), 1.65 (m, 6H), 1.30 (d, 6H, $J_{H\text{-}H}$ = 6.6 Hz), 1.24 (d, 6H, $J_{H\text{-}H}$ = 6.9 Hz), 1.09 (d, $J_{H\text{-}H}$ = 6.8 Hz, 6H). **^{13}C{^{1}H} NMR** (125.6 MHz, C_6D_6): δ = 168.7 (br, C-carbene), 153.5, 148.3, 138.4, 136.0, 128.2, 128.1, 127.7, 126.0, 124.5, 124.0, 121.0, 123.2, 29.2, 28.6, 25.9, 24.1, 23.0.

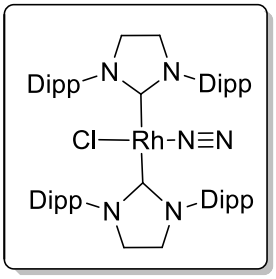


Synthesis of [Rh(IPr)(O$_2$)(Phen)Cl] (2-56): A 25 mL round bottomed flask was charged with complex **2-48** (18 mg, 0.025 mmol) and 5 mL of C_6H_6 under an atmosphere of N_2 and firmly sealed with a septa. The solution was then exposed to a steady stream of O_2 or air for 30 seconds. An immediate change in colour from dark violet to bright yellow-orange was observed. The reaction mixture was then filtered with 0.45 μm PTFE (Teflon) syringe filter, and all volatiles removed *in vacuo*. We were unable to purify compound **2-56** as it is highly unstable, and decomposes to **2-18** along with molecular rhodium upon standing. **^{1}H NMR** (600 MHz, C_6D_6): δ = 9.06 (d, 1H, $J_{H\text{-}H}$ = 3.2 Hz, Pyr*H*), 8.90 (d, 1H, $J_{H\text{-}H}$ = 4.2 Hz, Pyr*H*), 8.03 (br, 1H, Pyr*H*), 7.40 (br, 1H, Ar*H*), 7.31 (br, 2H, Ar*H*), 7.27 (d, 4H, $J_{H\text{-}H}$ = 7.1 Hz, Ar*H*), 7.17 (t, 1H, $J_{H\text{-}H}$ = 7.1 Hz, Ar*H*), 7.10 (br, 1H, Ar*H*), 6.90 (d, 1H, $J_{H\text{-}H}$ = 7.1 Hz, Ar*H*), 6.77 (br, 2H, C*H*=C*H*), 6.67 (br, 1H, Ar*H*), 3.78 (septet, 2H, C*H*), 3.81 (septet, 2H, C*H*), 1.68 (d, 6H, CH_3), 1.34 (d, 6H, $J_{H\text{-}H}$ = 5.7 Hz, CH_3), 1.28 (br, 6H, CH_3), 1.08 (d, 6H, CH_3).**^{13}C{^{1}H} NMR** (125.6 MHz, C_6D_6): δ = 167.8 (d, C-carbene), 153.9, 148.7, 146.6, 139.1, 135.8, 129.6, 127.3, 126.8, 126.6, 125.5, 124.3, 123.8, 30.4, 26.5, 26.2, 24.6, 23.7.



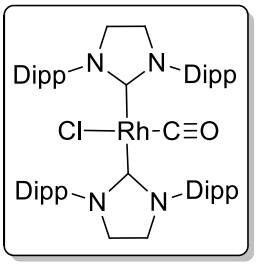
Synthesis of 2-59: In a nitrogen-filled glovebox, complex **2-58** (92 mg, 0.112 mmol) was added to a four dram vial and dissolved into MeCN (6 mL) and CF_3-Ph (7 mL). To this solution was added AgOTf (32 mg, 0.115 mmol) as a solid, and the resulting solution was stirred for 10 mins. The solution changed colour from blue to yellow, and a white precipitate began to form.

After this time, all volatiles were removed *in vacuo*. The product was extracted into CF_3-Ph (7 mL) and the mixture was passed through a small plug of Celite™. Evaporation of all volatiles resulted in the isolation of spectroscopically pure compound as a brown powder (52 mg, 0.53 mmol) in 47 % yield. Complex **2-59** is highly unstable in solution and rapidly decomposes to molecular rhodium. However, some X-ray quality brown plate-like crystals of complex **2-62** were obtained by slow diffusion of hexane into a concentrated acetonitrile solution of the product.**^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.70 (s, 4H Ar*H*), 7.65 (s, 4H Ar*H*), 3.2-2.2 (m, br, 8H, NCH_2), 1.98 (br s, 6H, CH_3CN), 1.44 (m. 24H, CH_3), 1.22 (m, 12H, CH_3).

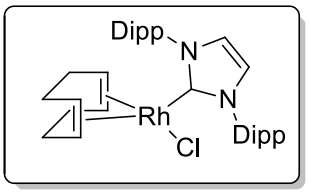


Synthesis of [Rh(SIPr)$_2$N$_2$Cl] (2-60): In a nitrogen-filled glovebox, a solution of SIPr (62.4 mg, 0.16 mmol) in 5 mL of THF was added to a solution of $[Rh(C_2H_4)_2Cl]_2$ (15.5 mg, 0.04 mmol) in THF (5 mL) in a round bottom flask. The resulting yellow solution was stirred for 24 hours at room temperature and all volatiles were removed *in vacuo*. The yellow residue was then triturated with cold hexanes and collected as a yellow solid by filtration (20.0 mg, 0.04 mmol) in 51 % yield. X-ray quality crystals were obtained by slow diffusion of hexane into a concentrated THF solution of the product. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ = 7.12 (t, 4H, $J_{H\text{-}H}$ = 7.2 Hz, Ar*H*), 6.98 (m, 8H, Ar*H*), 3.49 (br, 8H, NCH_2), 3.00 (m, 4H, C*H*), 1.31 (m, 4H, C*H*), 1.06-1.04 (m, 12H, CH_3), 0.94-0.93 (m, 36H, CH_3). **^{13}C{^{1}H} NMR** (125.6 MHz, CD_2Cl_2): δ =218.4 (d, $^1J_{Rh\text{-}C}$ = 37.8 Hz, *C*-carbene), 147.1, 144.6, 137.7, 126.4, 122.8, 121.8, 52.7 (N-*C*H$_2$), 38.9 (N-*C*H$_2$), 26.7, 26.8, 24.6, 24.3, 22.3, 21.7. **HRMS** (ESI-TOF, m/z) calculated for $C_{54}H_{76}ClN_6Rh$: 946.4875, found:

946.4889. **(EA)** Anal. Calcd for $C_{54}H_{76}N_4ClRh \cdot 1.15H_2O$: C 68.98, H 8.39, N 5.96; found C 69.07, H 8.52, N 5.82. **IR** (KBr): ν = 2107 (N-N, s) cm^{-1}.



Synthesis of [Rh(SIPr)$_2$(CO)Cl] (2-61): An oven-dried 50 mL round bottom flask was charged with complex **2-26** (25.0 mg, 0.03 mmol), and 10 mL of THF. The flask was firmly closed with a rubber septum, and purged with an atmosphere of CO from a balloon. An immediate colour change from blue to a dark yellow reaction mixture is observed, signaling formation of **2-61**. All volatiles were removed *in vacuo* and the residue was quickly washed with 2 mL of cold hexane (-20 °C) to obtain pure complex **2-61** as brownish-yellow powder (22.0 mg, 0.02 mmol) in 89 % yield. **^{1}H NMR** (500 MHz, C_6D_6): δ = 7.22 (t, 4H, $J_{H\text{-}H}$ = 7.1 Hz, Ar*H*), 7.05 (d, br, 8H, Ar*H*), 3.82-3.04 (m, br, 8H, NCH_2), 1.41 (m, 8H, C*H*), 1.22 (m, 24H, CH_3), 0.96 (m, 24H). **^{13}C{^{1}H} NMR** (125.6 MHz, C_6D_6): δ = 216.7 (d, $^1J_{Rh\text{-}C}$ = 39.9 Hz, *C*-carbene), 187.8 (d, $^1J_{Rh\text{-}C}$ = 80.0 Hz, *C*O), 163.7, 148.4 (br), 138.5, 128.9, 124.8, 124.1, 54.6 (N-*C*H_2), 28.6, 26.9, 24.7. **IR** (KBr): δ = 1945 (C-O, s) cm^{-1}. **HRMS** (ESI-TOF, m/z) Calculated for $C_{55}H_{76}ClN_4RhO$: 946.4763, found: 946.4792.



Synthesis of [Rh(IPr)(COD)Cl]: [Rh(COD)Cl]$_2$ (50.0 mg, 0.10 mmol), IPr-HCl (90.0 mg, 0.21 mmol), and NaHMDS (37.2 mg, 0.20 mmol) were combined as solids in an oven dried round bottom flask under argon sealed with a rubber septum. Anhydrous THF (10 mL) was added, and the mixture was allowed to stir for 3 hours at room temperature. The mixture

was diluted with ethyl acetate (10 mL) and filtered through Celite™, and all volatiles were remo5ved *in vacuo*. Purification by silica gel column chromatography using 100% EtOAc as an eluent gives [Rh(IPr)(COD)Cl] as a yellow powder (58.4 mg, 0.18 mmol) in 92 % yield. Spectral data matched the reported literature.[50]

2.5 References

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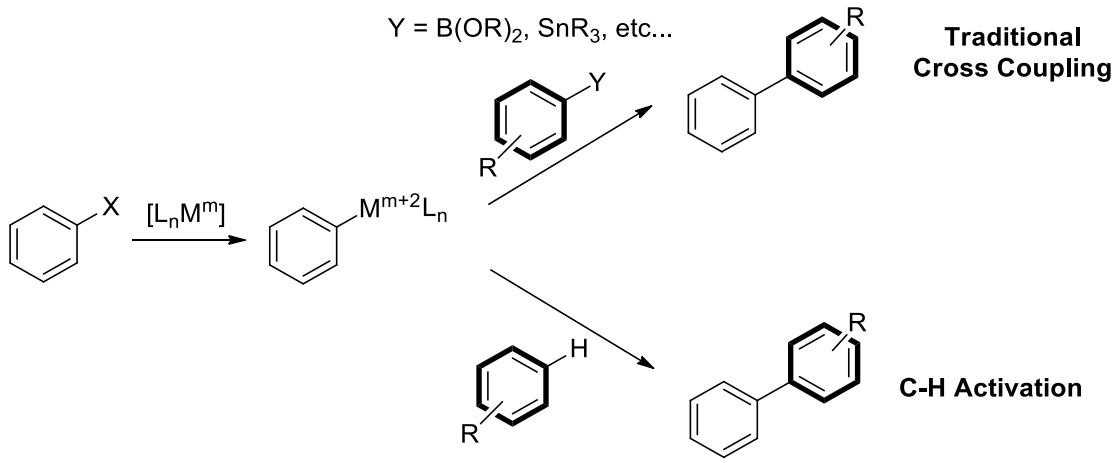
Chapter 3

Directed C-H Borylation with Rh-NHC Catalysts

3.1 C-H Activation

3.1.1 Introduction

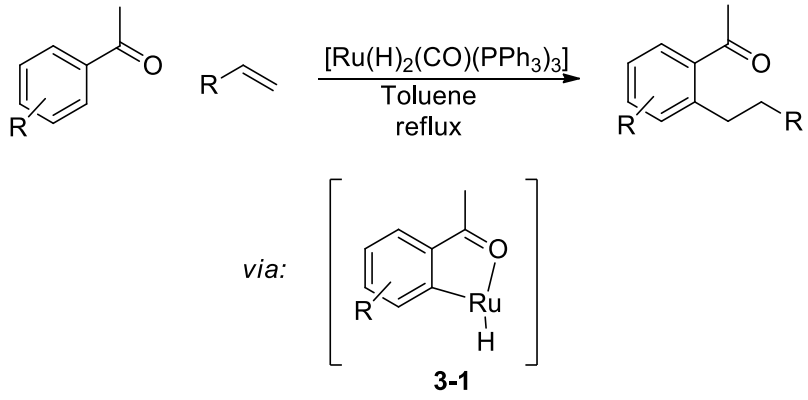
The functionalization of C-H bonds is an important field in synthetic chemistry, as it makes use of simple unactivated and readily available organic substrates.[1] A key example is C-H arylation, which obviates the need for pre-activation of substrates, which decreases synthetic steps and chemical waste, providing an environmentally friendly alternative to cross coupling reactions (Scheme 3-1).[2] Likely C-H activation has had the biggest impact on the functionalization of aromatic molecules, and has undergone explosive investigation in recent years.[2a, 2b, 3-5]



Scheme 3-1: Comparison of C-H activation/arylation and traditional cross coupling

Murai's 1993 report on the ruthenium catalyzed C-H alkylation of acetophenone derivatives with alkenes, with low (2 mol%) catalyst loadings (Scheme 3-2) had a huge impact on the field.[6] Although there were prior examples of stoichiometric C–H

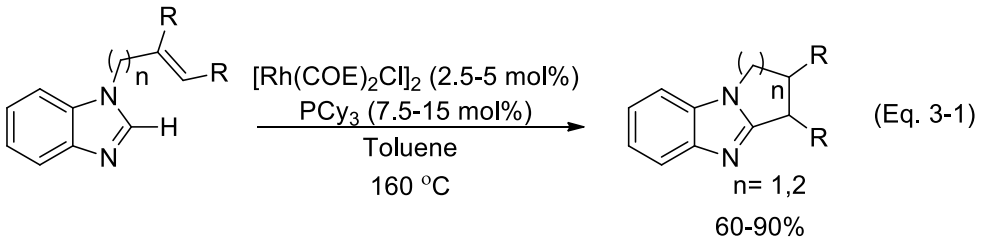
activations,[7,8] this report marked a major breakthrough in accomplishing synthetically useful catalytic methods for C–H functionalization. The reaction proceeds with complete regioselectivity for the C-H bonds ortho to the carbonyl moiety, indicating that the carbonyl acts as a directing group (**3-1**). Directed ortho Metallation (DoM) reactions are other examples of directed activation of C-H bonds that utilize stoichiometric amounts of strong lithium bases.[9] The Murai reaction further proceeds with a high selectivity for monoalkylation when multiple sites of possible activation were available, despite the elevated temperatures reported. This report was highly influential, and has spawned a great number of Lewis basic directing groups for C–H functionalization.[10]



Scheme 3-2: Murai's C-H alkylation reaction[6]

3.1.2 Rhodium Catalyzed C-H Functionalization Reactions

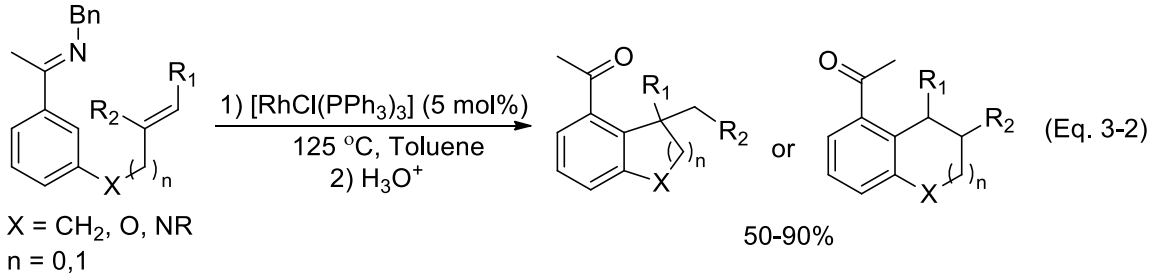
While many different metal catalysts have been reported, rhodium catalysts have been prominently featured in C-H activation reactions.[11] In 2001, Bergman and Ellman described the rhodium-catalyzed C-H activation/intramolecular alkene addition of benzimidazole derivatives (Eq. 3-1).[12] A combination of $[Rh(COE)_2Cl]_2$ and PCy_3 was found to be optimal, and the reaction was applicable with a variety of substituted alkenes, heteroaromatics and in inter or intramolecular systems.[13,14,15]



(Eq. 3-1)

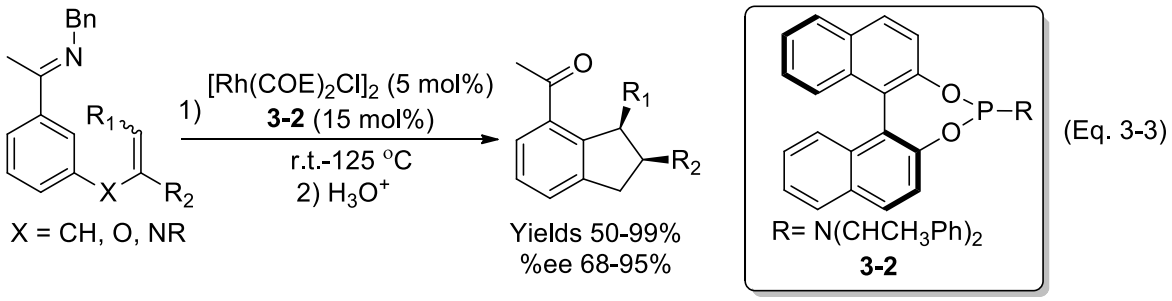
The rhodium catalyzed C-H arylation of heteroaromatics was also reported by Itami and coworkers, who demonstrated the effectiveness of Rh^{I} complexes bound to the strongly π-accepting $P(OCH(CF_3)_2)_3$.[16] While high temperatures were required, the reaction was found to be highly selective for the arylation of thiophenes and pyrroles in the β-position, the latter of which was important for the total synthesis of Lamellarins C and I,[17] and Dictyodendrins A and F.[18]

Rhodium catalyzed C-H alkylation reactions using chelation assisted methods have also been described in seminal reports from the laboratories of Kim,[19] Jun,[20] and Brookhart.[21] These transformations however were limited with respect to the alkene coupling partner, and typically only monosubstituted olefins were applicable. In an interesting report, in 2001 Bergman and Ellman described the intramolecular C-H alkylation of ketimines using Wilkinson's catalyst (Eq. 3-2).[22] The reaction was highly tolerant to the alkene moiety, and various substitution patterns were found to be tolerated.



(Eq. 3-2)

Impressively, the authors further described an enantioselective variant of this reaction by using chiral phosphoramidite ligand **3-2** in combination with $[Rh(COE)_2Cl]_2$ (Eq. 3-3).[22] The higher activity observed with this ligand translated to lower reaction temperatures being possible, which dramatically improved the enantioselectivity of the process. Unfortunately, relatively high catalyst loadings (5 mol% Rh) were still required.

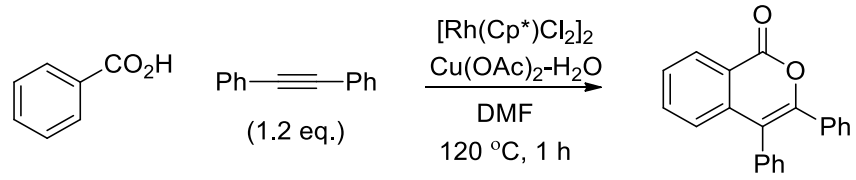


(Eq. 3-3)

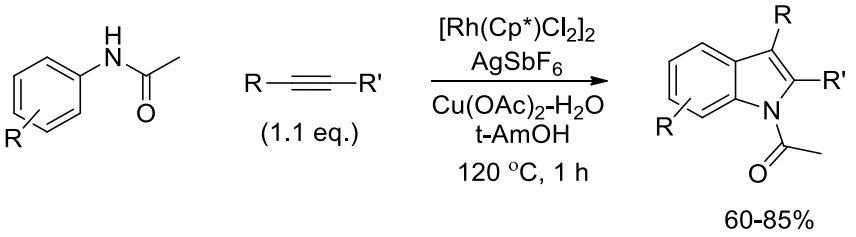
Since these reports, many researchers have described a variety of directed C-H functionalization procedures that are catalyzed by Rh^I complexes.[23] It should be pointed out that many of these processes require rather harsh conditions such as high temperatures, or high catalyst loadings.[16a, 23g, 24] The number of effective directing groups is limited, which may in part be due to the low Lewis acidity of Rh^I centers. The relatively small number of acceptable directing groups has certainly limited the potential of many of these reactions.

In 2007, Miura and Satoh described the oxidative C-H annulation of benzoic acids with alkynes which differed fundamentally in the catalyst structure (Eq. 3-4).[25] In contrast to previously reported C-H activation methods (*vide supra*) this procedure makes use of a Rh^{III} precursor. As the process is oxidative in nature, $Cu(OAc)_2$ was required as a terminal oxidant in order to regenerate the active Rh^{III} catalyst. Similarly, in 2008, Fagnou and coworkers described a rhodium catalyzed procedure for the synthesis of indoles from

acetanilides with internal alkynes in the presence of a silver salt that acts as a halide scavenger. (Eq. 3-5).[26] The transformation is incredibly functional group tolerant, and gives high yields in very short time frames.

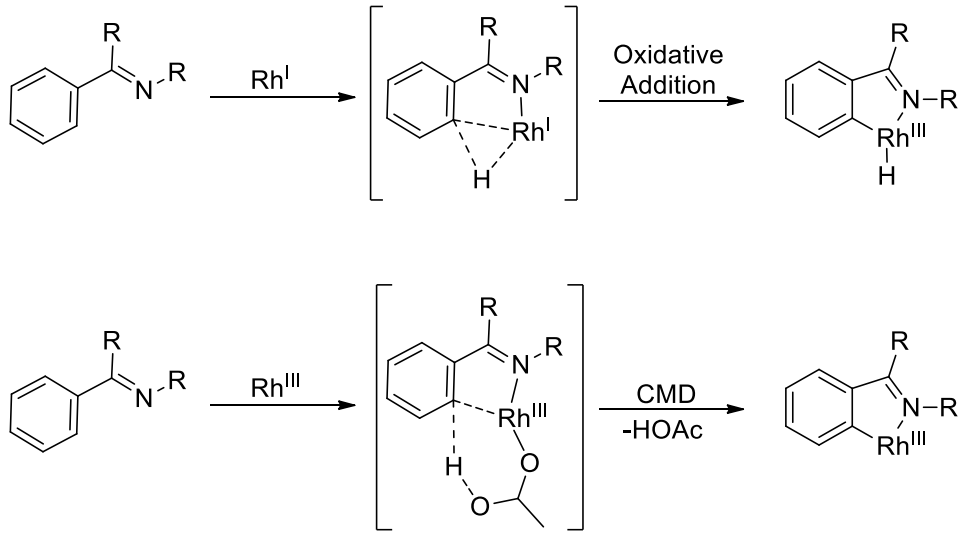


(Eq. 3-4)



(Eq. 3-5)

Atmospheric O_2 can be utilized as a terminal oxidant in presence of a substoichiometric amount of $Cu(OAc)_2$ cocatalyst, making this a truly mild transformation.[27] Similar methods were described by the same group for the synthesis of isoquinolines,[28] and isoquinolones.[29] In particular, $[Rh(Cp^*)Cl_2]_2/AgSbF_6$ is particularly effective, and has since been used in many C-H functionalization reactions by various research groups.[30] An important distinction should be made however, as the Rh^{III} catalyzed procedure varies mechanistically from Rh^{I} systems. These differences can have large ramifications for the outcome of the reactions. Two main mechanisms have dominated the literature for rhodium catalyzed C–H activation.[31] In general, Rh(I) catalysts are believed to undergo formal oxidative addition to C-H bonds,[23g, 24b, 32] while Rh(III) catalysts typically undergo base-assisted electrophilic metallation processes,[28, 33] commonly termed concerted metallation deprotonation (CMD) (Scheme 3-3).[31, 34]

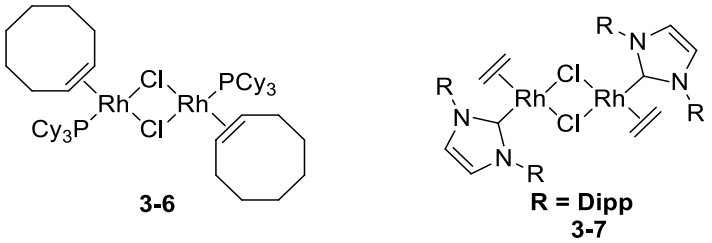


Scheme 3-3: General mechanistic differences in Rh^{I} vs. Rh^{III} C-H activation[20a, 33a, 35]

3.2 Results and Discussion

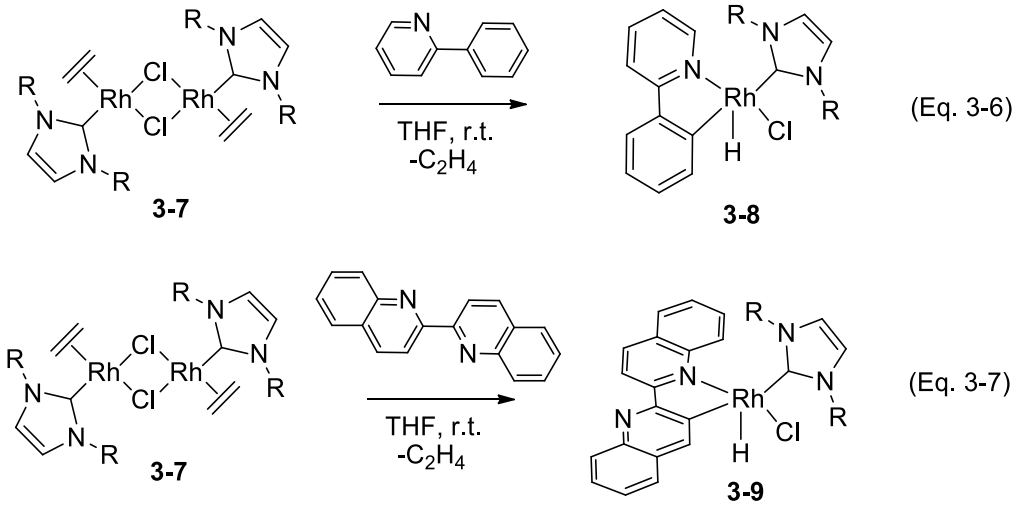
3.2.1 C-H activation with Rh-NHC complexes

While these reports on rhodium catalyzed C-H activation are impressive, known systems commonly require high catalyst loadings, high temperatures, extended reaction times and an excess of ligands.[31, 36] As such, we hypothesized that NHCs may offer increased catalytic activity through their ability to stabilize reactive metal centers. In addition, Chang and coworkers have shown that NHC ligands may provide benefits to C-H activation protocols over phosphines, by virtue of their increased trans effect.[37 38] We inferred complex **3-6** as the likely complex formed in situ under the catalytic system described by Bergman and Ellman for the alkylation and arylation of C-H bonds[12-14, 15] (Scheme 3-4). Complex **3-7** and the proposed complex **3-6** are both unsaturated and electron rich Rh^{I} systems that are similar in structure. As such, we proposed that **3-7** may be a potent C-H activation catalyst.



Scheme 3-4: Complex **3-7** and the likely product of the reaction of $[Rh(COE)_2Cl]_2$ with PCy_3[12]

To investigate the feasibility of employing dimeric Rh NHC complexes in C-H activation reactions, we conducted stoichiometric reactions involving complex **3-7** with 2-phenyl pyridine at room temperature (Eq. 3-6). Complex **3-7**, which features the IPr carbene, was chosen by virtue of its high stability and high yielding synthesis.[39] C-H activation could easily be observed in the ^{1}H NMR spectrum, which displayed the formation of a new resonance at -24.5 ppm with a $^1J_{Rh\text{-}C}$ value of 48.9 Hz, consistent with the formation of a Rh-H complex. The formation of this complex appeared to occur in very low conversion, as the ^{1}H NMR spectrum was primarily dominated by the two starting materials. All attempts to grow single crystals of C-H activated complex **3-8** were unsuccessful, however model complex **3-9**, which was instead coordinated to bis-quinoline, was attempted (Eq. 3-7). Similarly, a very low conversion was observed by ^{1}H NMR spectroscopy, however a Rh-H resonance could once again be observed at -14.7 ppm, ($^1J_{Rh\text{-}H}$ = 17.4 Hz). In addition, single crystals suitable for X-ray crystallography were obtained by slow diffusion of hexanes into a concentrated THF solution (Figure 3-1). The crystal structure of complex **3-9** clearly demonstrates successful C-H activation. The geometry of complex **3-9** appears to be pseudo-trigonal bipyrimidal with the hydride (not observed) likely occupying the fifth coordination site about the rhodium center.



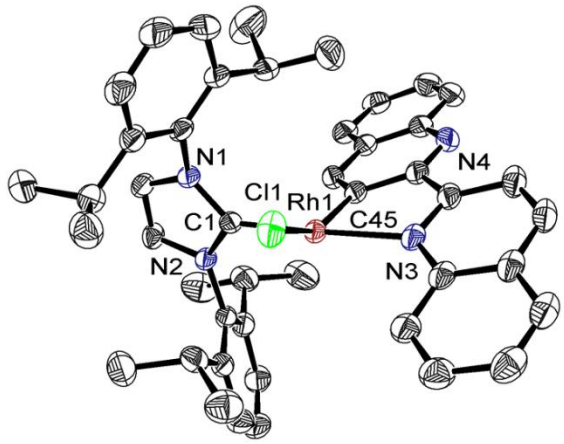
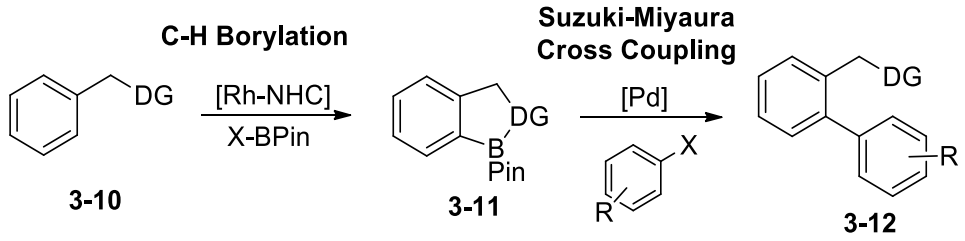


Figure 3-1: Crystallographically determined structure of **3-9**, displaying thermal ellipsoids drawn at the 50 % confidence level. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Rh(1)-C(1), 2.045(3); Rh(1)-C(45), 2.027(3); Rh(1)-N(3), 2.166(2); Rh(1)-Cl(1), 2.4170(8); N(1)-C(1), 1.352(3); N(2)-C(1), 1.337(3); C(45)-C(1), 91.56(11); C(45)-N(3), 82.90(11); C(1)-N(3), 174.47(10); C(45)-Cl(1), 152.33(8); C(1)-Cl(1), 93.59(8); N(3)-Cl(1), 91.37(7).

Delighted with the apparently well-controlled C-H activation process, we sought to exploit this activity in catalytic processes. While, as indicated previously, Rh(I) complexes have displayed reactivity in C-C bond forming reactions such as alkylation and arylation reactions, countless groups have detailed regioselectivity problems when multiple ortho C-H bonds are present.[23f-i, 40] This is particularly the case at elevated temperatures. This

presents a significant limitation to these methods, as they are hardly practical, and extremely limited in organic synthesis.

We hypothesized that if C-H functionalization could instead be affected to occur with the introduction of Lewis acidic group such as a boron center, the Lewis basic directing group would likely coordinate to the boron center forming **3-11** (Scheme 3-5), which would then prevent the reintroduction of the substrate into the catalytic cycle, resulting in selective mono-functionalization. The selection of a boron substituent seemed to be a reasonable target, considering the abundance of reports detailing rhodium catalyzed processes which involve the cleavage of H-B or B-B bonds, in particular for hydroboration reactions.[41] Rhodium catalysts are also known to be active in undirected C-H borylation reactions.[42] In addition, C-H borylations are highly attractive, as the products display remarkable utility in organic chemistry.[43]

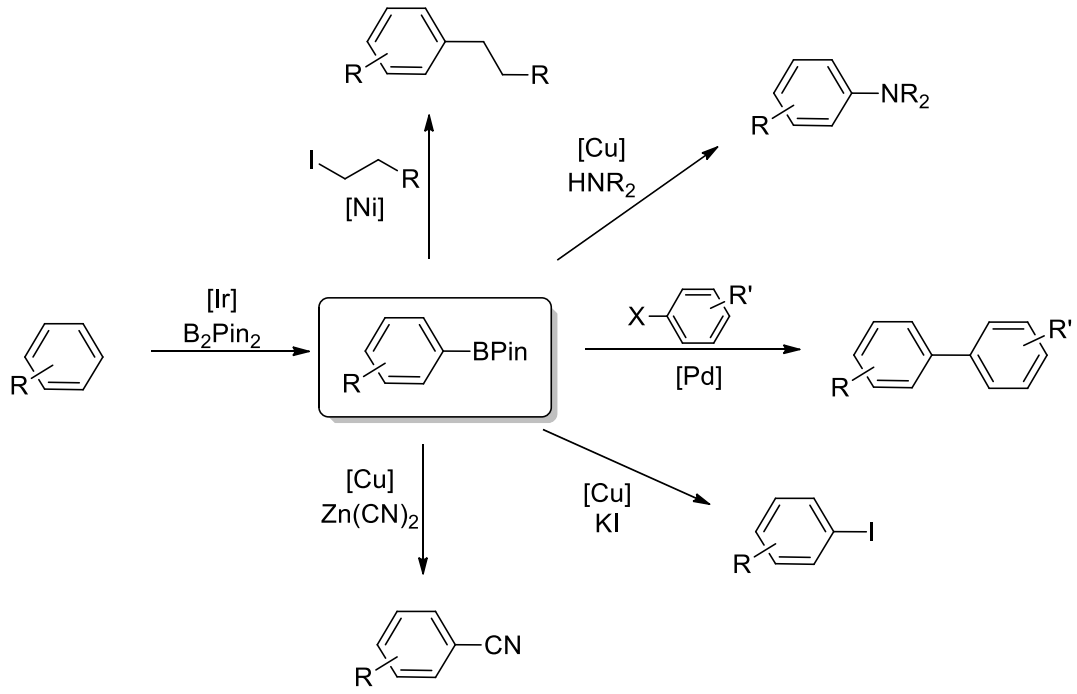


Scheme 3-5: Synthetic strategy for C-H borylation/arylation

3.2.2 C-H Borylation

C-H borylation reactions have an extensive history, and numerous reports from the laboratories primarily of Hartwig[44] and Smith[45] have demonstrated their vast applicability.[46] Typically, these procedures make use of simple iridium catalysts formed in situ from $[Ir(COD)OMe]_2$ and bipy type ligands.[47] As organoboron reagents have

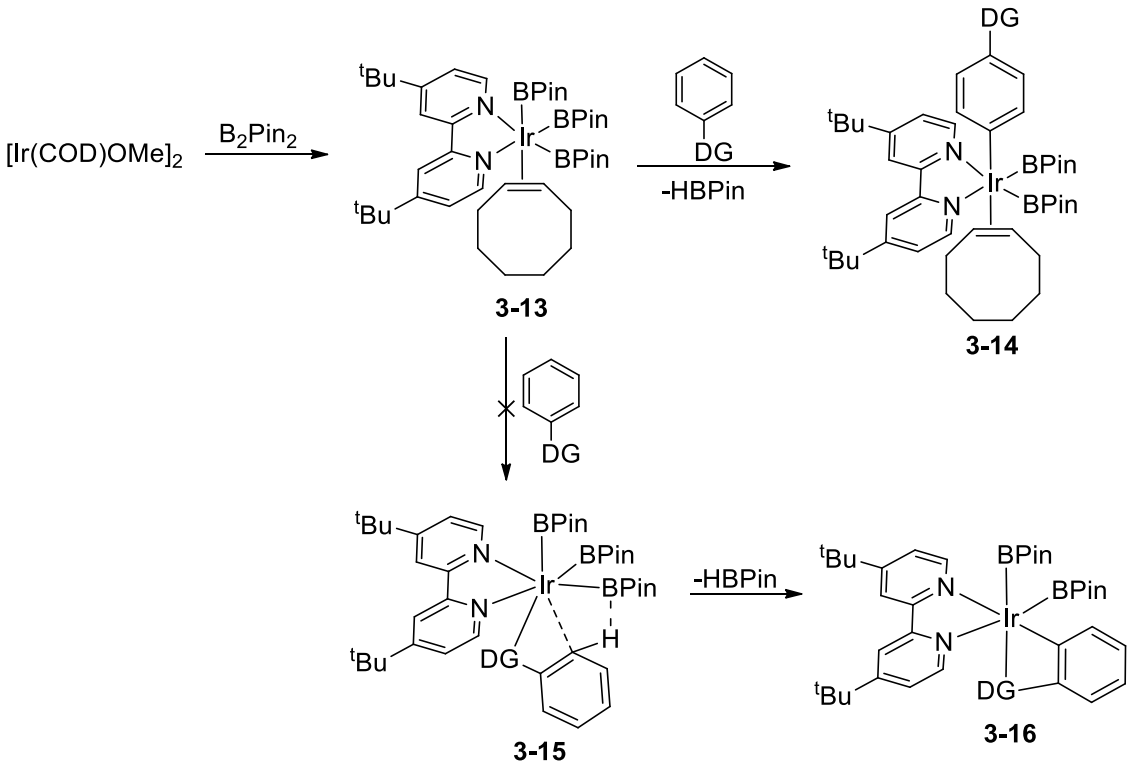
tremendous utility in organic chemistry,[43] it is no surprise that C-H borylation procedures have been combined with other bond forming processes giving rise to extremely complicated structures from simple organic substrates (Scheme 3-6).



Scheme 3-6: Synthetic utility of C-H borylation reactions[44f, 48]

An important distinction should be made however, as the processes described above, while incredibly impressive, display regiochemistry patterns that are almost completely dictated by the steric parameters of the substrate. As a result, selective C-H borylation reactions which occur at the ortho site, which would occur in the presence of a suitable directing group, are remarkably underdeveloped in comparison.[49] This is believed to be due to the lack of open coordination sites on the catalytically active iridium center, which cannot accommodate both the directing group as well as the aryl group resulting in **3-13** (Scheme 3-7). As a result, catalysts for directed C-H borylation reactions will likely

require the necessity of fundamentally different structures which can accommodate an increased coordination sphere, or operate under different mechanisms.

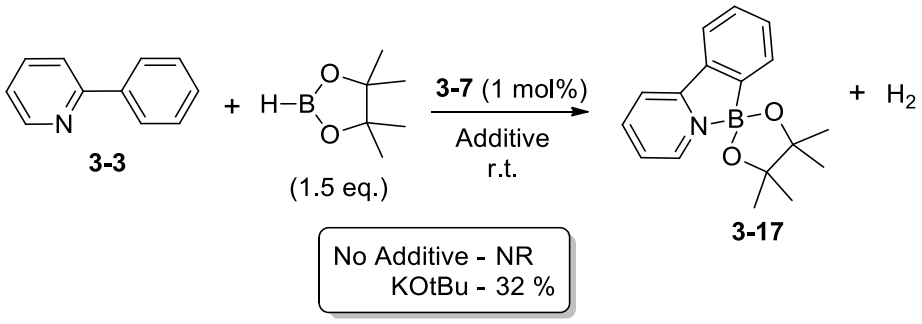


Scheme 3-7: Proposed mechanism of C-H activation with iridium complexes[44c]

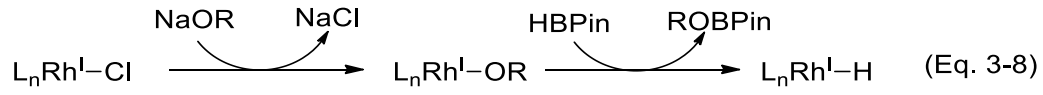
At the time we began our investigations into this field, we were aware of very few reports detailing transition metal catalyzed directed C-H borylation reactions. Sawamura and coworkers had reported their efforts directed towards C-H borylation of arenes with a variety of directing groups, catalyzed by iridium complexes bound to designer heterogeneous phosphine ligands.[50] In addition, Ishiyama and Miyaura reported the borylation of benzoate esters using a homogeneous iridium phosphine system.[51] Hartwig described the directed C-H borylation using silyl derived directing groups.[44g] Smith has detailed the outer-sphere directed C-H borylations of protected aniline and anisole

derivatives.[52] Finally, Snieckus has reported strategies detailing the ortho borylation of several substrates utilizing DoM procedures.[53] While these transformations are impressive, they have either a limited substrate scope, require the use of designer ligands, or require cryogenic conditions and exceptionally strong bases. Thus a user friendly method that was applicable to a wide variety of substrates was notably absent. This absence was in contrast to the plethora of reports detailing the somewhat analogous directed C-H silylation reactions.[54]

We began our investigation with the stoichiometric reaction of 2-phenyl pyridine, **3-3**, with 1 equivalent of HBPin in the presence of a catalytic amount (2 mol%) of **3-7** at room temperature. Monitoring the reaction by ^{1}H and ^{11}B NMR spectroscopy indicated that no product was being formed under the reaction conditions (Scheme 3-8). In line with observations made by Ishiyama, Miyaura and Hartwig in iridium catalyzed procedures,[55] we hypothesized that the presence of a basic ligand, such as an alkoxide would result in a Rh^{I}-H complex, which may facilitate product formation by a dehydrogenative route (Eq. 3-8).



Scheme 3-8: Initial Catalytic Screening for Directed C-H Borylation Reactions



Upon the addition of KOtBu (0.5 equivalents) to the reaction mixture, the immediate formation of gas was observed, and compound **3-17** could be observed by both ^{1}H and ^{11}B NMR spectroscopy in 32 % yield, as determined by ^{1}H NMR spectroscopy using 1,4-dimethoxy benzene as an internal standard. Importantly, no bis-borylation was observed, and the ^{11}B NMR spectrum of the reaction mixture displayed a signal with a significant upfield shift (δ 13.3 ppm). This effect is characteristic of 4-coordinate boron species, which helped to confirm our hypothesis of B-N coordination.[56] This was further confirmed by x-ray crystallographic analysis of single crystals of ethyl-substituted **3-18** obtained by slow evaporation of a diluted pentane solution, clearly demonstrating B-N coordination (Figure 3-2). Similar effects were observed by Fu and coworkers[57] with acetanilide derivatives, as well as Lassaletta and coworkers[58] with phenyl pyridine substrates.

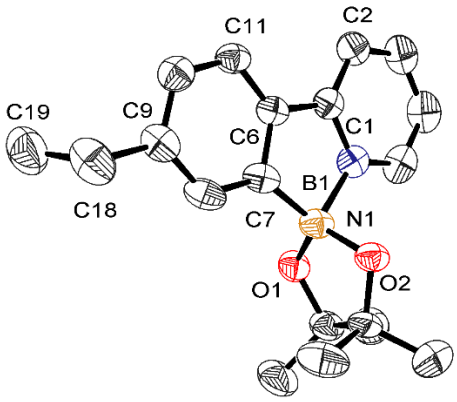
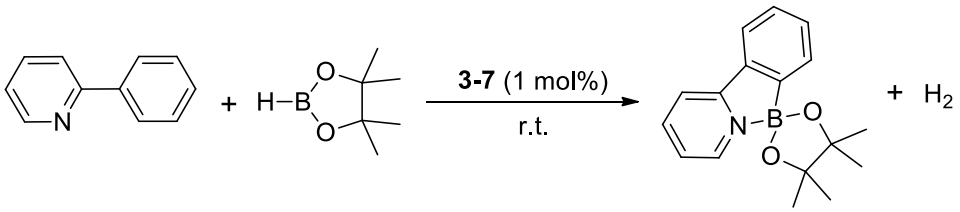


Figure 3-2: Crystallographically determined structure of **3-18**, displaying thermal ellipsoids drawn at the 50 % confidence level. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: N(1)-C(5), 1.3442(18); N(1)-C(1); 1.3535(17); N(1)-B(1), 1.694(2); C(1)-C(2), 1.3864; C(1)-C(6), 1.4710(18); C(7)-B(1), 1.623(2); O(1)-B(1), 1.49(4); O(2)-B(1), 1.493(5).

Despite the low yield obtained, ^{11}B NMR spectrum of the reaction mixture showed the full consumption of HBPin within one hour. The source for the decomposition of HBPin appeared to be a background reaction between the base and the HBPin, which resulted in the formation of B_2Pin_3 as a decomposition product, likely along with unobserved BH_3.[59] Therefore, conditions were investigated in order to help facilitate the reactivity of the catalyst while decreasing the decomposition of HBPin. A screening of bases indicated that strong alkoxide bases were most applicable in this transformation (Table 3-1). Weaker carbonate or phosphate bases such as K_2CO_3 or K_3PO_4 were completely ineffective under the reaction conditions, likely in part due to their decreased solubility. Longer reaction times were required for Cs_2CO_3 to be an effective base. NaOEt (0.25 equivalents) appeared to consistently give the best results. Different solvents were also screened, and aromatic solvents such as C_6H_6, toluene or $CF_3C_6H_5$ were found to be the most effective.

When the loading of HBPin was increased to 2 equivalents, the yield increased to 91 % (Table 3-2). Other boron containing reagents such as B_2Pin_2 were also investigated, but these reagents failed to give any observed product at all. ^{11}B NMR spectroscopy indicated the inability of complex **3-7** to activate the B-B bond at room temperature. Importantly, [Rh(IPr)(COD)Cl] displayed no observable activity under these reaction conditions.

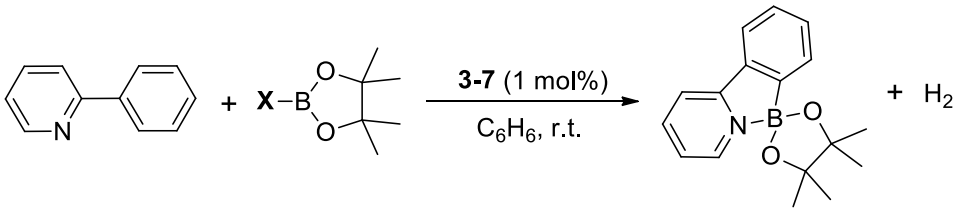
Table 3-1: Optimization of the C-H borylation of phenyl pyridine



Entry	Base (eq.)	Solvent	Yield (%)
1	KOtBu (0.5)	C_6H_6	32
2	KOtBu (0.25)	C_6H_6	70
3	NaOMe (0.25)	C_6H_6	32
4	NaOEt (0.25)	C_6H_6	84
5	Cs_2CO_3 (0.25)	C_6H_6	28
6[a]	Cs_2CO_3 (0.25)	C_6H_6	64
7	K_2CO_3 (0.25)	C_6H_6	0
8	K_3PO_4 (0.25)	C_6H_6	8
9	NaOEt (0.25)	THF	25
10	NaOEt (0.25)	Toluene	73
11	NaOEt (0.25)	$CF_3C_6H_5$	82

General Conditions: 2-phenyl pyridine (0.2 mmol), HBPin (0.35 mmol, **3-7** (0.002 mmol), with base in indicated solvent, and stirred for 4 hours at room temperature. yields determined by ^{1}H NMR spectroscopy using 1,4-dimethoxybenzene as an internal standard. [a]reaction run for 8 hours.

Table 3-2: Catalyst and reagent optimization for C-H Borylation



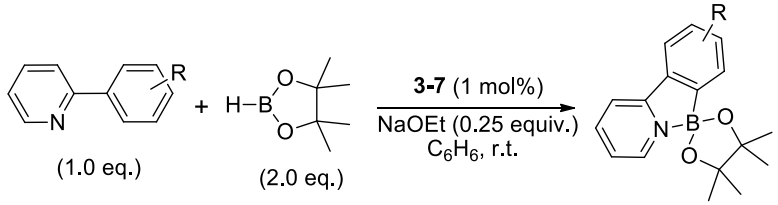
Entry	Catalyst (mol %)	X (eq.)	Yield (%)
1	**3-7** (1)	H (2)	91
2	**3-7** (2)	H (2)	70
3	**3-7** (0.5)	H (2)	30
4	**3-7** (1)	BPin (1.5)	NR
5	[Rh(IPr)(COD)Cl] (2)	H (2)	NR
6	[Rh(IPr)(COD)Cl] (2)	BPin (1.5)	NR

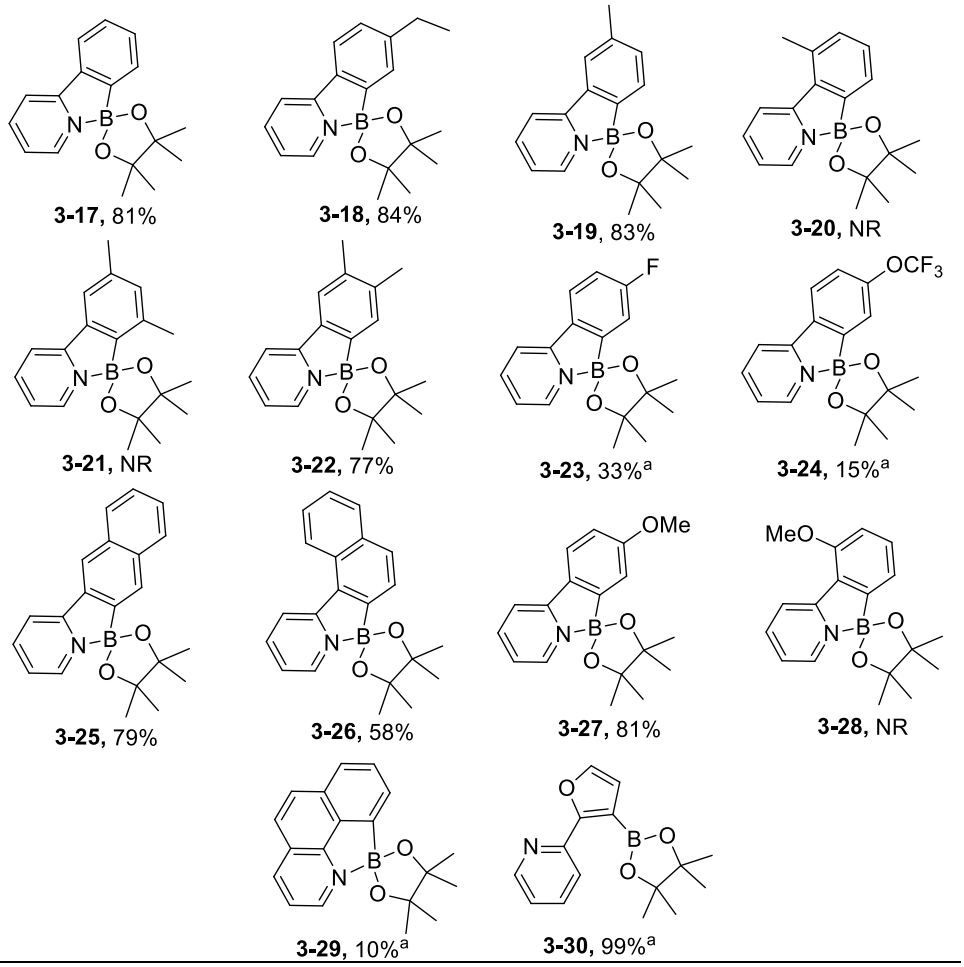
General Conditions: 2-phenyl pyridine (0.2 mmol), and NaOEt (0.05 mmol), were combined with HBPin and **3-7**, in C_6H_6, and stirred for 4 hours at room temperature. Yields determined by ^{1}H NMR spectroscopy using 1,4-dimethoxybenzene as an internal standard.

With the optimized conditions in hand, we sought to investigate the substrate scope of this transformation. A variety of 2-phenyl pyridines were subjected to the reaction conditions to investigate the steric and electron effects of the substrates (Table 3-3). Generally it was found that substrates that contained ortho substituents were completely unreactive. This was likely associated with their decreased ability to cyclometallate with the rhodium catalyst for steric reasons. Surprisingly however, naphthyl containing **3-26** appeared to be a viable substrate despite its substitution pattern. In line with the results of other groups, electron rich substituents were more effective than electron deficient.[23d, 23i] In addition, furan-containing **3-30** was formed in nearly quantitative conversion as determined by ^{1}H NMR spectroscopy. Unfortunately however, **3-30** proved to be remarkably unstable and decomposed rapidly preventing its isolation. The ^{11}B NMR spectrum of this species displays downfield shifting relative to the other compounds (δ = 30.7 ppm). This chemical shift may indicate the absence of an N-B coordination in this compound.

A proposed mechanism for this transformation is presented in Figure 3-3. After initial activation of the catalyst resulting in Rh^{I}-H **3-A**, oxidative addition of HBPin yields Rh^{III}-$(H)_2$ **3-B** complex, which undergoes reductive elimination of H_2. This is followed by the oxidative addition of the C-H bond resulting in **3-D**, which then undergoes product forming reductive elimination and regenerating Rh^{I}-H species **3-A**.

Table 3-3: C-H borylation of 2-phenyl pyridines catalyzed by Rh-NHC complex **3-7**[60]





General Conditions: 2-phenyl pyridine (0.5 mmol), and NaOEt (0.125 mmol), were combined with HBPin (1.0 mmol) and **3-7** (0.005 mmol) in C_6H_6, and stirred for 4 hours at room temperature Isolated yields. [a]Yields determined by ^1H NMR spectroscopy using 1,4-dimethoxybenezene as an internal standard.

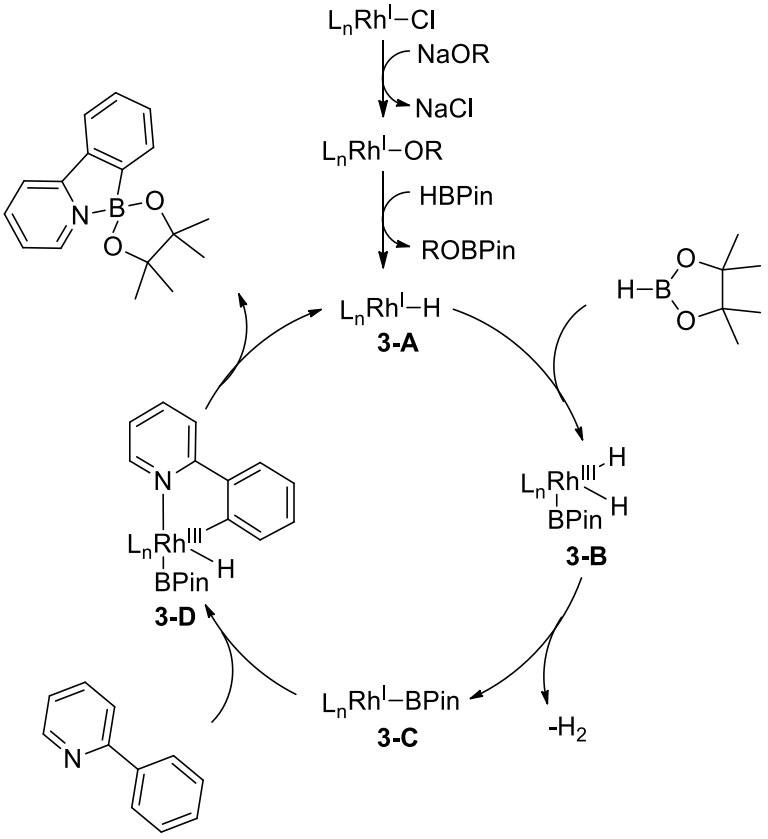
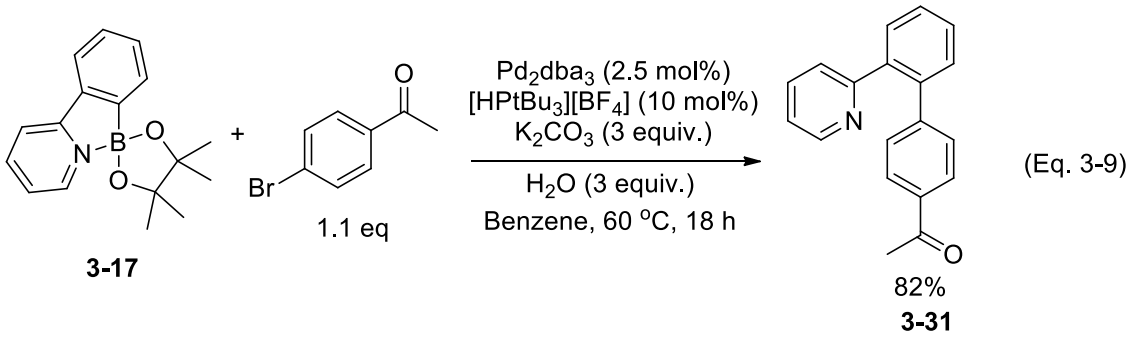
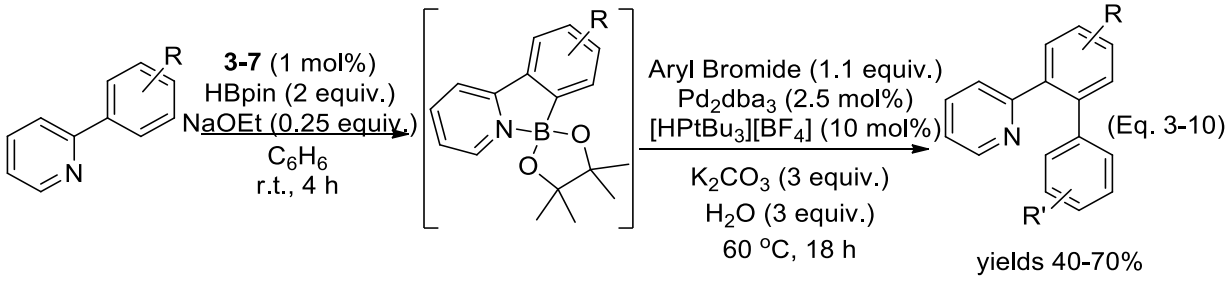


Figure 3-3: Proposed mechanism for the C-H borylation of phenyl pyridines

As previously indicated, we planned to take advantage of the selective formation of the monoborylated compounds **3-17** to **3-30** by subjecting them to Suzuki-Miyaura cross coupling conditions. In this regard, M. Sc. student Brandon Moore investigated cross coupling conditions under mild conditions. Conditions adapted from Suiginome[61] were found to be effective in the cross coupling of isolated compound **3-31** (Eq. 3-9).

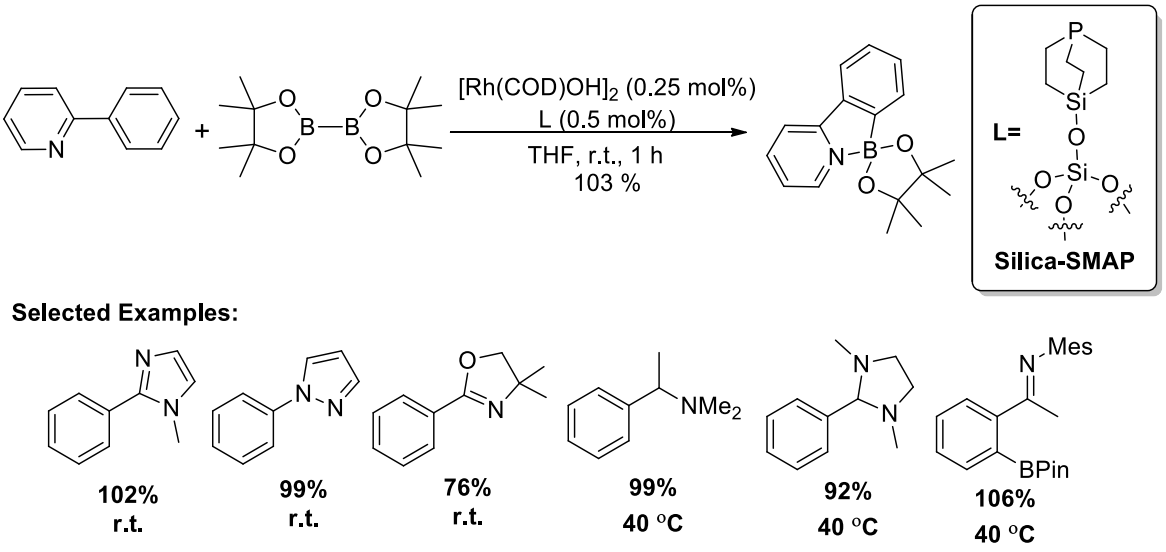


Brandon further demonstrated successful one-pot borylation/Suzuki-Miyaura cross coupling procedures. Different phenyl pyridines were reacted with HBPin under optimized conditions, and were then followed by Suzuki-Miyaura coupling protocols (Eq. 3-10). This was effected by the mere addition of the palladium catalyst, phosphine, base, aryl halide and H_2O to the original reaction mixture upon completion of the borylation. Acceptable yields (40-70 %) were obtained over two steps, and the products could be purified by column chromatography.



During the preparation of our manuscript, Yu[62] and Fu[57] reported palladium catalyzed directed borylations, while Lassaletta[58] and Ishiyama[63] reported iridium catalyzed examples. In addition, Sawamura reported the rhodium catalyzed C-H borylation of phenyl pyridine derivatives using heterogeneous phosphine ligands (Scheme 3-9).[64] Sawamura's system resulted in high yields over very short times even at low temperatures. Importantly, several nitrogen-based directing groups were reported to be effective at low

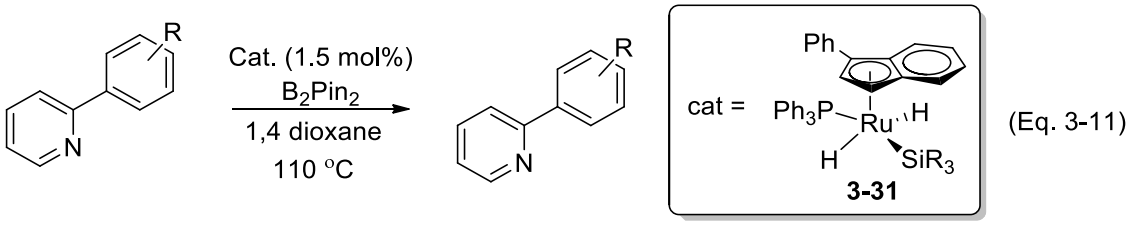
temperatures. The directing groups were further demonstrated to be complementary with the iridium catalyzed system that was previously reported by the same group.[50a] Caution must be used when judging this system however, as the yields reported are based on B_2Pin_2 even though this substrate is not the limiting reagent. As a result, some reported yields are above 100 %, even though that is technically impossible in the absence of alchemy. This report was later followed up by a second paper that demonstrated the C-H borylation of sp^3 C-H bonds.[65]



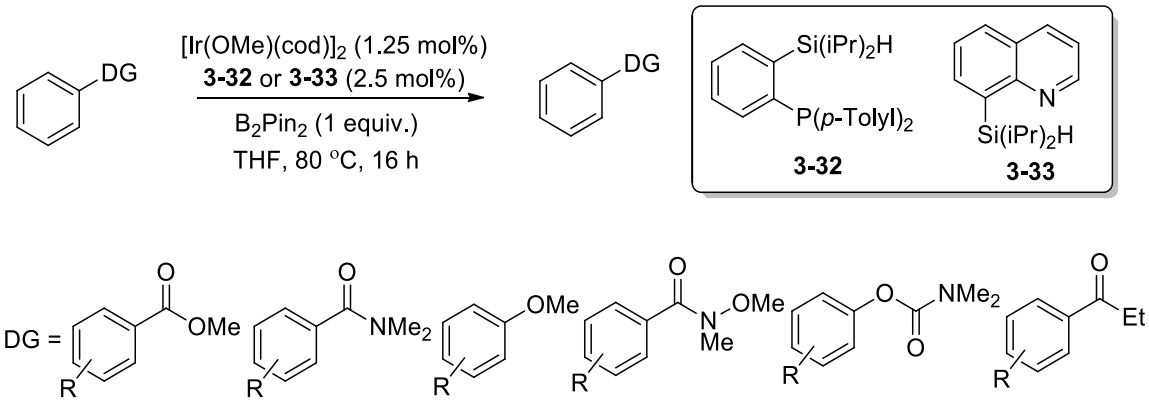
Scheme 3-9: Sawamura's reported rhodium system for C–H borylation[64]

In addition, Nolan reported the directed C-H borylation of phenyl pyridine derivatives catalyzed by a ruthenium indenyl hydride complex **3-31** (Eq. 3-10).[66] In a similar mechanistic proposal to ours, the authors implicated the importance of a Ru^{II}-H complex as an intermediate. Although no external base was required, temperatures as high as 115 °C were required in order to generate the active Ru^{II}-H upon loss of $HSiR_3$.

Unfortunately, no other directing groups were investigated. The applicability of complex **3-31** as a catalyst in C-H borylation reactions helped to confirm our mechanistic hypothesis.



Finally, a very impressive report by Smith appeared, which detailed directed C-H borylation reactions catalyzed by homogeneous iridium complexes coordinated to chelating silyl-phosphorus or pyridine ligands (Scheme 3-11).[67] A variety of directing groups were found to be applicable giving high yields and selectivities. Ligand **3-32** was found to form 1:1 complexes with the iridium center, and it was hypothesized that this ratio was crucial for creating open coordination sites on the metal resulting in high selectivity.



Scheme 3-10: Directed C-H borylations using chelating silyl phosphorus, or pyridine derived ligands.[67]

3.2.3 Investigations into Other Directing Groups

We applied the optimized conditions described above to various other directing groups (Chart 3-1). Unfortunately, in all cases, they failed to result in the formation of product, and quantitative decomposition of HBPin to B_2Pin_3 was observed by ^{11}B NMR spectroscopy. At higher temperatures (60 °C) pyrazole **3-35** did result in the formation of product in low yield, however we were unable to optimize for this substrate using the current conditions. This was surprising to us, as Sawamura had indicated a wide variety of viable directing groups in their Rh^I system (Scheme 3-9). We hypothesized that this lack of reactivity was associated with the presence of the external base, which decomposed the HBPin in the absence of an active catalytic use of this species.

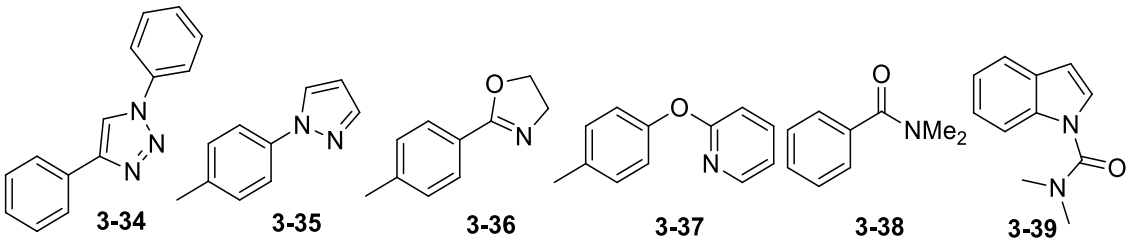
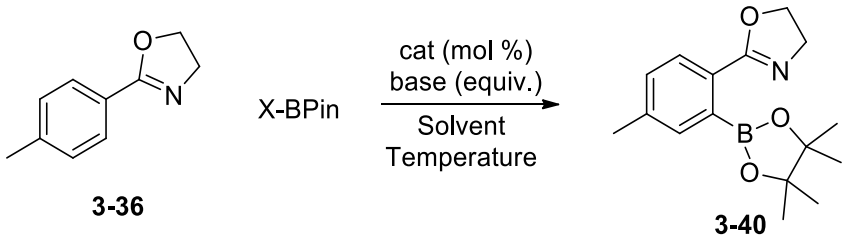


Chart 3-1: Other directing groups investigated

In order to test this hypothesis, we investigated the use of a preformed rhodium hydride complex which would obviate the need for the external base. As such, we chose to investigate the reactivity of commercially available $[HRh(PPh_3)_3CO]$ with **3-36** which features an oxazoline directing group (Table 3-4). These directing groups attracted our attention, as they are easily synthesized from aldehydes,[68] and have been described to be effective directing groups in other processes.[69] In addition, they have been reported to undergo facile hydrolysis to amides in the presence of a Lewis acid.[70] While treatment with HBPin resulted in complete return of starting material, the use of B_2Pin_2 at 60 °C instead

resulted in the formation of product in 39 % yield (Entry 7). The formation of **3-40** could be observed by GCMS and confirmed by both ^{1}H and ^{11}B NMR spectroscopy.

Table 3-4: C-H borylation of oxazoline-containing arenes



3-36 **3-40**

Entry	Catalyst (mol %)	X (eq.)	Solvent	Temperature (°C)	Yield (%)
1	[HRh(PPh$_3$)$_3$CO] (2)	H (1)	Toluene	RT	NR
2	[HRh(PPh$_3$)$_3$CO] (2)	BPin (1)	Toluene	RT	Trace
3	[HRh(PPh$_3$)$_3$CO] (2)	BPin (1)	Toluene	60	39
4	[HRh(PPh$_3$)$_3$CO] (2)	BPin (1)	THF	60	49
5	[HRh(PPh$_3$)$_3$CO] (2)	BPin (1)	Dioxanes	60	43
6	[Rh(IPr)(COD)Cl] (2)	BPin (1)	THF	60	NR
7	**3-7** (1)	BPin (1)	THF	60	NR

General Conditions: 3-36 (0.1 mmol), B_2Pin_2 (0.1 mmol) and indicated catalyst, stirred for 18 hours at indicated temperature. [a]yields determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

While the formation of **3-40** was only observed in low yield, it helps to confirm our mechanistic hypothesis implicating a Rh^{I} hydride complex as the active catalyst. In addition, it helps to confirm the detrimental effect of external bases. We are currently in the process of optimizing the catalyst structure for this reactions, in order to extend it to other directing groups.

3.3 Conclusions

Dimeric Rh-NHC complex **3-7** undergoes C-H oxidative addition to 2-phenyl pyridine (**3-17**) at room temperature, resulting in Rh^{III}-hydride complex **3-8** which was

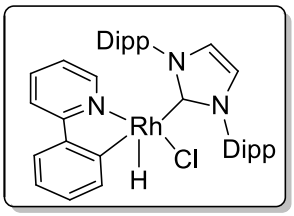
characterized by ^{1}H NMR spectroscopy. Single crystals of the analogous 2-2'-biquinoline derived complex **3-9** were obtained which confirmed the C-H activation. This complex represents a rare example of a crystallographically defined Rh complex, which underwent C-H oxidative addition.

We demonstrated the activity of complex **3-7** in directed C-H borylation reactions, which occur at room temperature with low catalyst loadings. Importantly, this process occurred with exclusive selectivity for mono-borylation. The transformation was combined with a Suzuki-Miyaura cross coupling reaction in one-pot, formally giving rise to C-H arylated products with exclusive selectivity for mono-arylation. We hypothesize that the reactive species in the C-H is a NHC-Rh^{I}-H complex, which is formed upon reaction with HBPin in the presence of an alkoxide base. This hypothesis was further corroborated by the activity of the commercially available $[HRh(PPh_3)_3CO]$ in similar reactions. To our knowledge, this catalyst has never previously been described in C-H functionalization reactions. We are currently in the process of further optimizing catalyst structure in hopes that this will allow for an expanded scope of directing groups. In particular, we hypothesize that dimeric Rh NHC catalysts similar to **3-7**, which instead contain basic ligands such as $[Rh(NHC)(C_2H_4)OAc]_2$ or $[Rh(NHC)(C_2H_4)OCH_3]_2$ may be more appropriate for these transformations.

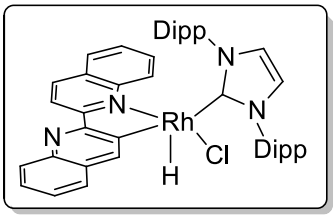
3.4 Experimental

General Considerations: Unless otherwise specified, all manipulations were carried out under an atmosphere of dry argon in oven–dried glassware, or under a nitrogen atmosphere in a glovebox (M. Braun) with oxygen and water levels $\leq$2 ppm. All solvents were distilled

from either CaH_2 (CH_2Cl_2, NEt_3) or Na/benzophenone (THF, C_6H_6, toluene, Et_2O), degassed via three freeze–pump–thaw cycles and stored under N_2 over molecular sieves (4Å) prior to use. Pinacolborane (HBPin) was purchased from Sigma Aldrich and purified by short path distillation and stored at –20 °C under a nitrogen atmosphere. 2–Phenylpyridine was purchased from Sigma Aldrich, distilled from CaH_2 and stored at –20 °C under a nitrogen atmosphere. 2–Phenylpyridines,[71] 1,3-diphenyl-1,2,3-triazole (**3-34**),[72] 4-tolyl-pyrazole (**3-35**),[73] 4-tolyl-oxazoline (**3-36**),[68] 2-(4-tolyloxy)pyridine (**3-37**),[74] and *N*,*N*-dimethyl-1H,indole-1-carboxamide (**3-39**)[75] were synthesized according to literature procedures.[68, 71] $[Rh(IPr)(C_2H_4)Cl]_2$ **(3-7)** was prepared according to our previously reported synthesis[39] and stored at –30 °C under a nitrogen atmosphere. $RhCl_3 \cdot 3H_2O$ and $Pd_2(dba)_3$ were generously donated by Johnson Matthey and used without further purification. NMR spectra were recorded on a Bruker Avance 400 or 500 MHz spectrometer where indicated. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using residual protonated solvent as an internal standard ($CDCl_3$, δ 7.26 ppm; CD_2Cl_2, δ 5.32 ppm; C_6D_6, δ 7.16 ppm). Boron NMR spectra (^{11}B) were recorded at 128 MHz and 160 MHz where indicated and are referenced to an external standard ($BF_3 \cdot OEt$, δ 0 ppm). Aluminum oxide was purchased from Sigma Aldrich (activated, basic, Brockmann Grade I, 58 Å porosity, pH 9.0–10.0). Flash grade silica gel (50 μm particle size, 60 Å porosity) was purchased from Silicycle. Elemental analyses were performed using a Thermo Scientific Flash 2000 CHNS Elemental Analyzer. High–resolution mass spectrometry (HRMS) was performed using a Micromass GCT (GC–Time of Flight Mass Spectrometer). X-ray data collection was performed on a Bruker SMART APEX II X-ray diffractometer.



Synthesis of 3-8: In a nitrogen–filled glovebox, 2-phenyl pyridine (4.2 mg, 0.027 mmol) in C_6D_6 (2.0 mL) was added to a solution of **3-7** (15 mg, 0.013 mmol) in C_6D_6 (2.0 mL) in a 20 mL vial, and the mixture was allowed to stir for 3 days, which resulted in an intractable mixture according to ^{1}H NMR spectroscopy. However, the formation of a new rhodium hydride complex was confirmed by the characteristic doublet in the ^{1}H NMR spectrum (500 MHz, C_6D_6) δ = -24.5 ppm, $^1J_{Rh\text{-}H}$ = 48.9 Hz.

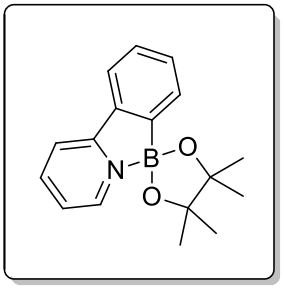


Synthesis of 3-9: In a nitrogen–filled glovebox, a solution of 2,2'–biquinoline (7.0 mg, 0.026 mmol) in C_6D_6 (2.0 mL) was added to a solution of **3-7** (15 mg, 0.013 mmol) in C_6D_6 (2.0 mL) in a 20 mL vial, and the solution was allowed to stir at RT for 10 days which resulted in an intractable mixture according to ^{1}H NMR spectroscopy. Single crystals were obtained by the slow diffusion of hexanes into a concentrated THF solution.

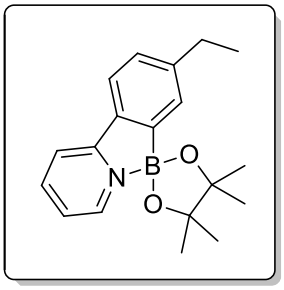
General procedure for the C-H borylation of phenyl pyridine derivatives:

In a nitrogen-filled glove box, an oven–dried round bottom flask was charged with NaOEt (8.5 mg, 0.125 mmol). A solution of substrate (0.5 mmol) and **3-7** (5.55 mg, 0.005 mmol) in 4 mL of benzene was added to the round bottom flask. A solution of HBPin (128 mg, 1.0 mmol) in 0.6 mL of benzene was added to the stirring mixture and the reaction was vigorously stirred for 4 hours. After this time, the flask was removed from the glovebox

and the contents were loaded directly onto a basic alumina column (eluted with ethyl acetate/hexanes mixtures). The organic fractions were then collected and concentrated *in vacuo*.

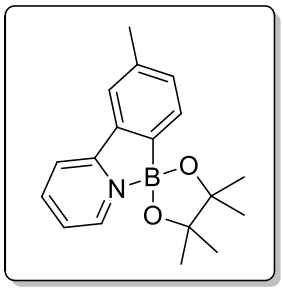


Synthesis of 3-17: Synthesized according to the general procedure using 2-(phenyl)pyridine (75.7 mg, 0.5 mmol), **3-7** (5.53 mg, 0.005 mmol) and HBPin (128 mg, 1 mmol) in C_6H_6 (4 mL). Purification was achieved by column chromatography using basic alumina eluting with a 7:3 EtOAc/hexanes mixture to afford a yellow powder (114 mg, 0.41 mmol) in 81 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.66 (d, 1H, $J_{H\text{-}H}$ = 5.5 Hz, Ar*H*), 7.95, (td, 1H, $J_{H\text{-}H}$ = 7.8, 1.5 Hz, Ar*H*) 7.79 (d, 1H, $J_{H\text{-}H}$ = 8.0 Hz, Ar*H*), 7.72 (d, 1H, $J_{H\text{-}H}$ = 7.2 Hz, Ar*H*), 7.65 (d, 1H, $J_{H\text{-}H}$ = 7.6 Hz, Ar*H*), 7.41 (td, 1H, $J_{H\text{-}H}$ = 7.3, 0.9 Hz, Ar*H*), 7.35 (dd, 1H, $J_{H\text{-}H}$ = 9.5, 3.4 Hz, Ar*H*), 7.29 (td, 1H, $J_{H\text{-}H}$ = 7.5, 1.1 Hz, Ar*H*), 1.43 (s, 12H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 156.7, 143.3, 141.9, 137.3, 131.6 (2 Carbons as determined by HSQC), 127.9, 122.8, 121.3, 117.5, 80.3, 27.1 (*C–B* bond not observed). **^{11}B NMR** (128 MHz, $CDCl_3$): δ = 13.3. **HRMS** (EI-TOF) calculated for [$C_{17}H_{20}BNO_2$]: 281.1587. Found: 281.1599. **(EA)** Anal. Calcd for [$C_{17}H_{20}BNO_2$]: C, 72.62; H, 7.17; N, 4.98. Found: C, 72.12; H, 6.93; N, 5.27.



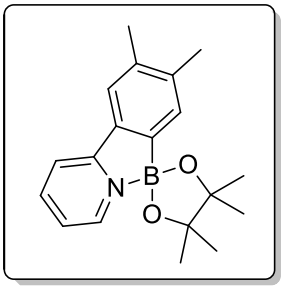
Synthesis of 3-18: Synthesized according to the general procedure using 2-(4-ethylphenyl)pyridine (91.5 mg, 0.5 mmol), **3-7** (5.53 mg, 0.005 mmol) and HBPin (128 mg, 1 mmol) in C_6H_6 (4 mL). Purification was achieved by column chromatography

using basic alumina eluting with 7:3 EtOAc/hexanes mixture to afford an off–white powder (130 mg, 0.42 mmol) in 84 % yield. Single crystals suitable for X-ray crystallography were obtained by evaporation of a diluted pentane solution. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.62 (d, 1H, $J_{H\text{-}H}$ = 4.1 Hz, Ar*H*), 7.90 (t, 1H, $J_{H\text{-}H}$ = 7.0 Hz, Ar*H*), 7.73 (d, 1H, $J_{H\text{-}H}$ = 7.6 Hz, Ar*H*), 7.56 (d, 1H, $J_{H\text{-}H}$ = 7.5 Hz, Ar*H*), 7.52 (s, 1H, Ar*H*), 7.30–7.28 (m, 1H, Ar*H*), 7.12 (d, 1H, $J_{H\text{-}H}$ = 7.1 Hz, Ar*H*), 2.68 (br q, 2H, $J_{H\text{-}H}$ = 7.3 Hz, CH_2), 1.43 (s, 12H, CH_3), 1.25 (t, 3H, $J_{H\text{-}H}$ = 7.0 Hz, CH_3). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 156.9, 148.0, 143.2, 141.8, 135.1, 131.3, 127.6, 122.2, 121.4, 117.3, 80.3, 29.5, 27.2, 15.6 (*C–B* bond not observed). **^{11}B NMR** (160 MHz, $CDCl_3$): δ = 13.3. **HRMS (EI)** calculated for [$C_{19}H_{24}BNO_2$]: 309.1900. Found: 309.1904. **(EA)** Anal. Calcd for $C_{19}H_{24}BNO_2$: C, 73.80; H, 7.82; N, 4.53. Found: C, 73.34; H, 8.05; N, 4.24.

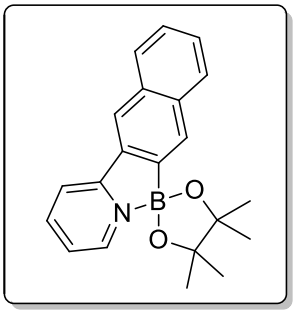


Synthesis of 3-19: Synthesized according to the general procedure using 2-(3-methylphenyl)pyridine (84.6 mg, 0.5 mmol), **3-7** (5.53 mg, 0.005 mmol) and HBPin (128 mg, 1 mmol) in C_6H_6. Purification was achieved by column chromatography using basic alumina eluting with 7:3 EtOAc/hexanes mixture to afford an off–white powder (122 mg, 0.41 mmol) in 83 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.62 (d, 1H, $J_{H\text{-}H}$ = 5.1 Hz, Ar*H*), 7.89 (t, 1H, $J_{H\text{-}H}$ = 7.6 Hz, Ar*H*), 7.73 (d, 1H, $J_{H\text{-}H}$ = 7.9 Hz, Ar*H*), 7.59 (d, 1H, $J_{H\text{-}H}$ = 7.3 Hz, Ar*H*), 7.44 (s, 1H, Ar*H*), 7.29 (t, 1H, $J_{H\text{-}H}$ = 6.3 Hz, Ar*H*), 7.21 (d, 1H, $J_{H\text{-}H}$ = 7.2 Hz, Ar*H*), 2.35 (s, 3H, CH_3), 1.41 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 156.7, 143.2, 141.7, 137.6, 137.4, 132.4, 131.4, 122.6, 121.9, 117.4, 80.2, 27.0, 21.4 (*C–B* bond not observed). **^{11}B NMR** (128 MHz, $CDCl_3$):

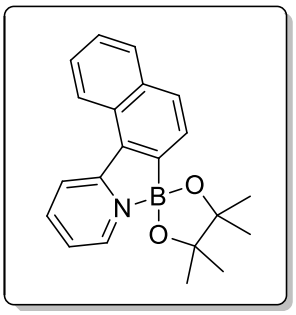
$\delta = 14.2$. **HRMS** (EI-TOF, m/z) calculated for [$C_{18}H_{22}BNO_2$]: 295.1744. Found: 295.1747. **(EA)** Anal. Calcd for $C_{18}H_{22}BNO_2$: C, 73.24; H, 7.51; N, 4.75. Found: C, 73.88; H, 7.98; N, 4.57.



Synthesis of 3-22: Synthesized according to the general procedure using 2-(3,4-dimethylphenyl)pyridine (91.4 mg, 0.5 mmol), **3-7** (5.53 mg, 0.005 mmol) and HBPin (128 mg, 1 mmol) in C_6H_6 (4 mL). Purification was achieved by column chromatography using basic alumina eluting with 7:3 EtOAc/hexanes mixture to afford an off–white powder (119 mg, 0.38 mmol) in 77 % yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.61 (d, 1H, $J_{H\text{-}H}$ = 5.2 Hz, Ar*H*), 7.88 (t, 1H, $J_{H\text{-}H}$ = 7.6 Hz, Ar*H*), 7.71 (d, 1H, $J_{H\text{-}H}$ = 7.9 Hz, Ar*H*,), 7.46 (s, 1H, Ar*H*), 7.41 (s, 1H, Ar*H*), 7.27 (t, 1H, $J_{H\text{-}H}$ = 6.4 Hz, Ar*H*), 2.31 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 1.43 (s, 12H, CH_3). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 156.9, 143.2, 141.6, 140.4, 136.1, 135.4, 132.9, 122.5, 122.1, 117.1, 80.2, 27.0, 20.3, 20.1 (*C–B* bond not observed). **^{11}B NMR** (160 MHz, $CDCl_3$): δ = 13.9. **HRMS** (EI-TOF, m/z) calculated for [$C_{19}H_{24}BNO_2$]: 309.1900. Found: 309.1913. **(EA)** Anal. Calcd for $C_{19}H_{24}BNO_2$: C, 73.80; H, 7.82; N, 4.53. Found: C, 74.19; H, 7.99; N, 4.57.

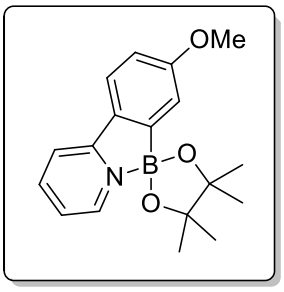


Synthesis of 3-25: Synthesized according to the general procedure using 2-(napthalen-2-yl)pyridine (102.5 mg, 0.5 mmol), **3-7** (5.53 mg, 0.005 mmol) and HBPin (128 mg, 1 mmol) in C_6H_6 (4 mL). Purification was achieved by column chromatography using basic alumina eluting with a 4:1 EtOAc/hexanes mixture to afford a white powder (131 mg, 0.39 mmol) in 79 % yield. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ = 8.72 (d, 1H, $J_{H\text{-}H}$ = 5.2 Hz, Ar*H*), 8.21 (s, 1H, Ar*H*), 8.13 (s, 1H, Ar*H*), 7.99–7.94 (m, 2H, Ar*H*), 7.91 (t, 2H, $J_{H\text{-}H}$ = 9.1 Hz, Ar*H*), 7.53 (t, 1H, $J_{H\text{-}H}$ = 7.1 Hz, Ar*H*), 7.49 (t, 1H, $J_{H\text{-}H}$ = 7.2 Hz, Ar*H*), 7.38 (t, 1H, $J_{H\text{-}H}$ = 5.4 Hz, Ar*H*), 1.49 (s, 12H, C*H*$_3$). **^{13}C NMR** (125 MHz, CD_2Cl_2): δ = 156.1, 143.5, 142.0, 136.2, 136.1, 133.7, 131.0, 128.9, 128.7, 127.3, 126.2, 123.7, 121.6, 118.8, 80.6, 27.3 (*C–B* bond not observed). **^{11}B NMR** (160 MHz, CD_2Cl_2): δ = 13.6. **HRMS** (EI-TOF, m/z) calculated for [$C_{21}H_{22}BNO_2$]: 331.1744, found: 331.1747. **(EA)** Anal. Calcd for $C_{21}H_{22}BNO_2$: C, 76.15; H, 6.69; N, 4.23. Found: C, 76.53; H, 6.95; N, 4.21.



Synthesis of 3-26: Synthesized according to the general procedure 2-(4-ethylphenyl)pyridine (102.4 mg, 0.5 mmol), **3-7** (5.53 mg, 0.005 mmol) and HBPin (128 mg, 1 mmol) in C_6H_6. Purification was achieved by column chromatography using basic alumina eluting with 3:2 hexanes/EtOAc mixture to afford a yellow powder (96 mg, 0.29 mmol) in 58 % yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.76 (d, 1H, $J_{H\text{-}H}$ = 5.0 Hz, Ar*H*), 8.33 (d, 1H, $J_{H\text{-}H}$ = 8.5 Hz, Ar*H*,), 8.28 (d, 1H, $J_{H\text{-}H}$ = 8.1 Hz, Ar*H*), 7.99 (t, 1H, $J_{H\text{-}H}$ = 7.7 Hz, Ar*H*), 7.91–7.88 (m, 3H, Ar*H*), 7.55 (t, 1H, $J_{H\text{-}H}$ =

7.6 Hz, Ar*H*), 7.47 (t, 1H, $J_{H\text{-}H}$ = 7.5 Hz, Ar*H*), 7.37 (t, 1H, $J_{H\text{-}H}$ = 7.4, Ar*H*), 1.43 (s, 12H, CH_3). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 157.7, 144.3, 141.6, 134.7, 133.7, 131.6, 129.8, 129.7, 128.5, 127.1, 125.3, 122.9, 121.9, 121.8, 80.8, 27.2 (*C–B* bond not observed). **^{11}B NMR** (160 MHz, $CDCl_3$): δ = 14.5. **HRMS** (EI-TOF, m/z) calculated for [$C_{21}H_{22}BNO_2$]: 331.1744. Found: 331.1747. **(EA)** Anal. Calcd for $C_{21}H_{22}BNO_2$: C, 76.15; H, 6.69; N, 4.23. Found: C, 76.33; H, 6.84; N, 4.44.



Synthesis of 3-27: Synthesized according to the general procedure using 2-(4-methoxyphenyl)pyridine (92.4 mg, 0.5 mmol), **3-7** (5.53 mg, 0.005 mmol) and HBPin (128 mg, 1 mmol) in C_6H_6 (4 mL). Purification was achieved by column chromatography using basic alumina eluting with with 7:3 EtOAc/hexanes mixture to afford an off–white powder (126 mg, 0.40 mmol) in 81 % yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.57 (d, 1H, $J_{H\text{-}H}$ = 5.2 Hz, Ar*H*), 7.87 (t, 1H, $J_{H\text{-}H}$ = 7.7 Hz, Ar*H*), 7.65 (d, 1H, $J_{H\text{-}H}$ = 7.9 Hz, Ar*H*), 7.56 (d, 1H, $J_{H\text{-}H}$ = 8.3 Hz, Ar*H*), 7.26–7.22 (m, 2H), 6.79 (d, 1H, $J_{H\text{-}H}$ = 8.1 Hz, Ar*H*), 3.86 (s, 3H, OCH_3), 1.41 (s, 12H, CH_3). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 162.8, 156.7, 143.0, 141.9, 130.0, 122.8, 121.5, 116.7, 116.4, 113.8, 80.2, 55.4, 27.2 (*C–B* bond not observed). **^{11}B NMR** (160 MHz, $CDCl_3$): δ = 13.0. **HRMS** (EI-TOF, m/z) calculated for $C_{18}H_{22}BNO_3$: 311.1693. Found: 311.1696. **(EA)** Anal. Calcd for $C_{18}H_{22}BNO_3$: C, 69.47; H, 7.13; N, 4.50. Found: C, 69.02; H, 7.09; N, 4.50.

General Procedure for the catalytic C-H borylation of 3-36 (Table 3-5): In a nitrogen-filled glovebox, a 1 dram vial was charged with **3-36** (0.1 mmol), B_2Pin_2 (0.1 mmol), and catalyst (2 mol%) were added as solids, and dissolved in the indicated solvent (0.8 mL). The vial was tightly sealed with a Teflon lined cap, and wrapped in electrical tape, then heated to the indicated temperature for 16 hours. Upon cooling the sample to room temperature, the mixture was diluted with $CHCl_3$ (3 mL) and 1,3,5-trimethoxy benzene was added as an internal standard. The reaction mixture was filtered through Celite and washed with $CHCl_3$. The yields listed were estimated by ^{1}H NMR spectroscopy. For **3-40**: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.65 (d, 2H, $J_{H\text{-}H}$ = 8.2 Hz, Ar*H*), 7.17 (d, 2H, $J_{H\text{-}H}$ = 8.2 Hz, Ar*H*), 4.56 (t, 2H, $J_{H\text{-}H}$ = 9.4 Hz, CH_2), 4.03 (t, 2H, $J_{H\text{-}H}$ = 9.4 Hz, CH_2), 2.38 (s, 3H, CH_3), 1.28 (s, 12H, CH_3). **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 27.4 ppm.

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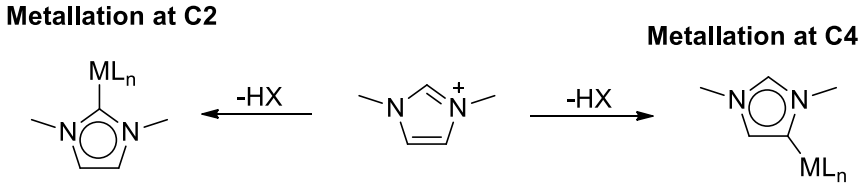
Chapter 4

1,2,3-Triazole Derived Mesoionic Carbene Complexes: Synthesis, Structure and Catalysis

4.1 Introduction

4.1.1 Abnormal Binding and Mesoionic Carbenes

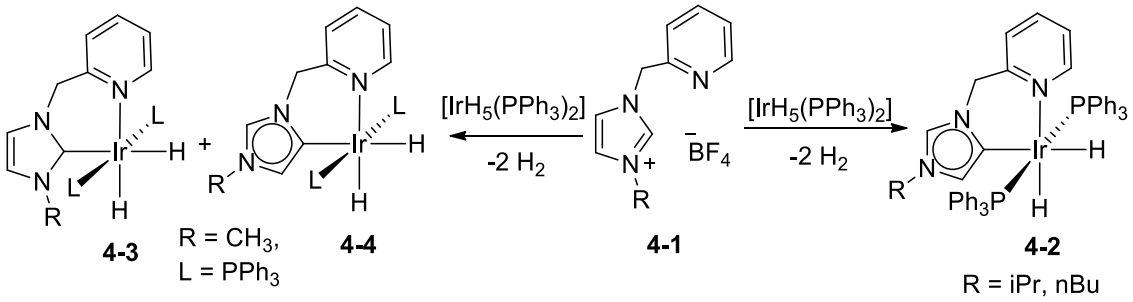
In the past decade there have been an increasing number of reports of metal carbene complexes that display unpredicted coordination chemistry,[1] most prominently, imidazole-derived carbenes coordinated at the C4 position instead of C2 (Scheme 4-1).[2] Preferential coordination at C4 over C2 is quite remarkable, as the pKa of the proton at C4 in imidazole has been calculated to be 33,[3] which is substantially higher than that calculated at C2 position (24). This large difference in pKa suggests that factors other than acidity are relevant for predicting the site of metallation.



Scheme 4-1: Comparison of metallation at either C2 or C4 of imidazolium ions

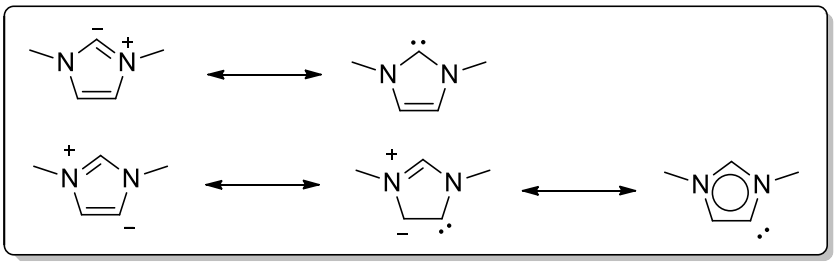
The first example of metallation at C4 was reported by Crabtree and coworkers in 2002 (Scheme 4-2).[4] While investigating the coordination of pyridine-functionalized imidazolium salt **4-1** to $[IrH_5(PPh_3)_2]$, Crabtree and co-workers found that complex **4-2** formed in preference to the expected product from metallation at C2. Importantly, no

isomerization of complex **4-2** to a C2-bound form was observed, even under forcing conditions. The same ligand also gave C4 metallation when reacted with osmium poly-hydride complexes,[5] and Li and coworkers have observed similar backbone metallation in the reaction of phosphine functionalized imidazolium salts with $[Ir(COD)Cl]_2$.[6]



Scheme 4-2: Crabtree's observed abnormal binding of NHCs to iridium[4, 7]

Due to the abnormal binding mode, ligands formed by metallation at C4 have been termed abnormal carbenes (aNHC).[4] As no neutral canonical structure can be obtained for these species (Scheme 4-3), the term mesoionic carbene (MIC) is likely a better description, however C4 bound imidazoles are still commonly termed aNHCs.[8]

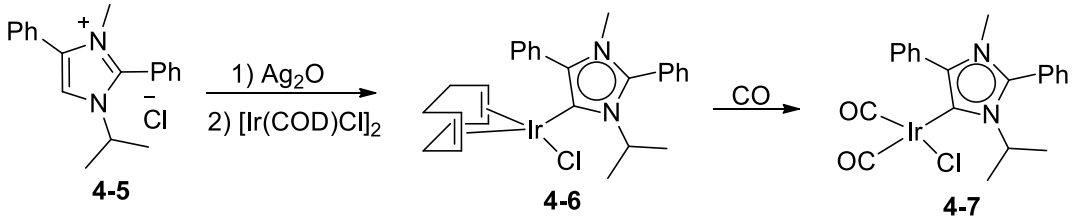


Scheme 4-3: Important resonance structures pertaining to NHCs and MICs

Several factors were identified for preferential C4 metallation of **4-1**. Crabtree observed that smaller wingtip groups such as CH_3 gave a mixture of C2 and C4 metallated products, while larger groups such as iPr or nBu groups favoured selective metallation at

C4.[7] The nature of the halide was also found to impact the site of metallation, as non-coordinating anions such as BF_4 led to C4 metallation, whereas coordinating anions such as halides favoured C2.[9]

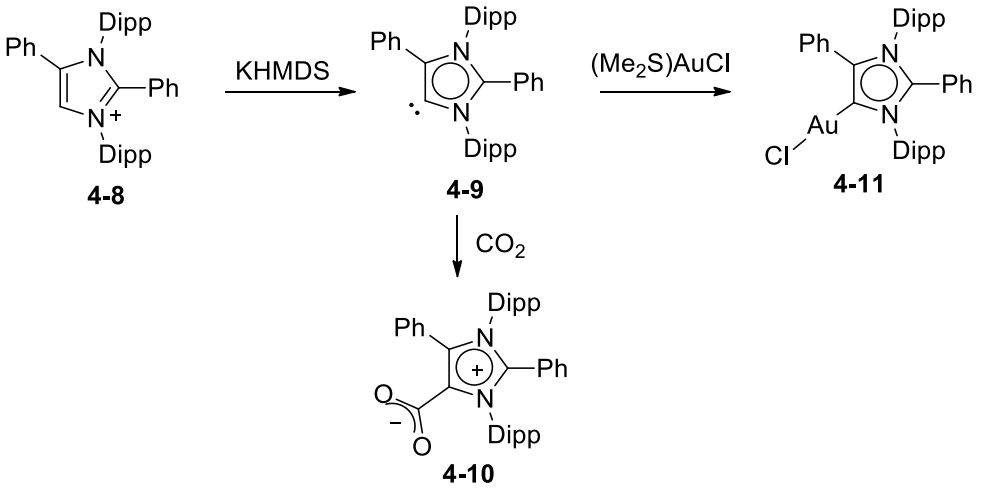
After these somewhat isolated reports, focus turned to finding general methods for selective C4 metallation.[10] In one successful method, the C2 site is blocked with an alkyl or aryl group to force metallation at C4,[10b, 11] and then common metallation strategies for NHCs can be used for the C4 site, albeit sometimes under more forcing conditions.[1] For example, treatment of C2 protected imidazolium salt **4-5** with Ag_2O results in an Ag-aNHC complex**,** which can be transmetallated to transition metals such as $[Ir(COD)Cl]_2$ to make **4-6** and finally **4-7** upon exposure to CO (Scheme 4-4).[12]



4-5 4-6 4-7

Scheme 4-4: Synthesis of Ir-MIC complex via Ag-MIC transmetallation[12]

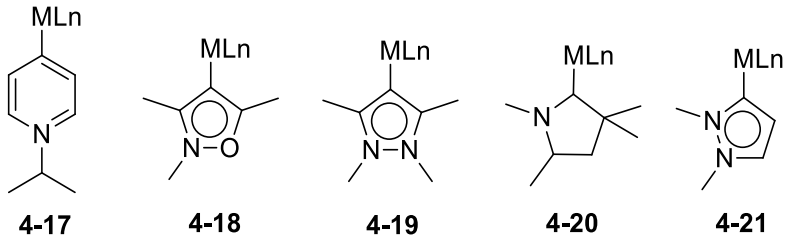
The C4 position of C2-protected imidazolium precursors can also be deprotonated in the presence of strong bases. In 2009, Bertrand described the deprotonation of **4-8** resulting in the isolation of free carbene **4-9** (Scheme 4-5).[13] Judicious choice of base, and substantial steric bulk around the carbene site was required in order to stabilize this highly reactive species, which could then be treated with $(Me_2S)AuCl$ or CO_2 resulting in stable aNHC adducts **4-10** and **4-11**.



Scheme 4-5: Bertrand's isolation of a free MIC and its activity towards transition metals and CO_2[13]

In this same paper, the authors reported the crystal structure of free carbene **4-9**, which allowed them to probe the validity of the carbene resonance structure. Consistent with the formation of a carbene,[14] lengthening of the endocyclic C-N and C-C bond lengths were observed, and the carbene bond angle was made more acute from the parent imidazolium salt.

A variety of other heterocycles can also be converted to carbenes that have decreased heteroatom stabilization of the carbene carbon (Scheme 4-6).[15] In many cases, similar methods to those described above can be utilized for the metallation of these ligands.[16] As new and exciting applications are discovered for these ligands, it is likely that more new libraries of ligand families will continually be investigated.

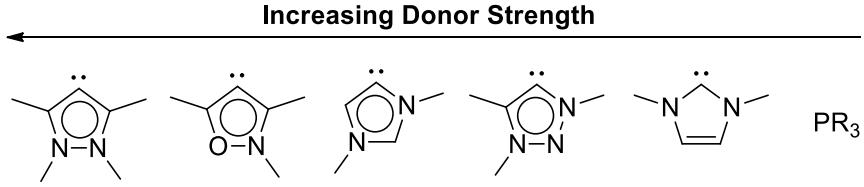


4-17 **4-18** **4-19** **4-20** **4-21**

Scheme 4-6: Selected list of non-imidazole derived carbenes

4.1.2 Electronic Implications of Abnormal Binding Modes

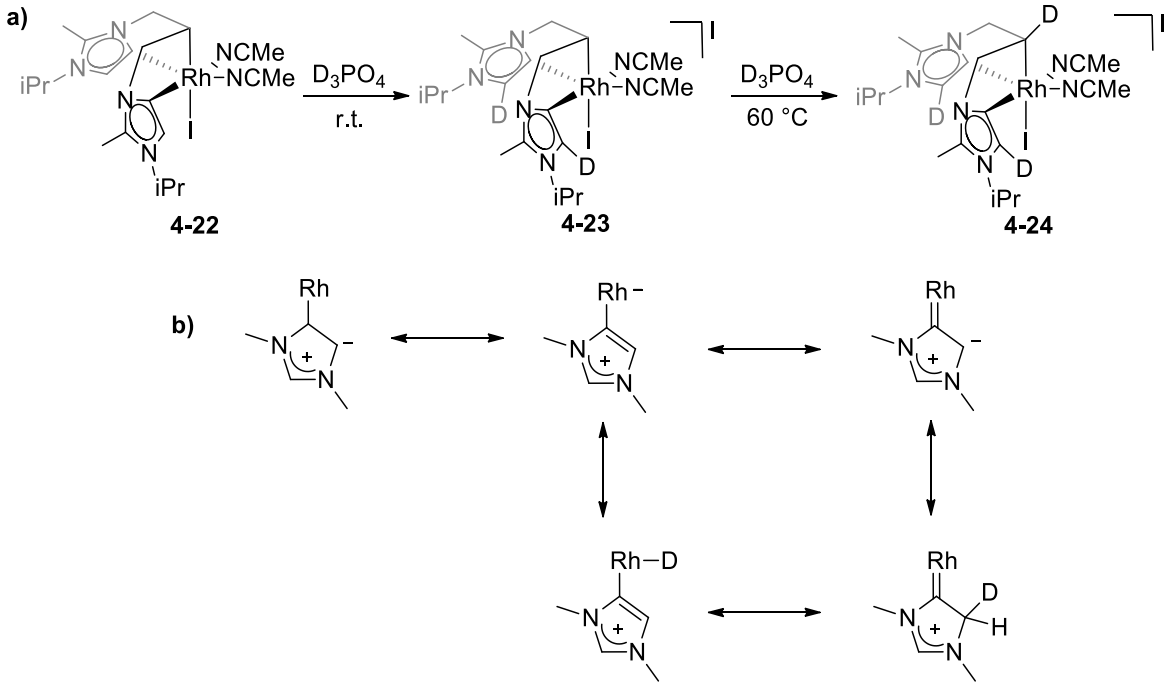
In addition to their unique bonding properties, MICs are interesting because they produce complexes which are more electron rich than even NHCs (Figure 4-1).[15c, 17] This can be rationalized by inductive effects provided by the pendant N groups flanking the carbene atom.[12] While MICs have decreased stabilization due to having only one adjacent donor atom, they also experience a decreased inductive stabilization, resulting in a higher electron density on the carbene carbon.



Scheme 4-7: Relative bond strengths of different MIC ligands compared to NHCs and phosphines

In some cases, these effects translate into complexes surpassing the catalytic activity of NHC complexes.[18] Importantly, various reports have also demonstrated the non-innocent behaviour of MICs while bound to a transition metal.[2, 7, 18b] For example, as shown in Figure 4-2a, deuterium is incorporated into the backbone of the rhodium-bound chelating aNHC ligand in **4-22** upon treatment with D_3PO_4.[18b] This cannot be explained by mere

protonolysis, and instead is likely associated with the mesoionic character of the carbene (Figure 4-2b). There is currently an active effort to utilize this behaviour of these ligands for catalysis.

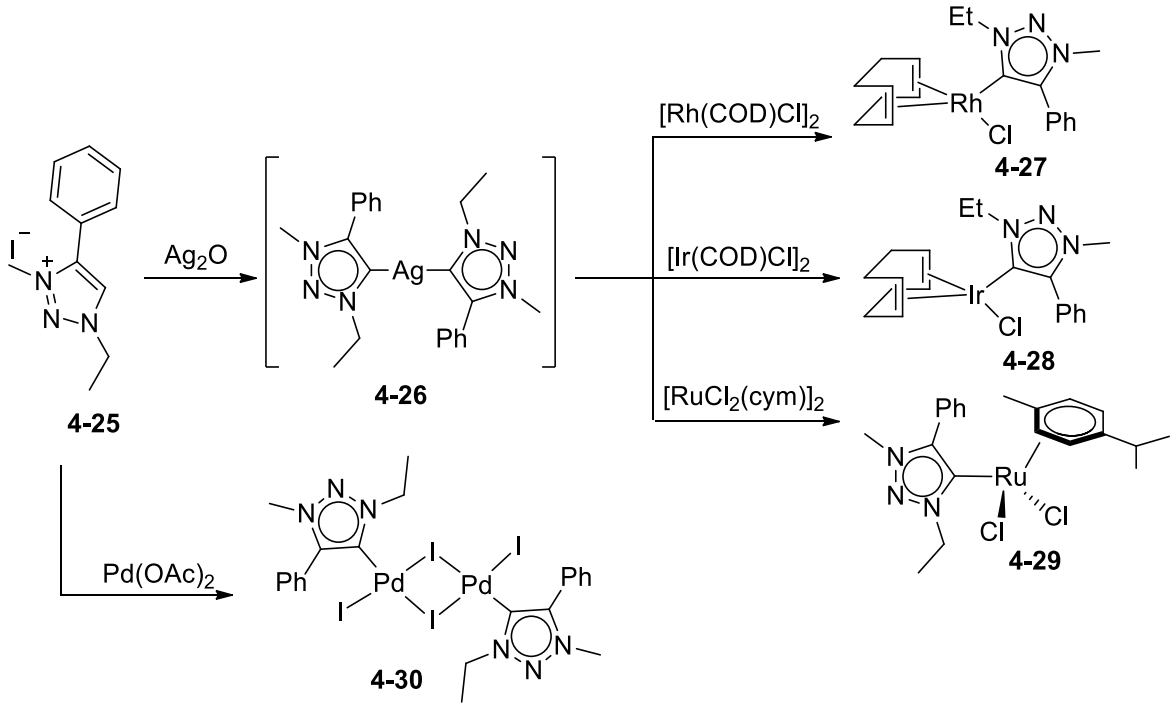


Scheme 4-8: a) Deuteration of Albrechts' chelating aNHC ligand, demonstrating mesoionic character and b) the proposed mechanism for deuteration[18b]

4.1.3 Triazole Derived MICS: 1,2,3-Triazol-5-ylidenes

In 2008, Albrecht and coworkers reported the synthesis of MIC ligands derived from alkylated 1,2,3 triazolium salts (tMICs).[19] The power of this route is that the carbene precursors can be easily synthesized by copper catalyzed Huisgen cycloaddtions which are commonly known as "Click" reactions,[20] followed by simple regioselective alkylation of the N3 nitrogen. The activation of **4-25** with Ag_2O resulted in Ag-tMIC complex **4-26** that could then be transmetallated to a variety of other transition metals (Scheme 4-7). Alternatively, similar to NHCs, **4-25** could be directly reacted with $Pd(OAc)_2$ in DMSO at

120 °C to form **4-30**. Similarly to aNHCs, these ligands were shown to be stronger donors than most NHC ligands, while being less strongly donating than aNHC ligands.[21] Most appealing about these ligands was their facile synthesis, indicating ready modification of their steric parameters, which is highly appealing for tuning catalytic behaviour.



Scheme 4-9: Albrecht's metalation of tMIC ligands[19]

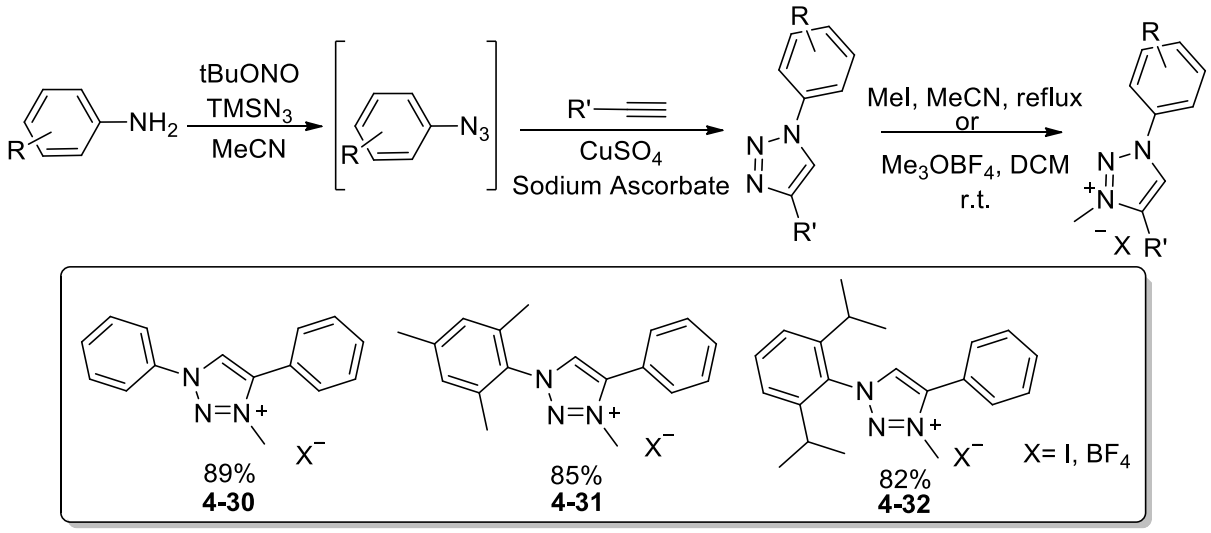
4.2 Results and Discussion

4.2.1 Isolation of Free tMIC Ligands and Their Metallation via Deprotonation

After Albrecht's initial report,[19] our group became interested in exploring the fundamental structure and coordination chemistry of these ligands, particularly with regard to new possible uses in catalysis. Historically, our group has employed free carbenes for the synthesis of metal complexes as opposed to the in situ generation of carbene from

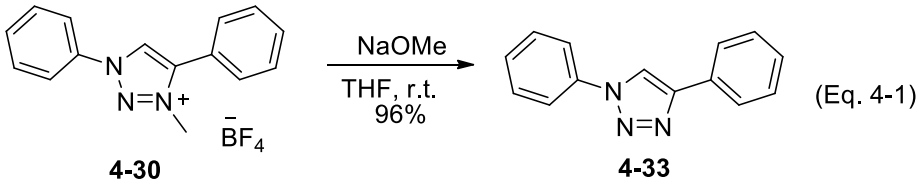
imidazolium salts and base. The former method is more likely to result in predicted structures to a higher degree than other methods.[22] In Albrecht's report however, the authors indicated that their attempts at metallating tMICs avoided the isolation of the free carbene, as they expected these species to be too unstable.[19] Indeed, the ligands that were originally reported were relatively small in nature, and could potentially decompose by the Wanzlick equilibrium (Scheme 1-2).[23] As a result, we hypothesized that incorporation of sterically larger wingtip groups around the carbene center would dramatically increase the relative stability of tMIC-based carbenes, potentially making them isolable.

The ligands displayed in Scheme 4-10 were chosen as initial candidates to test the stoichiometric deprotonation of tMIC salts. The synthesis of the parent triazoles was achieved by a convenient one-pot protocol reported by Moses and coworkers starting from simple anilines and acetylenes in high yields.[24] The alkylation proved slightly more difficult than was expected however, and extended reaction times in refluxing solvent were required for successful alkylation with a large excess of methyl iodide. Instead, the use of Meerwein's salt (Me_3OBF_4) was far more appealing as it gave complete conversion to product within a few hours stirring at room temperature in $PhCF_3$ or CH_2Cl_2.



Scheme 4-10: General synthesis of triazolium salts chosen for investigation

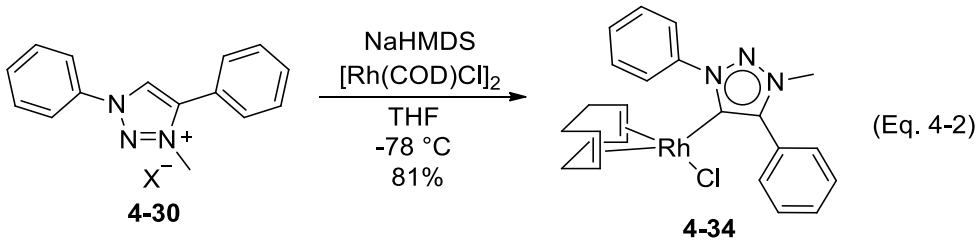
Based on our efforts with NHCs, we began investigating the deprotonation of tMIC salts with alkoxide bases such as KOtBu, or NaOMe, but we quickly found these bases were inappropriate choices. For example, when **4-30** was treated with 1.5 equiv. NaOMe in THF at room temperature, clean demethylation was observed giving the parent triazole **4-33** in near quantitative yield (Eq. 4-1). As a result, we opted to investigate the use of less nucleophilic bases such as NaHMDS, in hopes that this would decrease the possibility of demethylation.



(Eq. 4-1)

To further avoid the decomposition routes, we also examined the deprotonation of **4-30** in the presence of a transition metal, which would effectively trap the free carbene. Thus, **4-30** was reacted with 1.05 equiv. of NaHMDS at -78 °C in THF in the presence of

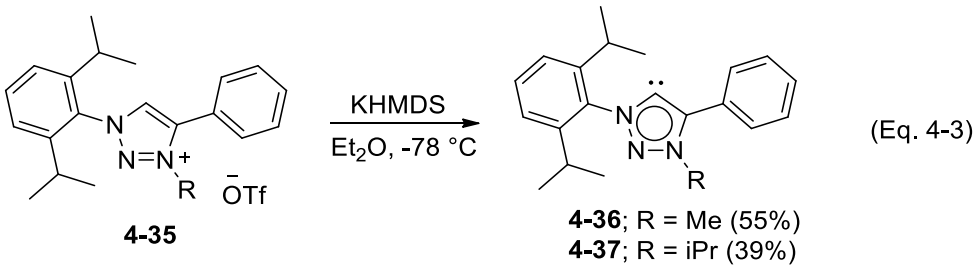
0.5 eq. of $[Rh(COD)Cl]_2$, followed by warming to room temperature (Eq. 4-2). This resulted in clean formation of air stable complex **4-34**, which was purified by silica gel column chromatography and isolated in 81% yield. Complex **4-34** was characterized by ^1H NMR, namely by the disappearance of the downfield resonance corresponding to the triazole C-H at 9.61 ppm (in Acetone-d_6). In addition, the ^{13}C NMR spectrum displayed a characteristic resonance at 171.93 ppm, with a $^1J_{Rh\text{-}C}$ = 46.3 Hz. Importantly, the formation of complex **4-34** clearly indicates the successful formation of the free carbene.



4-30 **4-34** (Eq. 4-2)

Thrilled with this result, we began expanding upon our results in order to make tMIC complexes of other transition metals using this procedure, and planned on continuing our attempts at isolation of the free carbene from triazolium salts **4-31** and **4-32**. Unfortunately, at this time, Bertrand and coworkers reported the synthesis and isolation of the free tMICs upon deprotonation from the corresponding triflate salts (Eq. 4-3).[25] This report described problems with carbene decomposition resulting from demethylation similar to what was observed in our hands, but the Bertrand group was able to overcome these problems by instead using a larger 2,6 diisopropylphenyl wingtip group, and an isopropyl alkyl group which resisted dealkylation relative to the methyl group. When both oxygen and moisture are excluded, methyl substituted **4-36** is stable at room temperature for only a few hours and decomposes at 50 °C. Isopropyl variant **4-37** is stable at room temperature for multiple days, and has a melting point of 120 °C. Importantly, Bertrand

also reported the x-ray crystal structure of **4-36**, which allowed the authors to probe the structure of the carbene. Similarly to aNHCs, the crystal structure displayed that the C5 bond angle becomes more acute upon deprotonation, consistent with an increase in s character in the σ-lone pair orbital, which is indicative of the formation of a carbene.



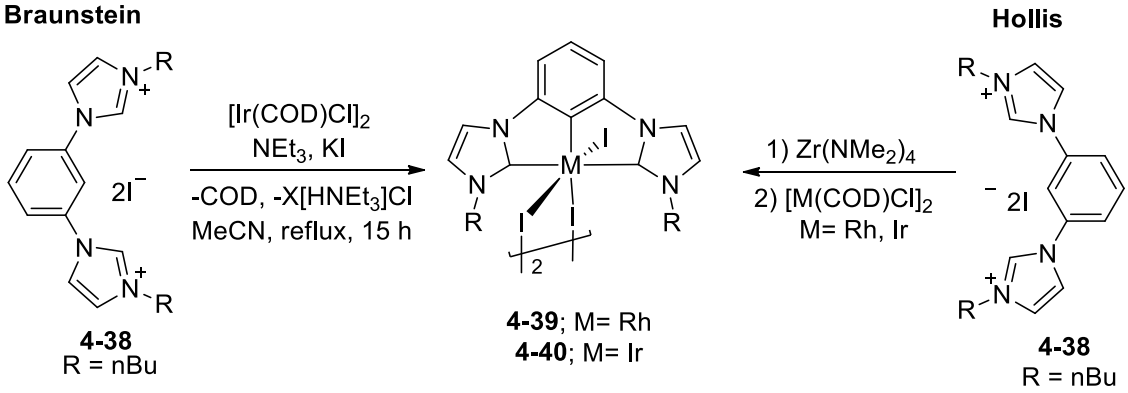
(Eq. 4-3)

Soon afterwards, there were several other reports of various transition metal complexes bound to tMIC ligands.[26] Almost exclusively, these ligands were simple derivatives of Albrecht's original reported ligands. In almost all cases, metallations were performed using transmetalation protocols, from intermediate Ag-tMIC complexes, which were themselves never isolated. From our perspective, one of the biggest selling points of these ligands was the ready tunability of the flanking wingtip groups for both electronic and steric modification. In this regard, none of the literature methods really brought this concept to fruition. Thus we became interested in advanced ligand architectures such as chelating and pincer-type ligands,[27] which featured a tMIC motif.

4.2.2 Investigation into Pincer-Type Complexes of tMIC Ligands

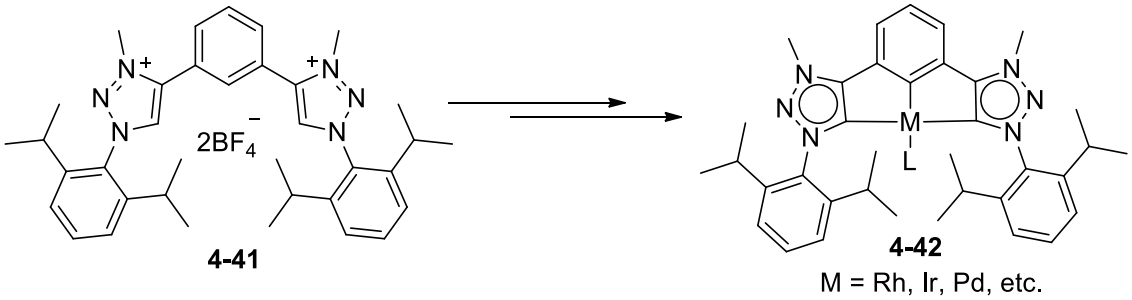
Pincer ligands derived from NHCs that feature a central phenyl backbone are quite rare, and only a few examples have been reported.[28] In contrast however, pincer ligands featuring phosphine, or pyridine groups have an extensive history in organometallic chemistry,[27] and display high activity in several organic transformations.[29] The dearth of

CCC pincer ligands in the literature is likely associated with difficulties in their metallation. Despite these difficulties, both Hollis[30] and Braunstein[28d] demonstrated the synthesis of complexes **4-39** and **4-40** from the same ligand ((**4-38**), Scheme 4-11). While Hollis activated **4-38** onto $Zr(NMe_2)_4$ followed by transmetalation to both rhodium and iridium, Braunstein was able to directly activate **4-38** by using a weak base such as triethyl amine in the presence of $[Ir(COD)Cl]_2$. Chianese and coworkers observed similar activation with benzimidazole derivatives, and documented the importance of steric parameters of the NHC ligand.[31]



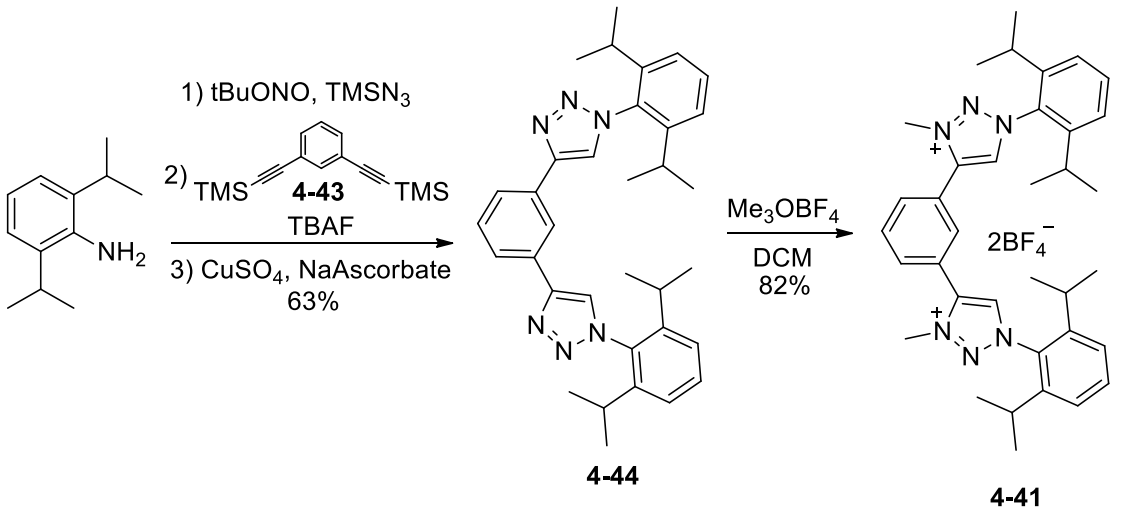
Scheme 4-11: The selective formation of rhodium and iridium CCC pincer complexes[28d, 32]

We hypothesized that triazolium salt **4-41** would be a suitable precursor for pincer complexes of general structure **4-42** (Scheme 4-12). The reported synthetic pathways for **4-39** and **4-40** were of great interest to us, as they avoided the isolation of the free carbene derived from **4-38**. Thus we elected to investigate the coordination of **4-41** to transition metals in the hopes of forming complexes of general structure **4-42**.



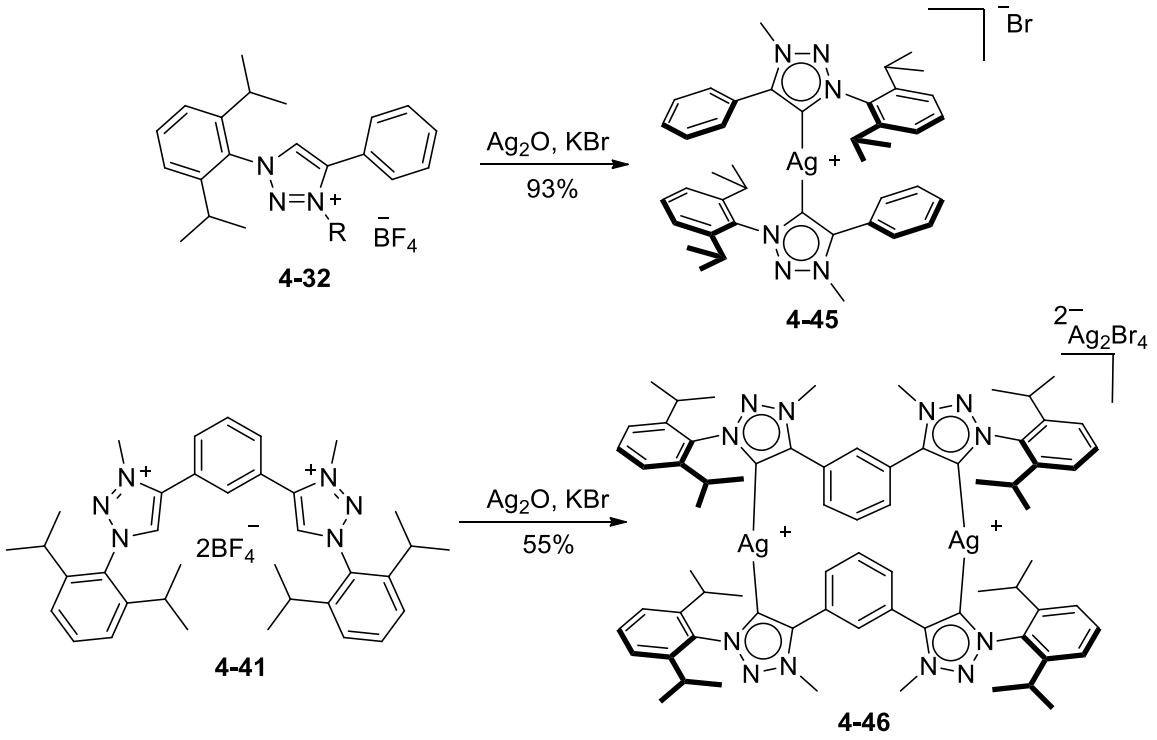
Scheme 4-12: Proposed preparation of pincer-type tMIC ligands

Ligand precursor **4-41** was synthesized by the protocol displayed in Scheme 4-13. TMS protected acetylene **4-43** was synthesized via Sonogashira coupling of 1,3-dibromobenzene, and was subjected to a copper catalyzed click reaction with 2,6-diisopropylphenyl azide after deprotection with TBAF. Conveniently a one pot procedure was developed in which the azide was synthesized, the TMS-diyne deprotected and the click reaction performed, all in a combined 63% yield. This was followed by regioselective methylation with Me_3OBF_4 in CH_2Cl_2 giving **4-41** in 82% yield.[33] The ^1H NMR spectrum of **4-41** was highly symmetrical, and only a single resonance was observed for the trz-CH_3 group.



Scheme 4-13: Synthesis of tMIC ligand precursors for pincer complexes

In order to investigate the coordination chemistry of **4-41**, we pursued the possibility of activating it with Ag_2O prior to the transmetalation to other transition metals (Scheme 4-14).[34] Thus, the light sensitive Ag-tMIC complexes **4-45** and **4-46** could be synthesized under very mild conditions by modification to a procedure reported by Cavell and coworkers.[35] Quantitative formation of **4-45** was observed upon reaction of **4-41** with 3.5 eq. of Ag_2O in acetonitrile, after extended reaction times (3 days). This procedure was found to be general, as similar behaviour was observed with **4-32**. Clean deprotonation of the C-H was clearly evident by ^1H NMR spectroscopy, which clearly showed the disappearance of the signals at 8.98 and 8.84 ppm for **4-32** and **4-45** respectively. The identities of the complexes were predicted based on HRMS of the two complexes which gave m/z values of 745.3143 for **4-45**, indicative of a compound with the formula $[(tMIC)_2Ag]^+$, and 667.2581 for **4-46**, which is the cationic fragment of $[(tMIC)_2Ag_2]^{2+}$. The low yield obtained with **4-46** was attributed to the formation of insoluble oligomeric complexes which that may have been removed during filtration.



Scheme 4-14: Activation of **4-32** and **4-41** with Ag_2O

At this time, although several Ag-tMIC complexes had been reported as intermediates for transmetalation, not a single crystal structure had been reported. Ag-NHC species are known to crystallize in a wide variety of complex structures, and can exhibit complicated equilibria making their characterization difficult.[36] While all attempts to crystallize **4-45** were unsuccessful, single crystals suitable for x-ray diffraction were obtained of **4-46** by slow diffusion of hexanes into a concentrated CH_2Cl_2 solution. The crystal structure of **4-46** confirmed the dimeric structure which was purposed based on the HRMS data, and elucidated the anion of the complex as $[Ag_2Br_4]^{2-}$. Similar such complexes have been reported by Crowley using related ligands on gold.[37]

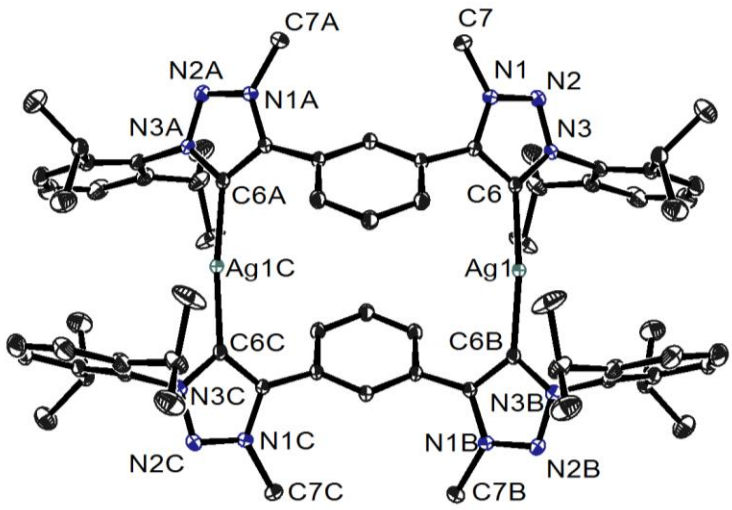
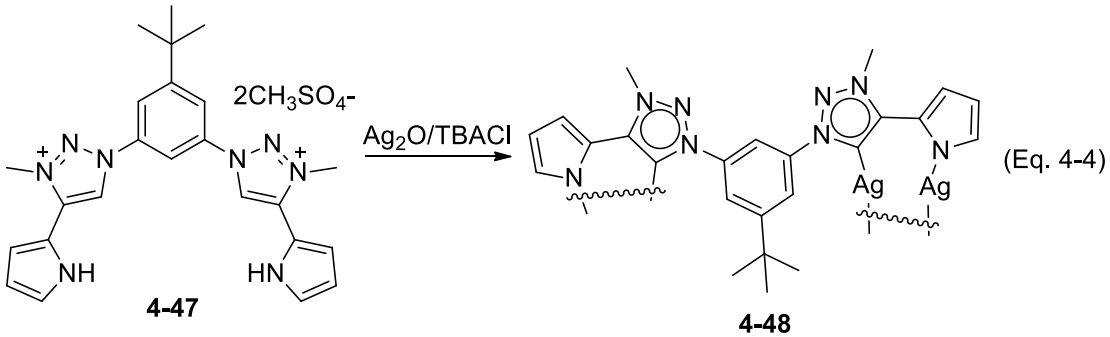


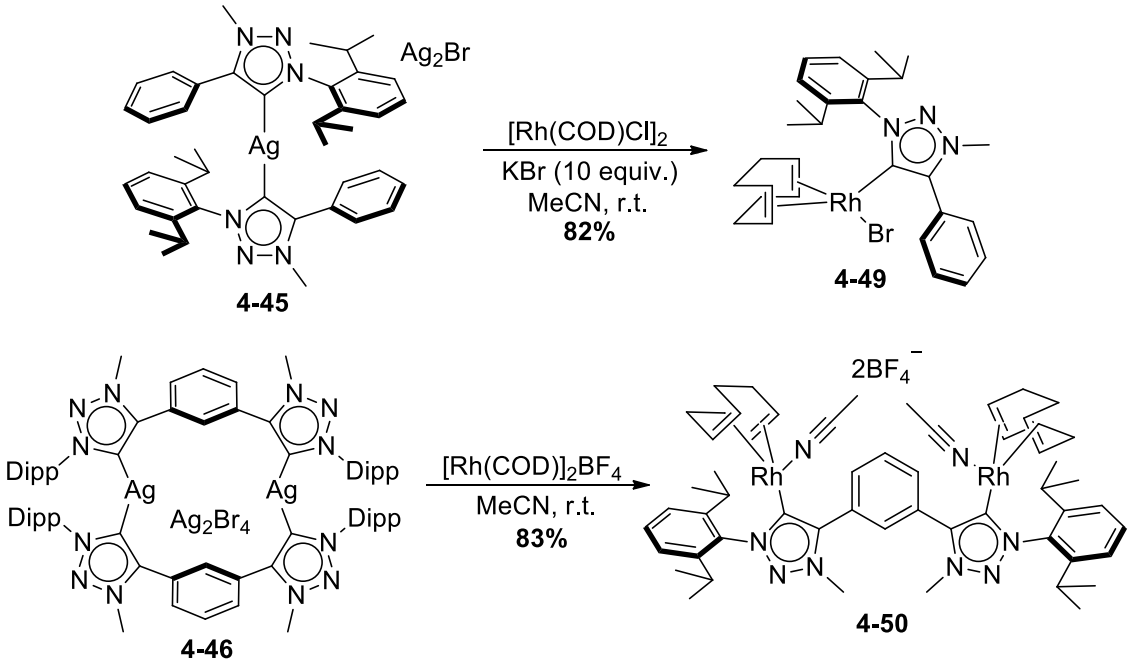
Figure 4-1: Crystallographically determined structure of **4-46** displaying thermal ellipsoids drawn at the 50 % confidence level. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Ag(1)−C(6), 2.075(7); N(2)−N(3), 1.340(8); N(1)−N(2), 1.321(9); N(3)−C(6), 1.350(8); N(1)−C(7), 1.477(9); C(6)−Ag(1)−C(6B), 173.9(3)

While our manuscript was in preparation, Bielawski and coworkers reported the synthesis of tMIC ligand precursor **4-47** and Ag complex **4-48** (Eq. 4-4).[38] A crystal structure of complex **4-48** was reported which helped the authors confirm the identity of the highly complicated species. Similar to complex **4-46**, complex **4-48** appeared to exhibit a substantially rigid structure, which may be an important factor in the crystallization of Ag-tMIC complexes.[39] The transmetallation of **4-48** to ruthenium was also reported.



Interested in the synthesis of Rh-tMIC complexes, we first treated **4-45** with 1 equivalent of $[Rh(COD)Cl]_2$ in MeCN at room temperature (Scheme 4-15). A large excess (10 equivalents) of KBr was added to the reaction mixture in order to avoid halide scrambling. This resulted in the formation of complex **4-49**, which could be purified by column chromatography. The ^{13}C NMR spectrum of **4-49** displayed a characteristic carbene peak at 173.5 ppm, with a $^{1}J_{Rh\text{-}C}$ = 48.09 Hz. Single crystals suitable for x-ray crystallography were grown from the slow evaporation of a CH_2Cl_2 solution of **4-49**, and permitted the unambiguous assignment of the Rh-tMIC complex as that shown in structure **4-49**, (Figure 4-4).

Similarly, bidentate MIC–Ag derivative **4-46** was transmetallated to cationic $[Rh(COD)_2]BF_4$, which resulted in the formation of bimetallic cationic complex **4-50**, Chelated complexes were never observed, regardless of the initial rhodium loading. Interestingly, complex **4-50** exhibits a very symmetrical ^{1}H NMR spectrum, indicative of the presence of only one complex. This is in contrast to the results of Hollis and coworkers, who found a similar neutral bimetallic rhodium NHC complex that exists as an interconverting mixture of two diastereomeric complexes.[40] Similarly to **4-49**, the ^{13}C NMR spectrum of **4-50** displays a characteristic peak at 166.8 ppm coupled to Rh ($^{1}J_{Rh\text{-}C}$ = 47.17 Hz). Single crystals suitable for x-ray crystallography of complexes **4-50** were grown from the slow diffusion of hexanes into a concentrated 1:1 CH_2Cl_2:THF solution (Figure 4-2). The crystal structure of complex **4-50** shows substantial twisting (53.51°) of the two triazole moieties about the central phenyl ring, which positions the rhodium centres anti to one another, likely for steric reasons. The positioning of the metals in such a manner may be associated with the failure to form bidentate complexes.



Scheme 4-15: Transmetallation of Ag-tMIC complexes to Rh[33]

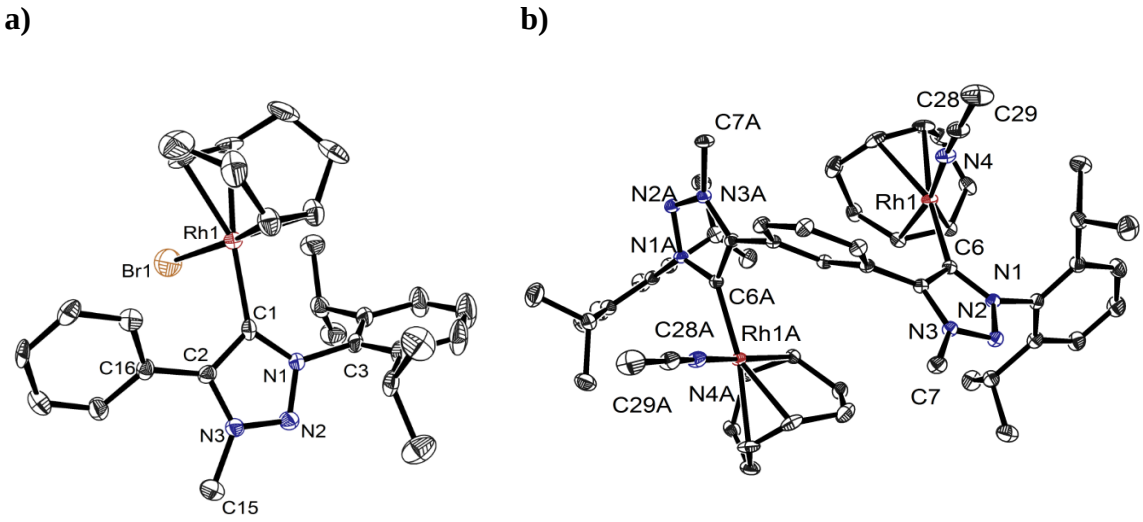
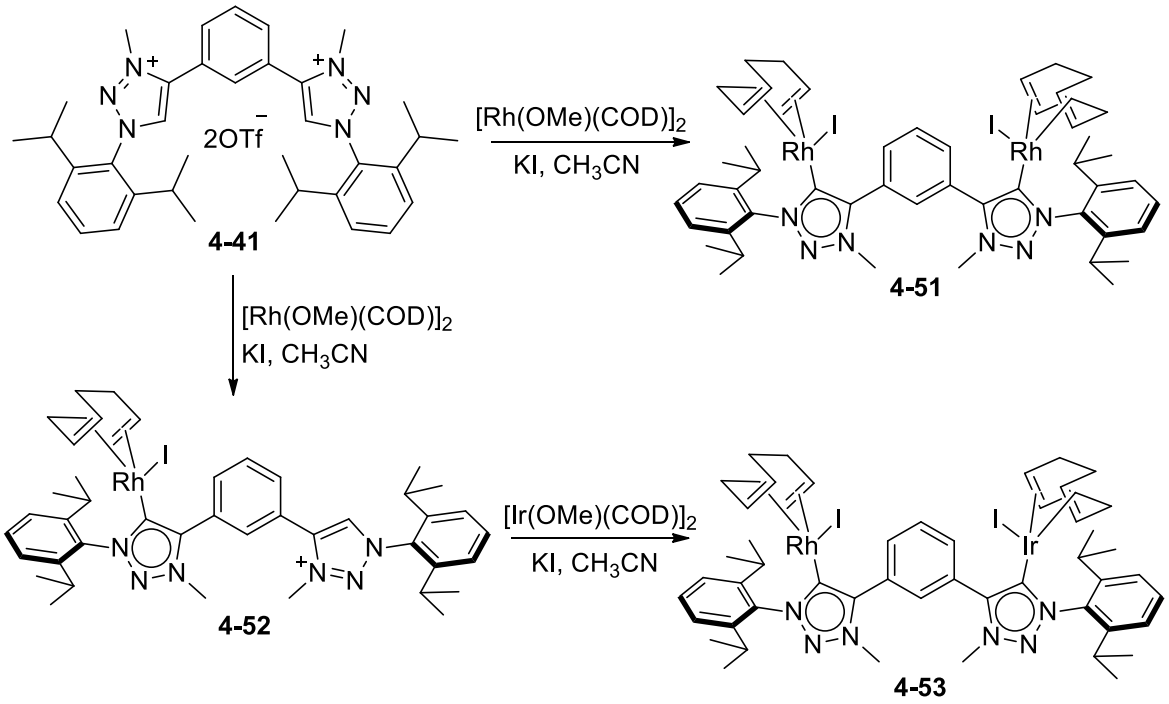


Figure 4-2: Crystallographically determined structure of (a) **4-49** and (b) **4-50** displaying thermal ellipsoids drawn at the 50 % confidence level. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: a) **4-49**: Rh(1)−C(1), 2.044(6); Rh(1)−Br(1), 2.4937(10); C(2)−C(16), 1.465(9); N(1)−C(3), 1.436(7); N(1)−C(1), 1.372(8); N(2)−N(3), 1.308(7); N(3)−C(15), 1.483(8); Br(1)−Rh(1)−C(1), 87.54(17). b) **4-50**: Rh(1)−C(6), 2.048(4); Rh(1)−N(4), 2.060(3); C(28)−C(29), 1.459(6); N(2)−N(3), 1.314(4); N(1)−N(2), 1.346(4); N(1)−C(6), 1.361(5); N(3)−C(7), 1.468(4); N(4)−Rh(1)−C(6), 86.70(13).

A similar report appeared shortly after our paper by Cowie's group, which described the synthesis of neutral complex **4-51** by directly reacting the triflate salt of **4-41** with $[Rh(COD)OMe]_2$ as a metal precursor (Scheme 4-16).[41] In this case, it was possible to obtain monometallic complexes **4-52** by using lower loadings of metal precursor, however once again no cyclometallation was observed. This method did however, allow for the formation of mixed bimetallic Rh/Ir complex **4-53**, upon the treatment of monometallic **4-52** with $[Ir(OMe)(COD)]_2$.

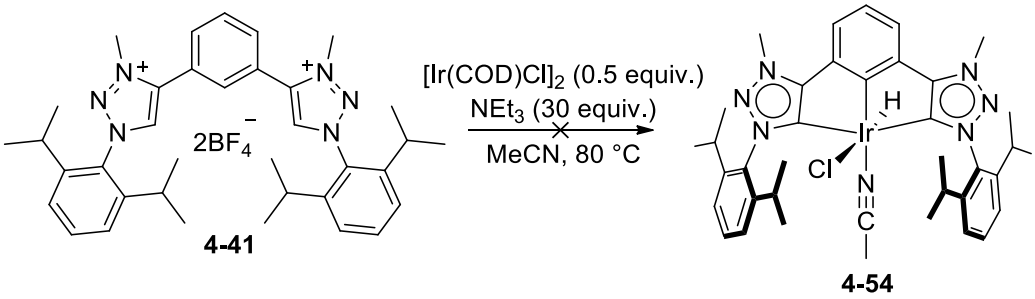


Scheme 4-16: Cowie's reported synthesis of bimetallic rhodium/iridium tMIC complexes[41]

In further attempts to isolate pincer type complexes, the transmetallation of **4-46** to other rhodium precursors such as $[Rh(COE)_2Cl]_2$ and $[Rh(C_2H_4)_2Cl]_2$ was also

investigated, but unfortunately the resulting species were very unstable, giving intractable mixtures along with elemental rhodium. The higher oxidation state [$RhCl_3$] was also investigated, as Bergman and Tilley previously reported it to undergo cyclometallation with pincer ligands derived from oxazolines.[42] Unfortunately, however, this metal precursor was ineffective as it failed to undergo any observable transmetalation as indicated by ^{1}H NMR spectroscopy, and the parent Ag-tMIC complex was recovered.

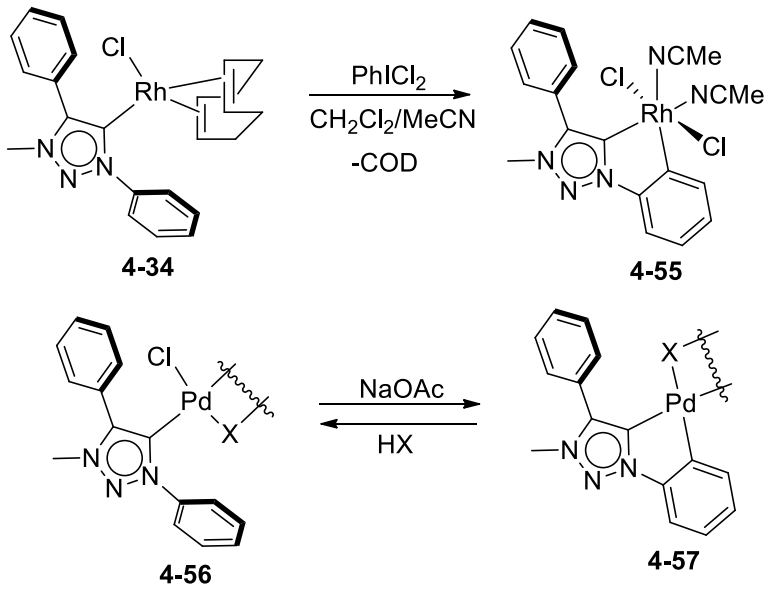
Conditions reported by Braunstein,[28d] and adapted by Chianese[31] for the formation of Ir-CCC pincer complexes were also investigated on ligand **4-41** (Scheme 4-17). But in all cases, the weak bases utilized failed to produce any observable product, and complete recovery of starting material was observed. This may be associated with the decreased acidity of the triazolium salt in comparison to imidazoles, or related to the increased steric environment around the carbene carbon.[31]



Scheme 4-17: Failed attempt at metallation onto iridium

The inability of ligand **4-41** to cyclometallate under all investigated conditions is likely explained by a later report by Albrecht and coworkers, detailing the importance of higher oxidation state metals for cyclometallation of tMIC ligands to occur.[43] For example, rhodium complex **4-34** only undergoes cyclometallate upon oxidation to Rh^{III} complex **4-55**. Similarly, Pd^{II} complex **4-56** undergoes reversible cyclometallation in the presence of

NaOAc to form **4-57** (Scheme 4-18). In addition, a further hindrance may be observed in that most examples of successfully cyclometallated tMIC ligands undergo cyclometallation at the more electron rich wingtip group bound to the N substituent of the triazoles, which is unavailable in ligand precursor **4-41**.



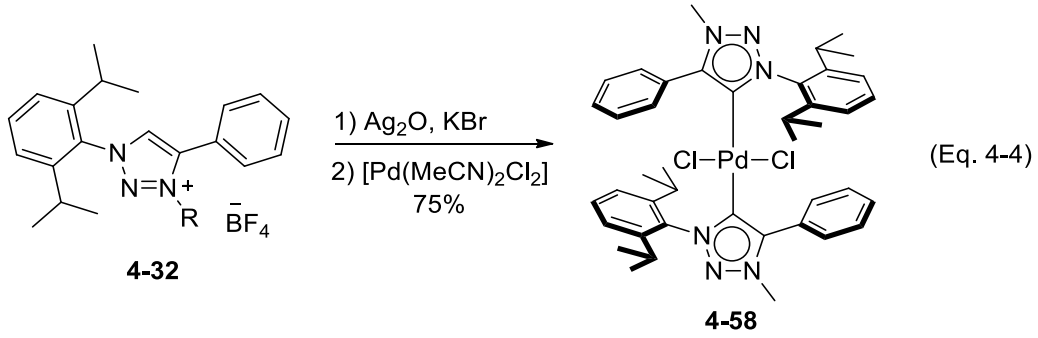
Scheme 4-18: Cyclometallation of tMIC ligands with higher oxidation state metals[43]

Current efforts are being directed to encourage cyclometallation by investigating transmetallation of **4-46** onto higher oxidation state metals such as $Pd(OAc)_2$. Furthermore, alternative routes that involve the direct activation of **4-41** and similar derivatives onto transition metals are also being investigated.

4.2.3 Development of Pd-tMIC complexes for Cross Coupling

As we imagined the greater electron donating capability of the tMIC ligands would be beneficial in palladium catalyzed cross coupling reactions, we sought to synthesize Pd-tMIC complexes and investigate their catalytic activity. Accordingly, treatment of **4-32**

with Ag_2O was followed with transmetalation to [Pd(MeCN)Cl_2] resulting in the formation of bis(tMIC) Pd complex **4-58** in 75% overall yield (Eq. 4-4).[44] The ^{1}H NMR spectrum of **4-58** was highly fluxional and very broad resonances were observed, however the ^{13}C NMR spectroscopy displayed the characteristic carbene resonance at 162.9 ppm, confirming coordination to palladium. Single crystals suitable for X-ray crystallography were obtained upon slow diffusion of hexanes into a concentrated solution of **4-58** in CH_2Cl_2 (Figure 4-3). Similar complexes had been reported previously by Fukuzawa and coworkers, and displayed marginal reactivity in Mizoroki-Heck reactions requiring temperatures of 150 °C.[45]



(Eq. 4-4)

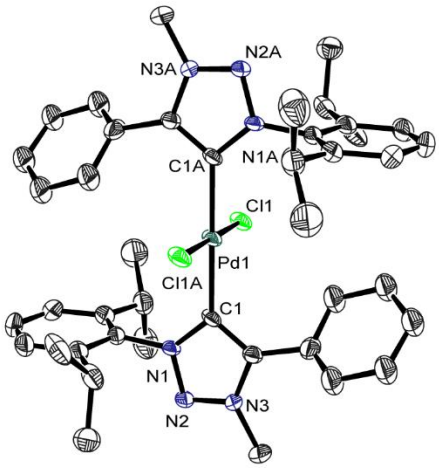
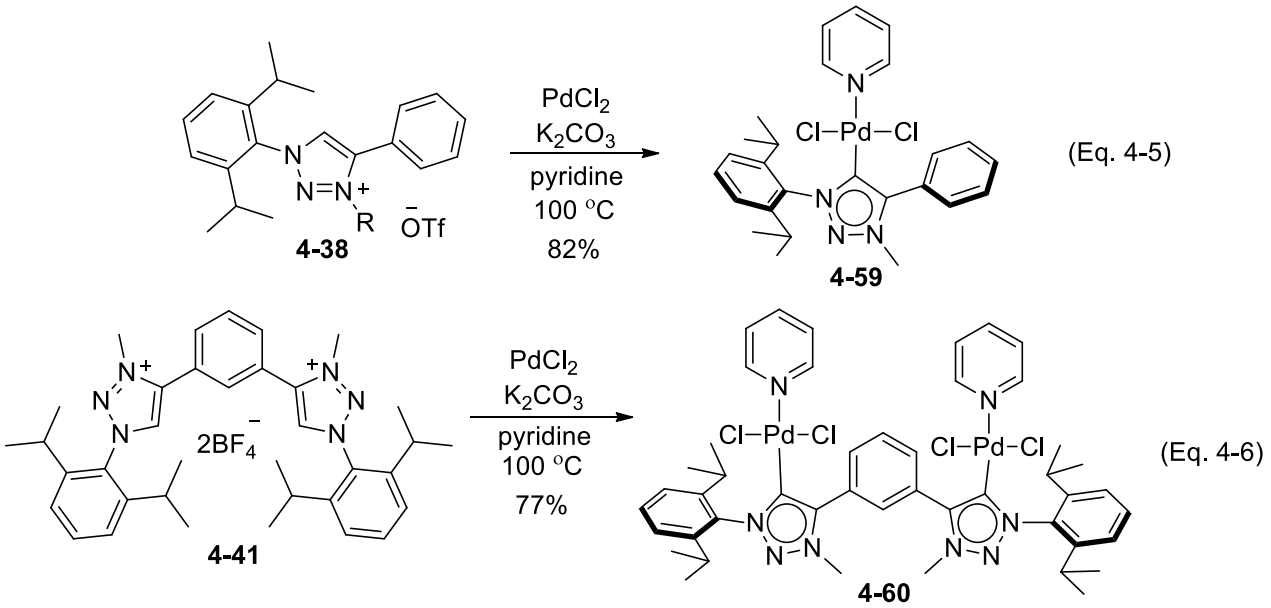


Figure 4-3: Crystallographically determined structure of **4-58** displaying thermal ellipsoids drawn at the 50 % confidence level. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Pd(1)−C(1), 2.022(6); Pd(1)−Cl(1), 2.3512(15); N(1)−C(1), 1.382(7);

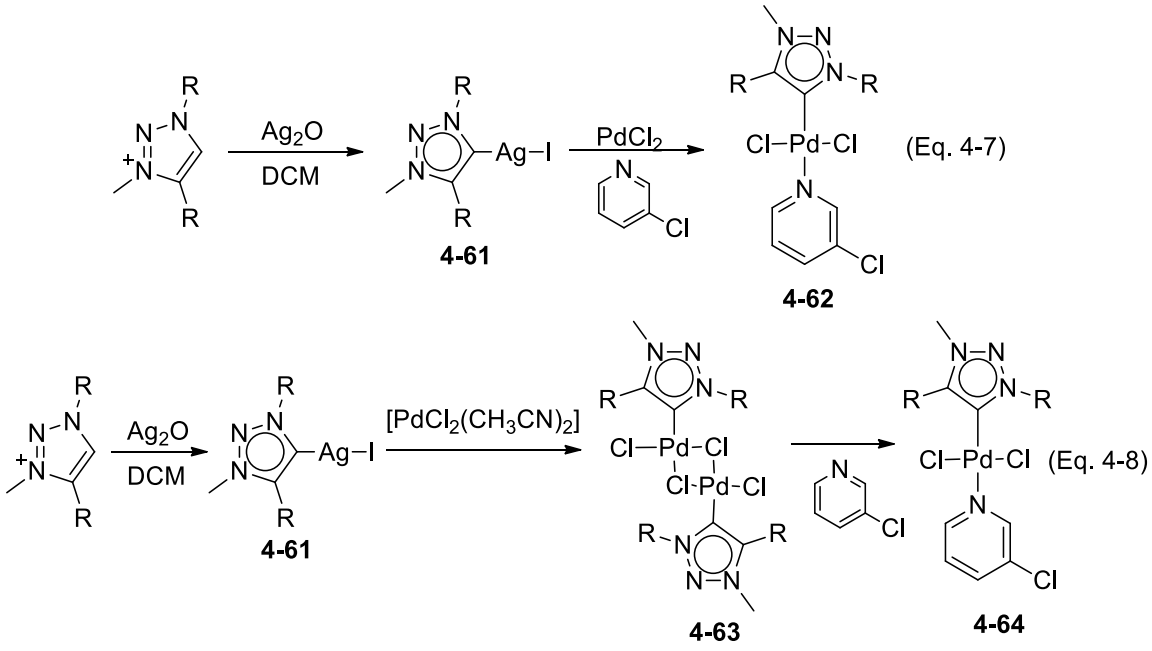
N(2)−N(1), 1.344(7); N(2)−N(3), 1.306(7); C(1)−Pd−C(1A), 180.000(1); C(1)−Pd(1)−Cl(1), 90.35(17); Cl(1)−Pd(1)−Cl(2), 180.0.

Thus, in direct analogy with Pd-NHC complexes, it seemed more appropriate to investigate mono(tMIC) complexes as cross coupling catalysts,[46] as the analogous NHC complexes have displayed higher activity.[47] While several different Pd-NHC complexes have been reported in the literature, the PEPPSI family of catalysts reported by Organ and coworkers were particularly appealing.[48] This is due to their high activity in a variety of transformations despite their remarkable stability, as well as their facile synthesis and purification.

The synthesis of tMIC PEPPSI complexes was accomplished in an analogous manner to NHC derivatives reported by Organ.[49] Thus treatment of the corresponding triazolium salts **4-38** and **4-41** with $PdCl_2$ and K_2CO_3 in pyridine resulted in the formation of air and moisture stable complexes **4-59** and **4-60** respectively, which could be purified by column chromatography in good overall yield (Eqs. 4-5 and 4-6). The formation of these complexes could be monitored by ^{1}H NMR spectroscopy, which clearly showed the disappearance of the characteristic C-H peak from the triazole starting materials. Once again, complex **4-60** was bimetallic in nature, and in our hands, complex **4-60** was obtained regardless of the M:L loading ratio. Single crystals of complexes **4-59** and **4-60** were obtained by the slow diffusion of hexanes into concentrated CH_2Cl_2 solutions (Figure 4-4). Similar to the case with rhodium, the triazole rings in complex **4-60** are twisted about the central phenyl ring with the palladium centres situated anti to each other.



While our manuscript was in preparation, Albrecht and Trzeciak reported very similar PEPPSI complexes derived from tMIC ligands (Eq. 4-7).[50] Their synthesis instead relied on the transmetalation of Ag-tMIC complexes to $PdCl_2$ in pyridine. In addition, after our manuscript was published, yet another report of tMIC PEPPSI complexes appeared from Hong and coworkers using a similar transmetalation strategy (Eq. 4-8).[51] In both of these cases, the PEPPSI catalysts were analyzed for their reactivity in the Suzuki-Miyaura coupling reaction.



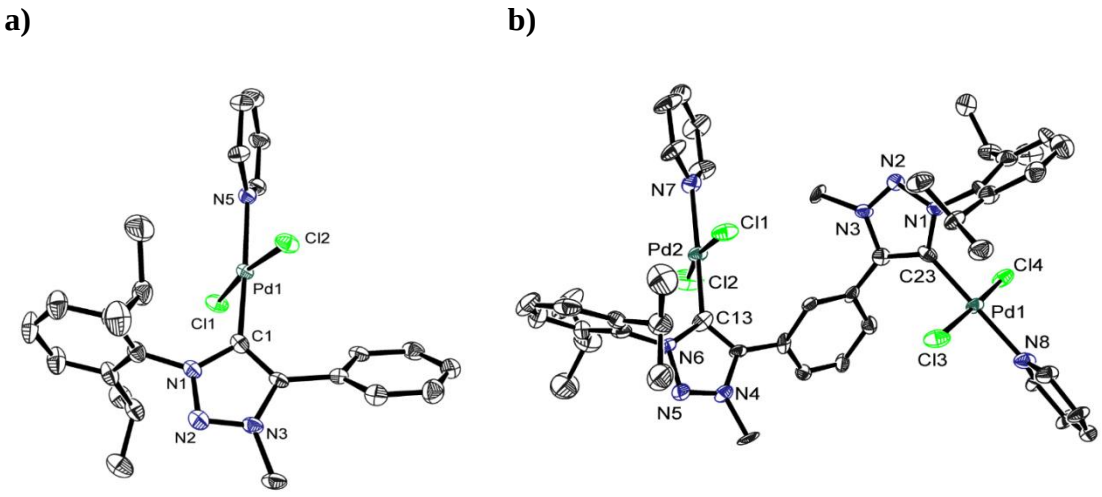
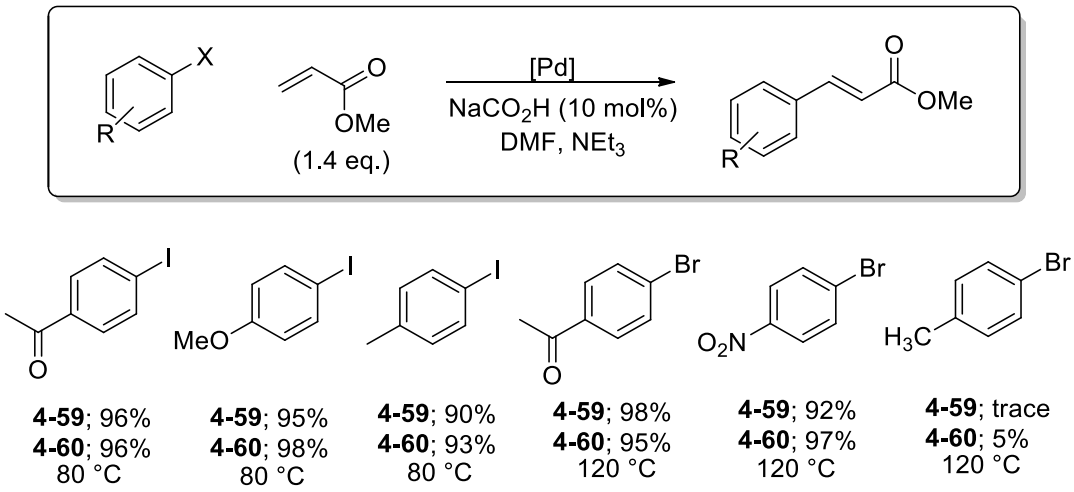


Figure 4-4: Crystallographically determined structure of (a) **4-59** and (b) **4-60** displaying thermal ellipsoids drawn at the 50 % confidence level. Hydrogen atoms omitted for clarity. Selected interatomic distances [Å] and angles [°]: a) **4-59**: Pd(1)−C(1), 1.977(5); Pd(1)−Cl(1), 2.3066(13); Pd(1)−Cl(2), 2.3003(13); N(1)−C(1), 1.367(6); N(2)−N(1), 1.316(6); N(2)−N(3), 1.306(7); Pd(1)−N(5), 2.116(4); C(1)−Pd−N(5), 176.70(17); C(1)−Pd(1)−Cl(1), 89.15(15); C(1)−Pd(1)−Cl(2), 87.84(15); Cl(1)−Pd(1)−Cl(2), 172.02(5). For b) **4-60**: Pd(1)−C(23), 2.004(13), Pd(2)−C(13), 2.000(13); Pd(2)−Cl(1), 2.322(4); Pd(2)−Cl(2), 2.324(4); Pd(1)−Cl(3), 2.299(4); Pd(1)−Cl(4), 2.297(4); N(6)−C(13), 1.358(15); N(1)−C(23), 1.349(14); N(2)−N(1), 1.349(13); N(6)−N(5), 1.350(13); N(2)−N(3), 1.300(12); N(4)−N(5), 1.304(12); Pd(2)−N(7), 2.145(11); Pd(1)−N(8), 2.103(11); C(13)−Pd(2)−N(7), 178.8(5); C(23)−Pd(1)−N(8), 178.5(5);

C(13)−Pd(2)−Cl(1), 88.3(3); C(13)−Pd(2)−Cl(2), 87.5(3); C(23)−Pd(1)−Cl(4), 89.7(4); C(23)−Pd(1)−Cl(3), 88.5(4); Cl(3)−Pd(1)−Cl(4), 173.34(15); Cl(1)−Pd(2)−Cl(2), 168.63(16).

We instead decided to investigate the activity of complexes **4-59** and **4-60** in the Mizoroki-Heck reaction of aryl halides with methyl acrylate (Scheme 4-19). Sodium formate was found to be a necessary additive for catalytic turn over, likely needed to reduce the Pd(II) precatalyst to Pd(0). Although aryl iodides were reactive under these conditions, high temperatures were required for activated aryl bromides, and non-activated aryl bromides or chlorides were completely inactive. This in stark contrast to NHC catalysts described by Organ, which are able to activate the substantially less reactive aryl chlorides. Complete inhibition of catalytic activity was observed when elemental mercury was added to the reaction mixture, which likely implicates the decomposition of the Pd-tMIC complexes to palladium nanoparticles under the reaction conditions.[52] Similar results were reported by Albrecht and Trzeciak in the Suzuki-Miyaura reaction.[50] These results highlight the binding differences between NHCs and tMICs, suggesting that tMICs may not be appropriate as ligands in cross coupling reactions.



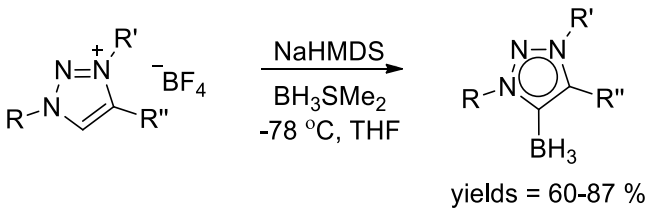
Scheme 4-19: Mizoroki-Heck coupling with Pd-tMIC complexes.

Shortly after these reports, Albrecht described some interesting results in the chemistry of Au-tMIC complexes.[53] Modest catalytic activity was observed in the aldol reaction of isocyanoacetates with benzaldehyde, however upon the addition of $AgBF_4$, substantially higher activity was observed. Through careful analysis, the authors determined that the active catalyst was likely a triazole-free gold species. Specifically, the authors implicated either a ligandless Au^+ ion, or as a gold aggregate such as a cluster or a nanoparticle as the catalytically active species. Dynamic light scattering was used to detect the formation of nanoparticles upon the addition of $AgBF_4$ to a mixture containing the gold complex and substrate, indicating that the silver reagent is likely involved in the liberation of the MIC from the complex.

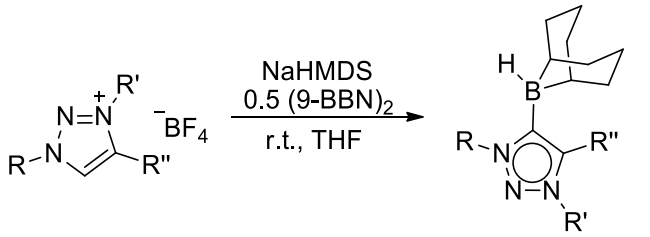
These results, in combination with ours, may point to the lability of tMIC ligands from transition metals. This may indicate that tMIC may have a more limited role in palladium catalyzed cross coupling than their NHC relatives. As a result, our group began exploring alternative avenues for the use of tMIC ligands in catalysis with main group metals.

Specifically, postdoctoral fellow Patrick Eisenberger and exchange student Luiza Baptista de Oliveira Freitas investigated the coordination of tMIC ligands to boron reagents.[54] It was hypothesized that the increased electron density donated from the tMIC ligand would translate to higher hydridic character of the resulting borohydride. The synthesis of borane tMIC complexes can be conveniently performed by the one-pot deprotonation/metallation procedure in Eq. 4-9. The resulting products were found to be

efficient catalysts for the reduction of aromatic ketones in the presence of Lewis acid promoters.



(Eq. 4-9)



(Eq. 4-10)

Patrick further demonstrated the metallation of these ligands onto 9-BBN using a similar protocol (Eq. 4-10). The resulting complexes were found to be effective catalysts in the reduction of various aldimines, ketimines, and *N*-heterocycles in the presence of $[Ph_3C][B(C_6F_4)]$ which acts as a hydride abstractor. These giving rise to valuable secondary amines. Current efforts in our group are being carried out by Patrick Eisenberger and Brian Bestvater which are dedicated to developing enantioselective variants of this system using alternative ligand structures, and investigating the scope of the reaction to include more diverse substrates.

4.3 Conclusions

This chapter has detailed my efforts to investigate the coordination chemistry of tMIC ligands with selected transition metal and main group elements, and the use of the resulting complexes in catalysis. In particular, I demonstrated some of the few examples of metallating tMIC ligands without the use of Ag_2O, towards transition metals as well as

the first examples of the preparation of boron–tMIC complexes. Taking advantage of the facile synthetic potential of tMICs we investigated the possibility of using these ligands for more advanced architectures such as pincer ligands. While we have been unsuccessful to date with the formation of bidentate complexes using this particular architecture, we believe there is great promise in this field.

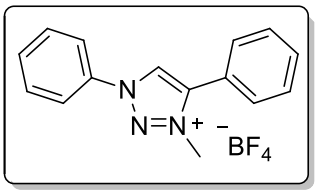
In addition, results from our group have indicated that tMIC ligands may present significantly different bonding structures compared to more traditional NHCs. In particular we observed the lability of tMICs from palladium in the Mizoroki-Heck reaction of aryl halides with acrylates. This is an important factor, as it should not be assumed that tMICs can act as mere surrogates for NHCs.

4.4 Experimental

General considerations: All manipulations were carried out under an atmosphere of dry argon in oven dried glassware, or under a nitrogen atmosphere in a glovebox (M. Braun) with oxygen and water levels ≤2 ppm. All solvents were distilled from Na/benzophenone (THF, Et_2O, toluene, benzene, Ph-CF_3) or CaH_2 (CH_2Cl_2, NEt_3) under argon, and degassed via three freeze-pump-thaw cycles then stored over 4 Å molecular sieves prior to use. $[Rh(COD)_2Cl]_2$,[55] 1,3-Bis[(trimethylsilyl)ethynyl]benzene,[56] 1,4-diphenyl-1*H*-1,2,3-triazole, 1-(2,4,6-trimethylphenyl)-4-phenyl-1*H*-1,2,3-triazole and 1-(2,6-diisopropylphenyl)-4-phenyl-1*H*-1,2,3-triazole[57] were prepared according to previously reported literature procedures. $[Rh(COD)_2]BF_4$, and $PdCl_2$ were generously donated by Johnson-Matthey. Ag_2O was purified by Soxhlet extraction with H_2O, and stored under N_2 in the dark. All other reagents were purchased from commercial suppliers and used without

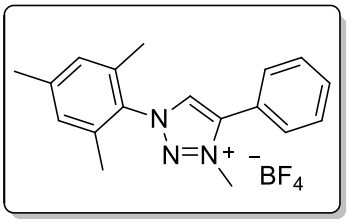
further purification. ^{1}H NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using residual protonated solvent as an internal standard (CD_3CN, 1.94 ppm, C_6D_6, 7.15 ppm; $CDCl_3$, 7.26 ppm). ^{13}C NMR spectra were recorded at 100 MHz. Chemical shifts are reported as above using the solvent as an internal standard (CD_3CN, 118.26 ppm, C_6D_6, 128.0 ppm; $CDCl_3$, 77.16). Assignments of the ^{1}H and ^{13}C{^{1}H} NMR spectra were made using ^{1}H-^{1}H gs-COSY, ^{1}H-^{13}C-HSQC and ^{1}H-^{13}C-HMBC NMR experiments. X-ray data collection was performed on a Bruker SMART APEX II X-ray diffractometer.

Synthesis of Ligand Precursors:

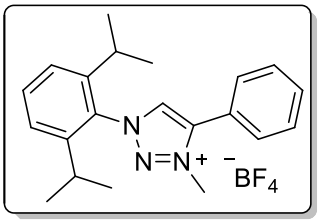


Synthesis of 4-30: In a nitrogen-filled glovebox, 1,4-diphenyl-1*H*-1,2,3-triazole (175 mg, 0.79 mmol) and Me_3OBF_4 (150 mg, 1.03 mmol) were combined as solids in a 20 mL vial and then dissolved in CH_2Cl_2 (5 mL). The heterogeneous suspension was stirred at room temperature for 16 hours. The vial was removed from the glovebox, and MeOH (1 mL) was added, and stirring continued for 30 minutes. The product was then precipitated in Et_2O, and isolated by filtration and further washed with Et_2O then dried under vacuum resulting in an off-white solid in (226.9 mg, 0.70 mmol) 89 % yield. **^{1}H NMR** (Acetone-d_6, 400 MHz): δ = 9.53 (s, 1H, Trz-*H*), 8.15-8.13 (m, 2H, Ar*H*), 7.94-7.92 (br m, 2H, Ar*H*), 7.81-7.80 (m, 3H, Ar*H*), 7.74-7.72 (m, 3H, Ar*H*), 4.59 (s, 3H, Trz-C*H*$_3$). **^{13}C{^{1}H} NMR** (Acetone-d_6, 100 MHz): δ = 145.1, 136.2, 132.9, 132.7, 131.4, 130.6, 130.5, 128.0, 123.6,

122.7, 39.8. **HRMS** (ESI-TOF, m/z) calculated for [$C_{15}H_{14}N_3$]: 236.11822, found 236.11822.

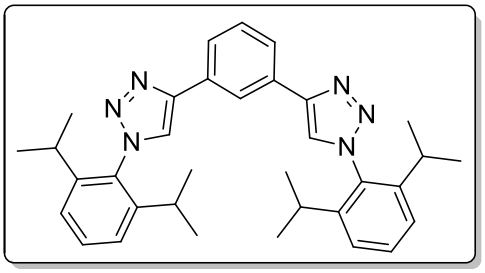


Synthesis of 4-31: In a nitrogen-filled glovebox, 1-(2,4,6-trimethylphenyl)-4-phenyl-1*H*-1,2,3-triazole (208 mg, 0.79 mmol) and Me_3OBF_4 (150 mg, 1.03 mmol) were combined as solids in a 20 mL vial and CH_2Cl_2 (4 mL), and CF_3Ph (6 mL) were added. The heterogeneous suspension was stirred at room temperature for 16 hours. The vial was then removed from the glovebox, and MeOH (1 mL) was added, and stirring continued for 30 minutes. The product was then precipitated with Et_2O, and isolated by filtration and further washed with Et_2O then dried under vacuum resulting in an off-white solid in (244.7 mg, 0.68 mmol) 85 % yield. **^{1}H NMR** (Acetone-d_6, 400 MHz): δ = 9.21 (s, 1H, Ar*H*), 7.98-7.96 (m, 2H, Ar*H*), 7.74-7.72 (m, 3H, Ar*H*), 7.25 (s, 2H, Ar*H*), 4.62 (s, 3H), 2.42 (s, 3H, C*H*$_3$), 2.21 (s, 6H, C*H*$_3$). **^{13}C{^{1}H} NMR** (Acetone-d_6, 100 MHz): δ = 145.1, 143.3, 135.7, 132.6, 131.6, 130.7, 130.5, 130.3, 123.6, 39.1, 21.2, 17.1. **HRMS** (ESI-TOF, m/z) calculated for [$C_{18}H_{20}N_3$]: 278.1655, found 278.1653.



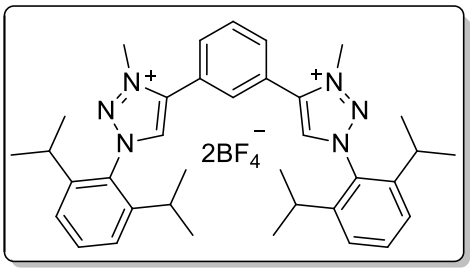
Synthesis of 4-32: In a nitrogen-filled glovebox, 1-(2,6-diisopropylphenyl)-4-phenyl-1*H*-1,2,3-triazole (200 mg, 0.66 mmol) and Me_3OBF_4 (390 mg, 2.64 mmol) were combined as solids in a 50 mL round bottom flask and dissolved in CF_3Ph (10 mL) and CH_2Cl_2 (5 mL). The heterogeneous suspension was stirred at room temperature for 48 hours. The flask was removed from the box, MeOH (1 mL) was added,

and stirring continued for 30 minutes. The product was then precipitated with Et_2O and isolated by filtration and further washed with Et_2O, then dried under vacuum resulting in an off-white solid in 88 % yield (235 mg, 0.58 mmol). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.98 (s, 1H, Trz-*H*), 8.10-8.09 (m, 2H, Ar*H*), 7.64-7.60 (m, 4H, Ar*H*), 7.38 (d, 2H, J_{H-H}= 7.92 Hz, Ar*H*), 4.65 (s, 3H, Trz-CH_3), 2.49 (sept, 2H, J_{H-H}= 6.75 Hz, iPr-C*H*), 1.26 (d, 6H, J_{H-H}= 6.75 Hz, iPr-CH_3), 1.22 (d, 6H, J_{H-H}= 6.75 Hz, iPr-CH_3). **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ = 145.8, 144.6, 133.0, 132.3, 131.0, 130.9, 130.4, 129.9, 124.9, 121.4, 40.3, 29.0, 24.7, 24.1. **HRMS** (EI-TOF, m/z) calculated for [$C_{21}H_{26}N_3$]: 320.2127, found 320.2119.



Synthesis of 4-44: Tertbutyl nitrite (1.01 mL, 8.43 mmol) was added to a stirring solution of 2,6-diisopropylaniline (1.06 mL, 5.62 mmol) in MeCN (40 mL) under argon in a 250 mL round bottom flask at 0 ºC. This was followed by the addition of $TMSN_3$ (0.89 mL, 6.74 mmol). The solution was stirred for 15 minutes at 0 °C, and then slowly warmed to room temperature and stirring continued for an additional 3 hours. The evolution of N_2 gas was observed as the solution reached room temperature. To the resulting mixture, 1.14 g (4.21 mmol) of 1,3-*bis*[(trimethylsilyl)ethynyl]benzene was added as a solid, and then a 1M solution of TBAF in THF (8.4 mL, 8.4 mmol) was added dropwise, resulting in a deep black solution. A solution of $CuSO_4$ (178 mg, 1.12 mmol), and sodium ascorbate (1.11 g, 5.62 mmol) in 10 mL of H_2O was then added to the reaction mixture and the resulting solution was allowed to stir at room temperature for 18 hours. After this time, 50 mL of

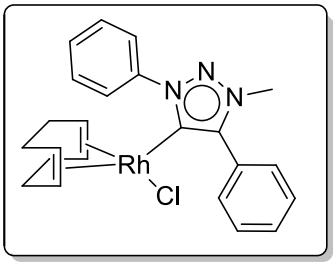
$CHCl_3$ and was added, and the organic layer was washed with H_2O (50 mL). The organic layer was then dried with $MgSO_4$, and filtered, and all volatiles were removed *in vacuo*. Precipitation was performed by the slow addition of the reaction mixture to hexanes stirring at 0 ^oC, and the product was isolated by filtration as a white powder (1.89 g, 3.54 mmol) in 63 % yield. **^{1}H NMR** (Acetone-d_6, 400 MHz): δ = 8.70 (s, 2H, Trz-*H*), 8.60 (s, 2H, Trz*H*), 7.97 (dd, 2H, $J_{H\text{-}H}$ = 7.70, 1.5 Hz, Ar*H*) 7.56-7.52 (m, 3H, Ar*H*), 7.38 (d, 4H, $J_{H\text{-}H}$ = 7.8 Hz, Ar*H*), 2.30 (septet, 4H, $J_{H\text{-}H}$ = 6.9 Hz, iPr-C*H*), 1.16 (t, 24H, $J_{H\text{-}H}$ = 6.9 Hz, iPr-CH_3). **^{13}C{^{1}H} NMR** (CD_3CN, 100 MHz): δ = 147.7, 146.9, 134.5, 132.7, 131.8, 130.4, 126.1, 124.9, 124.7, 123.7, 28.4 (confirmed by HSQC), 24.4, 24.1. **HRMS** (EI-TOF, m/z) calculated for [$C_{34}H_{40}N_6$]: 532.3314, found 532.3307.



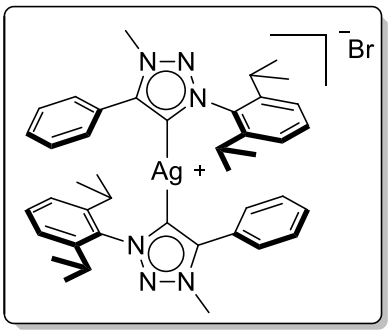
Synthesis of 4-41: In a nitrogen-filled glovebox, 1,3-*bis*(2,6-diisopropylphenyl-1,2,3-triazole)benzene **4-44** (250 mg, 0.47 mmol) and Me_3OBF_4 (200 mg, 1.4 mmol) were combined as solids in a 100 mL round bottom flask. CH_2Cl_2 (10 mL) was added, and the heterogeneous suspension was stirred at room temperature for 36 hours. The flask was removed from the box, and MeOH (2 mL) was added, and stirring continued for 30 minutes. Removal of all volatiles i*n vacuo* resulted in compound **4-41** as an off-white solid (284.2 mg, 0.39 mmol) in 82 % yield. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.84 (s, 2H, Trz-*H*), 8.47 (br s, 1H, Ar*H*), 8.07 (dd, 2H, $J_{H\text{-}H}$ = 7.92, 1.47 Hz, Ar*H*), 7.88 (t, 1H, $J_{H\text{-}H}$= 7.92 Hz, Ar*H*), 7.66 (m, 2H, Ar*H*), 7.40 (d, 4H, $J_{H\text{-}H}$ = 7.92 Hz, Ar*H*), 4.55 (s, 6H, Trz-CH_3), 2.39 (septet, 4H, $J_{H\text{-}H}$ = 6.8 Hz, iPr-C*H*), 1.25 (d, 12H, $J_{H\text{-}H}$ = 6.75 Hz, iPr-CH_3), 1.22 (d, 12H, $J_{H\text{-}H}$= 6.75 Hz, iPr

C*H*$_3$).**^{13}C{^{1}H} NMR** (CD_3CN, 100 MHz): δ = 146.6, 142.6, 142.8, 134.1, 134.0, 132.5, 131.8, 131.7, 125.8, 124.6, 40.3 (Trz-*C*H$_3$), 29.2 (iPr-*C*H), 24.6 (iPr-*C*H$_3$), 23.8 (iPr-*C*H$_3$). **HRMS** (EI-TOF, m/z) calculated for $[C_{36}H_{46}N_6]^{2+}$: 281.1886, found 281.1881.

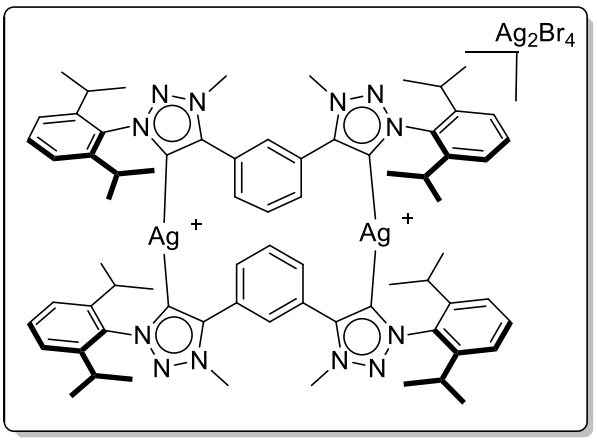
Synthesis of tMIC complexes:



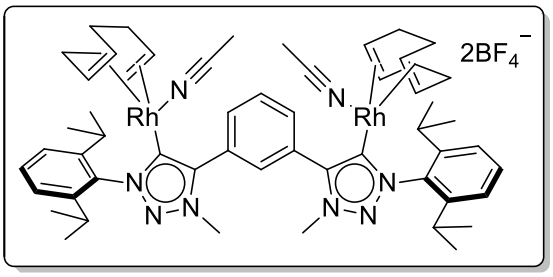
Synthesis of 4-34: Compound **4-30** (40.0 mg, 0.123 mmol), NaHMDS (23.8 mg, 0.13 mmol), and $[Rh(COD)Cl]_2$ (30.5 mg, 0.06 mmol) were combined as solids in a 25 mL Schlenk flask under argon. The flask was cooled to -78 °C and anhydrous THF (10 mL) was added. The solution was stirred at -78 °C for 20 minutes, and then allowed to warm to room temperature. Stirring was continued for another 3 hours at room temperature. The flask was then exposed to air, diluted with CH_2Cl_2 (10 mL) and filtered through a plug of Celite^{TM} and evaporated. Purification was carried out by silica gel column chromatography eluting with 3:1 hexanes:ethyl acetate, which resulted in a yellow/orange powder (48.0 mg, 0.99 mmol) in 81 % yield. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ = 8.80 (br m, 2H, Ar*H*), 8.21 (br m, 2H, Ar*H*), 7.60-7.55 (br m, 6H, Ar*H*), 4.95 (m, 2H, olefinic C*H* of COD), 4.12 (s, 3H, C*H*$_3$), 2.74 (br m, 2H, olefinic C*H* of COD), 2.07-2.18 (br m, 2H, C*H*$_2$ of COD), 1.54-1.84 (br m, 6H, C*H*$_2$ groups of COD). **^{13}C{^{1}H} NMR** ($CDCl_3$, 125 MHz): δ = 171.9 ($^1J_{Rh-C}$ = 46.3 Hz), 144.8, 140.0, 130.6, 129.7, 129.6, 128.9, 128.6, 128.4, 124.2, 96.2 ($^1J_{Rh-C}$ = 7.3 Hz), 95.7 ($^1J_{Rh-C}$ = 7.3 Hz), 69.5 ($^1J_{Rh-C}$ = 14.9 Hz), 67.5 ($^1J_{Rh-C}$ = 14.9 Hz), 37.5, 32.7, 32.3, 29.8, 29.0. **HRMS** (EI-TOF, m/z) calculated for $[C_{25}H_{31}N_3Rh]$: 476.1573, found 476.1582.



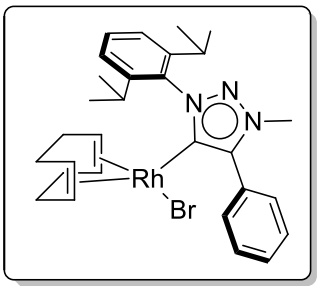
Synthesis of 4-45: In a nitrogen-filled glovebox, Ag_2O (20 mg, 0.086 mmol), **4-32** (20 mg, 0.049 mmol), and KBr (29 mg, 0.25 mmol) were added as solids to 20 mL vial and dissolved in MeCN (5 mL), and stirred with the exclusion of light for 3 days at room temperature. A white precipitate began to form after 6 hours. After this time, the opaque solution was diluted with CH_2Cl_2 (10 mL) and filtered through a plug of Celite^{TM}, and all volatiles were removed *in vacuo*. Precipitation of a concentrated CH_2Cl_2 solution into hexanes, followed by filtration resulting in an off-white powder (23.1 mg, 0.023 mmol) in 93 % yield. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.71 (m, 4H, Ar*H*), 7.55 (br, 8H, Ar*H*), 7.31 (d, 4H, $J_{H\text{-}H}$ = 7.63 Hz, Ar*H*), 4.25 (s, 6H, Trz-CH_3), 2.28 (septet, 4H, $J_{H\text{-}H}$ = 6.46 Hz, iPr-C*H*), 1.27 (d, 12H, $J_{H\text{-}H}$ = 6.46 Hz, iPr-CH_3), 1.15 (d, 12H, $J_{H\text{-}H}$ = 6.46 Hz, iPr-CH_3). **^{13}C{^{1}H} NMR** ($CDCl_3$, 125 MHz): δ = 172.4 (*C*-carbene), 148.7, 145.1, 135.9, 131.4, 130.5, 129.6, 129.4, 126.9, 124.4, 37.9, 28.7, 24.5, 24.3. **HRMS** (ESI-TOF, m/z) calculated for [$C_{42}H_{50}N_6Ag$]: 745.3148, found 745.3143.



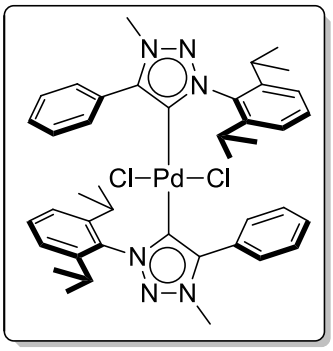
Synthesis of 4-46: In a nitrogen-filled glovebox, compound **4-41** (80 mg, 0.108 mmol), Ag_2O (92 mg, 0.38 mmol) and KBr (140 mg, 1.08 mmol) were combined as solids in a 20 mL vial. MeCN (6 mL) was added and the mixture was stirred with the exclusion of light for 3 days at room temperature. Formation of a white precipitate was observed after about 6 hours. After this time, the opaque solution was diluted with CH_2Cl_2 (10 mL) and filtered through a plug of Celite™, and all volatiles were removed *in vacuo*. The product was precipitated from a CH_2Cl_2 solution into hexanes, and collected by filtration as a light brown solid (56.2 mg, 0.030 mmol) in 55% yield. Single crystals suitable for X-ray analysis were achieved by a slow diffusion of hexanes into a concentrated CH_2Cl_2 solution. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.03 (s, 2H, Ar*H*), 7.85 (m, 4H, Ar*H*), 7.79 (m, 2H, Ar*H*), 7.56 (t, 4H, $J_{H\text{-}H}$= 7.63 Hz, Ar*H*), 7.34 (d, 8H, $J_{H\text{-}H}$= 7.63 Hz, Ar*H*), 4.39 (s, 12H, Trz-C*H*$_3$), 2.29 (septet, 8H, $J_{H\text{-}H}$= 6.65 Hz, iPr-C*H*), 1.26 (d, 24H, $J_{H\text{-}H}$= 6.65 Hz, iPr-C*H*$_3$), 1.18 (d, 24H, $J_{H\text{-}H}$ = 6.65 Hz, iPr-C*H*$_3$). **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ = 172.4 (*C*-carbene), 147.4, 145.1, 135.6, 131.6, 131.5, 130.9, 130.5, 128.5, 124.5, 38.9, 28.8, 24.5, 24.4. **HRMS** (ESI-TOF, m/z) calculated for $[C_{72}H_{88}N_{12}Ag_2]^{2+}$: 667.2835, found 667.2581.



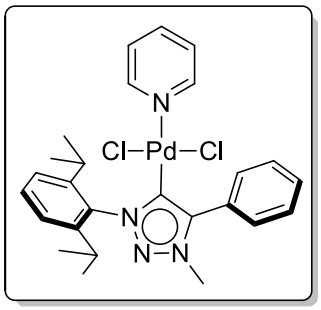
Synthesis of 4-50: In a nitrogen-filled glovebox, a solution of complex **4-46** (20.0 mg, 0.01 mmol) in MeCN (2 mL) was added to a 20 mL vial containing $[Rh(COD)_2]BF_4$ (17.4 mg, 0.043 mmol) in MeCN (2 mL). A white precipitate was observed almost immediately. The resulting solution was stirred at room temperature for 16 hours with the exclusion of light, then diluted with CH_2Cl_2 (5 mL) and filtered through a plug of Celite™ and all volatiles were removed *in vacuo*. The residue was washed with hexanes resulting in a yellow powder (22.2 mg, 0.02 mmol) in 81 % yield. Single crystals suitable for X-ray analysis were achieved by the slow diffusion of hexanes into concentrated CH_2Cl_2:THF (1:1) solution. **^{1}H NMR** (CD_3CN, 400 MHz): δ = 8.85 (s, 1H, Ar*H*), 8.16 (dd, 2H, J_{H-H}= 7.63, 1.47 Hz, Ar*H*), 7.98 (t, 1H, J_{H-H}= 7.75 Hz, Ar*H*), 7.70 (t, 2H, J_{H-H}= 7.63 Hz, Ar*H*), 7.50 (d, 4H, J_{H-H}= 7.63 Hz, Ar*H*), 4.44 (br m, 2H, olefinic-C*H* of COD), 4.46 (br m, 2H, olefinic-C*H* of COD), 4.30 (s, 6H, Trz-CH_3), 3.66 (br m, 2H, olefinic-C*H* of COD), 2.44 (br m, 2H, olefinic-C*H* of COD), 2.42 (br m, 4H, iPr-C*H*), 1.97 (s, 6H, Rh-CH_3CN), 1.89 (br m, 8H, CH_2 of COD), 1.77 (br m, 8H, CH_2 of COD), 1.40 (d, 12H, J_{H-H} = 6.75 Hz, iPr-CH_3), 1.16 (d, 12H, J_{H-H}= 6.75 Hz, iPr-CH_3). **^{13}C{^{1}H} NMR** (CD_3CN, 100 MHz): δ = 166.8 (d, *C*-carbene, J_{Rh-C}= 47.2 Hz), 146.7, 135.9, 133.7, 132.4, 132.3, 130.5, 129.8, 129.5, 125.2, 95.0 (d, J_{Rh-C} = 7.4 Hz, olefinic-*C*H of COD), 85.9 (d, J_{Rh-C} = 11.1 Hz, olefinic-CH of COD), 77.6 (d, J_{Rh-C} = 12.9 Hz, olefinic-*C*H of COD), 38.6, 32.7, 31.2 (2 overlaid peaks, as determined by ^{1}H-^{13}C-HSQC), 29.7, 29.4, 25.9, 23.5. **HRMS** (ESI-TOF, m/z) calculated for $[C_{56}H_{74}N_8Rh_2]^{2+}$: 532.2074, found 532.2013.



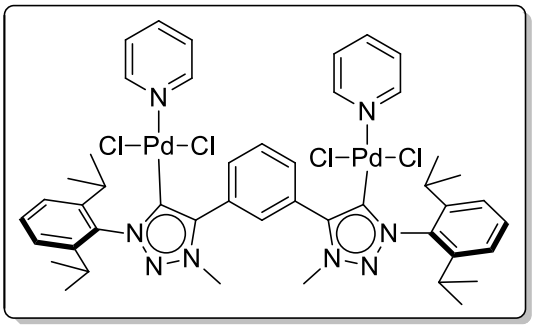
Synthesis of 4-48: In a nitrogen-filled glovebox, a solution of complex **4-45** (19.0 mg, 0.023 mmol) in MeCN (2 mL) was added to a 20 mL vial containing a solution of $[Rh(COD)Cl]_2$ (11.4 mg, 0.023 mmol) and KBr (27.4 mg, 0.23 mmol) in 5 mL of MeCN. The resulting yellow solution was allowed to stir at room temperature overnight with exclusion of light. After this time CH_2Cl_2 (10 mL) was added and the solution was filtered through a plug of Celite™. All volatiles were removed *in vacuo*, and the residue was washed with hexanes resulting in a yellow solid (22.9 mg, 0.04 mmol) in 82 % yield. Single crystals suitable for X-ray analysis were achieved by slow evaporation of a concentrated CH_2Cl_2 solution. **^{1}H NMR** ($CDCl_3$, 400 MHz, 253K): δ = 8.20 (m, 2H, Ar*H*), 7.60-7.51 (m, 4H, Ar*H*), 7.45 (br, 1H, Ar*H*), 7.26 (br, 1H, Ar*H*), 4.68-4.63 (br, 2H, olefinic-C*H* of COD), 4.09 (s, 3H, Trz-CH_3), 3.38 (septet, 1H, iPr C*H*, $J_{H\text{-}H}$= 6.46 Hz), 3.28 (br, 1H, olefinic-C*H* of COD), 2.89 (br, 1H, olefinic-C*H* of COD), 2.12-1.98 (m, 4H, 2 x CH_2 of COD), 1.93 (m, 2H, CH_2 of COD), 1.72-1.69 (m, 3H, iPr-C*H* and CH_2 of COD), 1.55 (d, 3H, $J_{H\text{-}H}$ = 6.46 Hz, iPr-CH_3), 1.18 (d, 3H, $J_{H\text{-}H}$ = 6.46 Hz, iPr CH_3), 1.14 (d, 3H, $J_{H\text{-}H}$= 6.75 Hz, iPr CH_3), 1.04 (d, 3H, $J_{H\text{-}H}$ = 6.75 Hz, iPr CH_3). **^{13}C NMR** ($CDCl_3$, 100 MHz, 293K): δ = 173.5 (d, $^1J_{Rh\text{-}C}$= 48.09Hz, *C*-Carbene), 145.6, 136.1, 130.8, 130.7, 129.6, 128.7, 128.5, 125.9, 124.0, 95.5 (br, olefinic-*C* of COD), 78.8 (d, $^1J_{Rh\text{-}C}$= 12.9 Hz, olefinic-*C* of COD), 37.5 (Trz-*C*H_3), 33.5, 32.1, 29.2, 28.9, 28.9, 28.6, 26.5, 26.1, 23.8, 22.5. **HRMS** (EI-TOF, m/z) calculated for $[C_{29}H_{37}BrN_3Rh]^+$: 609.1226, found 609.1202.



Synthesis of 4-58: In a nitrogen-filled glovebox, compound **4-32** (20.0 mg, 0.049 mmol), Ag_2O (20.0 mg, 0.086 mmol), and KBr (29.0 mg, 0.25 mmol) were added as solids to a 50 mL round bottom flask and MeCN (5 mL) was added. The suspension was stirred with the exclusion of light for 3 days. After this time, the solution was filtered diluted with CH_2Cl_2 (5 mL) and filtered through Celite^{TM}, and all volatiles were removed *in vacuo*. The residue was dissolved in MeCN (5 mL), and [$Pd(MeCN)_2Cl_2$] (6.4 g, 0.0245 mmol) was added. The solution was stirred for 16 hours at room temperature under N_2 atmosphere, after which it was diluted with CH_2Cl_2 (5 mL) and then filtered through Celite^{TM} and evaporated. Complex **4-58** was then precipitated from a CH_2Cl_2/hexanes mixture as a yellow powder and was collected by filtration (16.9 mg, 0.02 mmol) in 83% yield. Single crystals were grown from a slow diffusion of hexanes into a concentrated CH_2Cl_2 solution. **^{1}H NMR** (CD_3CN, 600 MHz): δ = 7.96 (br, 3H, Ar*H*), 7.69 (d, 1H, $J_{H\text{-}H}$= 7.69 Hz, Ar*H*), 7.64 (t, 1H, $J_{H\text{-}H}$= 7.93 Hz, Ar*H*), 7.55 (m, 2H, Ar*H*), 7.49 (t, 1H, $J_{H\text{-}H}$= 7.55 Hz, Ar*H*), 7.40 (d, 1H, $J_{H\text{-}H}$= 7.93 Hz, Ar*H*), 7.35 (t, 2H, $J_{H\text{-}H}$= 7.55 Hz, Ar*H*), 7.31 (d, 2H, $J_{H\text{-}H}$= 7.93 Hz, Ar*H*), 7.25 (br, 3H, Ar*H*), 3.98 (s, 6H, Trz-CH_3) 2.36-2.25 (m, 4H, iPr-C*H*), 0.95 (d, 12H, $J_{H\text{-}H}$= 6.80 Hz, iPr-CH_3), 0.90 (d, 12H, $J_{H\text{-}H}$= 6.80 Hz, iPr-CH_3). **^{13}C{^{1}H} NMR** (CD_3CN, 100MHz): δ = 162.9 (Pd-C), 147.3, 146.8, 137.2, 132.2, 131.5, 131.2, 129.9, 129.4, 124.7, 38.4, 29.2, 26.2, 22.9. **(EA)** (%) Anal. Calcd for: $C_{41}H_{49}N_6Cl_2Pd{\cdot}1.75C_6H_{14}{\cdot}0.4CH_2Cl_2$: C 63.1, H 7.58, N 8.51; found C 63.35, H 7.34, N 8.26.



Synthesis of 4-59: Triazolium salt **4-38** (224.0 mg, 0.55 mmol), K_2CO_3 (490.0 mg, 2.75 mmol) and $PdCl_2$ (88.7 mg, 0.5 mmol) were combined as solids in a 25 mL Schlenk flask under air. Pyridine (3.5 mL) was added to the above mixture, and the suspension was heated to 100 ^oC for 24 hours under air. The insoluble $PdCl_2$ was noticeably consumed throughout the reaction. The resulting yellow solution was cooled to room temperature, and all volatiles were removed *in vacuo*. The residue was taken up in 15 mL of CH_2Cl_2 and the resulting solution was filtered through Celite^{TM}, and all volatiles were removed *in vacuo*. The product was purified by silica gel chromatography, eluting with 100% CH_2Cl_2 resulting in the product as a pale yellow powder that was precipitated from CH_2Cl_2/hexanes mixture and isolated by filtration (235 mg, 0.45 mmol) in 82 % yield. Single crystals were grown from a slow diffusion of hexanes into a concentrated CH_2Cl_2/THF solution. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.72 (d, 2H, $J_{H\text{-}H}$ = 5.05 Hz, *o*-pyr-*H*), 8.21 (d, 2H, $J_{H\text{-}H}$ = 7.57 Hz, Ar*H*), 7.61-7.55 (m, 5H, Ar*H*), 7.39 (d, 2H, $J_{H\text{-}H}$ = 7.88 Hz, *m*-Dipp-*H*), 7.17 (t, 2H, $J_{H\text{-}H}$ = 6.62 Hz, *m*-pyr-*H*), 4.14 (s, 3H, trz-CH_3), 2.80 (septet, 2H, $J_{H\text{-}H}$ = 6.75 Hz, iPr-C*H*), 1.44 (d, 6H, $J_{H\text{-}H}$ = 6.75 Hz, iPr-CH_3), 1.09 (d, 6H, $J_{H\text{-}H}$= 6.75 Hz, iPr-CH_3). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 153.5, 151.5, 146.8 (Pd-*C*), 139.3, 137.6, 131.3, 130.9, 130.2, 129.0, 127.2, 125.2, 124.2, 124.1, 37.8, 29.0, 26.3, 23.0. **HRMS** (ESI-TOF, m/z) Calculated for [$C_{26}H_{30}ClN_4Pd$]: 539.1227 found 539.1222. **(EA)** (%) Anal. Calcd for: $C_{26}H_{30}N_4Cl_2Pd{\cdot}0.7C_6H_{14}$: C 57.02, H 6.31, N 8.81; found C 57.14, H 6.10, N 8.83.



Synthesis of 4-60: Triazolium salt **4-41** (162.4 mg, 0.22 mmol, 0.55), K_2CO_3 (305 mg, 2.2 mmol) and $PdCl_2$ (71 mg, 0.4 mmol) were weighed in air as solids, and combined in a 25 mL Schlenk flask. Pyridine (3.5 mL) was added to the above mixture, and the suspension was heated to 100 ^oC for 24 hours under air. The insoluble $PdCl_2$ was noticeably consumed throughout the reaction. The resulting yellow solution was cooled to room temperature, and all volatiles were removed *in vacuo*. The residue was then taken up in CH_2Cl_2 (15 mL) and the resulting suspension was filtered through Celite^{TM}, and all volatiles were removed *in vacuo*. The product was purified by silica gel chromatography, eluting with 100% CH_2Cl_2, resulting in the product as a yellow powder that was precipitated from CH_2Cl_2/hexanes mixture and isolated by filtration (165 mg, 0.17 mmol) in 77 % yield. Single crystals were grown from a slow diffusion of hexanes into a concentrated CH_2Cl_2 solution. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.78 (d, 4H, $J_{H\text{-}H}$ = 6.55 Hz, *o-pyr*), 8.52 (m, 3H, Ar*H*), 7.90 (t, 1H, $J_{H\text{-}H}$ = 7.81 Hz, Ar*H*), 7.64 (t, 2H, $J_{H\text{-}H}$ = 6.55 Hz, *p-pyr*), 7.56 (t, 2H, $J_{H\text{-}H}$ = 7.81 Hz, Ar*H*), 7.38 (d, 4H, $J_{H\text{-}H}$ = 7.81 Hz, Ar*H*), 7.21 (t, 4H, $J_{H\text{-}H}$ = 6.55 Hz, *m-pyr*, Ar*H*), 4.27 (s, 6H, trz-CH_3), 2.81 (septet, 4H, $J_{H\text{-}H}$ = 6.55 Hz, iPr-C*H*), 1.45 (d, 12H, $J_{H\text{-}H}$ = 6.55 Hz, iPr-CH_3), 1.09 (d, 12H, $J_{H\text{-}H}$ = 6.55 Hz iPr-CH_3). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 151.4, 146.8, 143.3, 142.1 (Pd-C), 137.8, 135.0, 132.7, 132.6, 131.4, 129.7, 127.9, 124.4, 124.1, 38.6, 29.1, 26.3, 23.0. **HRMS** (ESI-TOF, m/z) calculated for [$C_{46}H_{54}N_8Pd_2$]: 1072.1239, found 1072.1298. **(EA)** (%) Anal. Calcd for: $C_{46}H_{54}N_8Cl_4Pd_2 \cdot 1.9C_6H_{14} \cdot 1.2CH_2Cl_2$: C 52.55, H 6.25, N 8.37; found C 52.88, H 5.95, N 8.06.

General procedure for the Mizoroki-Heck reaction with Pd-tMIC complexes (Scheme 4-17): Catalyst (0.002 mmol, 2 mol% Pd), sodium formate (0.02 mmol, 10 mol%), and aryl halide (0.2 mmol, 1 eq.) were added to a oven dried 50 mL Schlenk flask under argon. Dry, degassed DMF (2.5 mL) was added, followed by methyl acrylate (0.28 mmol, 1.4 eq), and NEt_3 (0.5 mL). The solution was then heated for the indicated time at the indicated temperature, after which, the CH_2Cl_2 and NEt_3 were removed under vacuum. The remaining residue was dissolved in 10 mL of EtOAc and filtered through Celite™. Coupled products were then purified by column chromatography using hexanes/EtOAc as an eluent. Spectra of products matched those previously reported.[58]

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Chapter 5

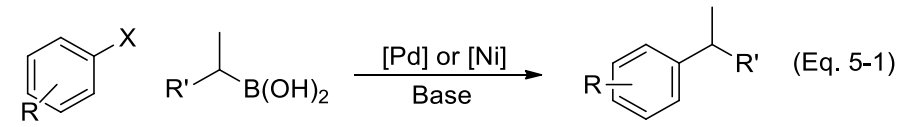
Pd-NHC Catalyzed Desulfinative Cross Coupling Reactions

5.1 Pd Catalyzed Cross Couplings

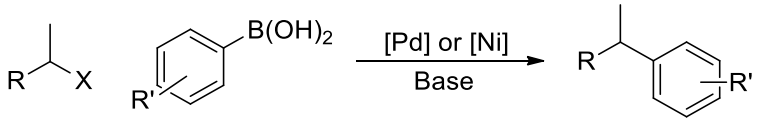
5.1.1 Introduction

Transition metal catalyzed cross coupling has undergone an unparalleled growth in development in the last few decades, and is now at a remarkable level of refinement.[1] Of the different types of cross coupling, the Suzuki-Miyaura cross coupling is particularly attractive due to its relatively mild nature and the low environmental impact of boron.[2] In addition, the starting boronic acids or the corresponding boronic esters can be readily synthesized, typically display high bench stability,[3] and undergo facile transmetallation to transition metals.[4]

Until only recently however, Suzuki-Miyaura cross couplings have been restricted to bond forming reactions between two sp^2 centers or linear sp^3 centers. In contrast, reports detailing the Suzuki-Miyaura cross coupling of chiral sp^3 containing boranes or derivatives (Eq. 5-1) or chiral electrophiles (Eq. 5-2) have only recently appeared.[5] The cross coupling of chiral sp^3 centers in particular has great potential in organic synthesis as it represents the possibility of preparing enantiomerically enriched products.



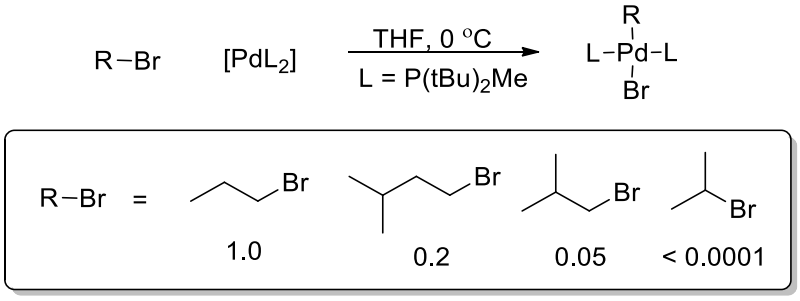
(Eq. 5-1)



(Eq. 5-2)

A number of problems typically plague sp^3 cross coupling reactions however. The decreased ability of a transition metal to undergo an oxidative addition[6] or transmetalation[7] to hindered alkyl halides or boronic acids respectively represents a major obstacle to be overcome for the successful cross coupling of these substrates. While there have been several reports of palladium catalyzed cross couplings with branched alkyl boron species,[5f, 7-8] branched alkyl electrophiles have lagged in comparison.

It has been proposed that oxidative addition of alkyl halides with palladium complexes takes place via an S_N2 type pathway.[9] In direct accordance with this, Fu has demonstrated that the steric bulk of a substrate has a significant effect on the rate of oxidative addition on alkyl halides (Scheme 5-1).[6] It should therefore be no surprise that very few examples of palladium catalyzed Suzuki-Miyaura cross coupling reactions of secondary alkyl halides have been reported.[10] In contrast, nickel complexes typically undergo oxidative additions involving radical intermediates,[11] and are less impacted by steric bulk. As a result, there have been many examples of Ni catalyzed cross coupling reactions of secondary alkyl halides.[12] Importantly, the radical nature of this reaction has also been exploited in the enantioselective cross couplings of racemic branched electrophiles.[5b, 13]



Scheme 5-1: Rate of oxidative addition of different alkyl halides onto Pd described by Fu.[6]

In addition, the propensity of alkyl palladium species to undergo β-hydride elimination presents a divergent pathway which results in the formation of alkenes as unwanted by products (Figure 5-1).[14] As such, for desired product forming reductive elimination to occur, competing β-hydride elimination must be suppressed. Alternatively, reductive elimination can be facilitated by the use of large, bulky ligands.

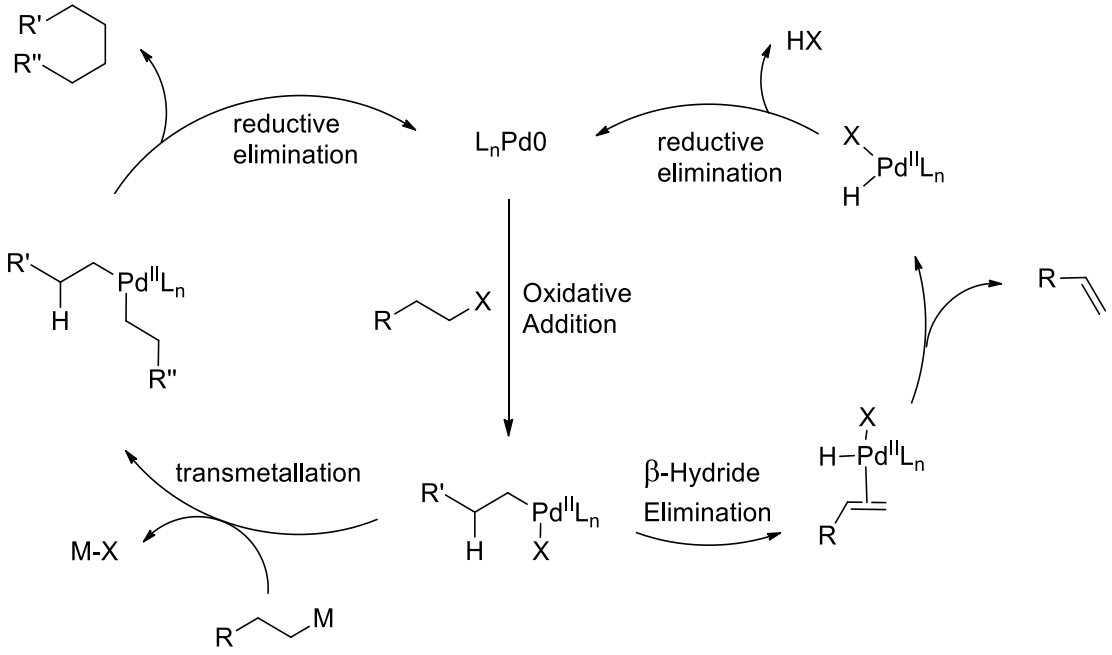
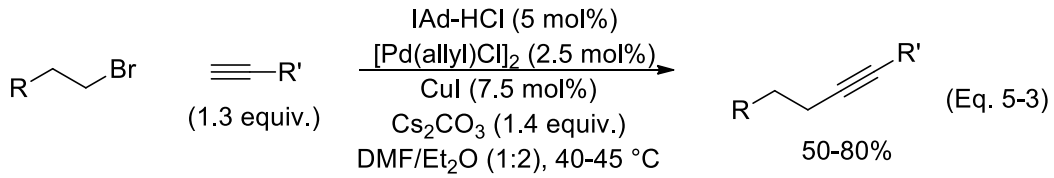


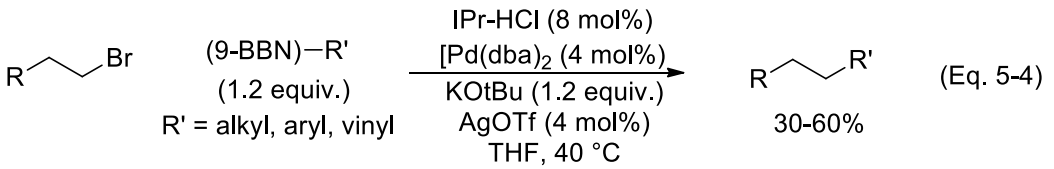
Figure 5-1: Competing pathways in sp^3-sp^3 cross coupling

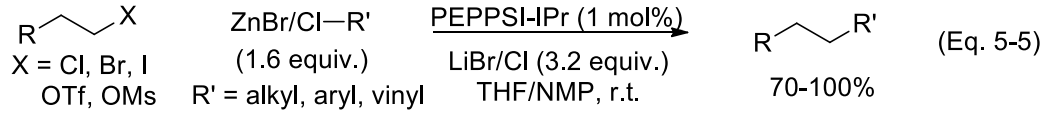
5.1.2 Sp^3 Cross Coupling with Pd-NHC catalysts

As indicated in Section 1.7.1, Pd-NHC complexes have a long history in cross coupling,[15] however, this is almost entirely in the the cross coupling of C-B and C-X compounds bearing sp^2 centers. The first report of a Pd-NHC complex catalyzing a process involving an sp^3 hybridized electrophile was reported by Fu and coworkers in 2004.[16] This process involved the Sonogashira reaction of primary alkyl halides, and proceeded in good

yield, which occurred under mild conditions (Eq. 5-3). All phosphines screened were ineffective, however sterically encumbered NHCs resulted in the formation of product. The catalyst was formed in situ from a combination of $[Pd(allyl)Cl]_2$ and an imidazolium salt. Similar results were demonstrated soon afterwards by Caddick and coworkers, who described the sp^3-sp^3 Suzuki-Miyaura reaction utilizing alkyl primary 9-BBN reagents (Eq. 5-4).[17]



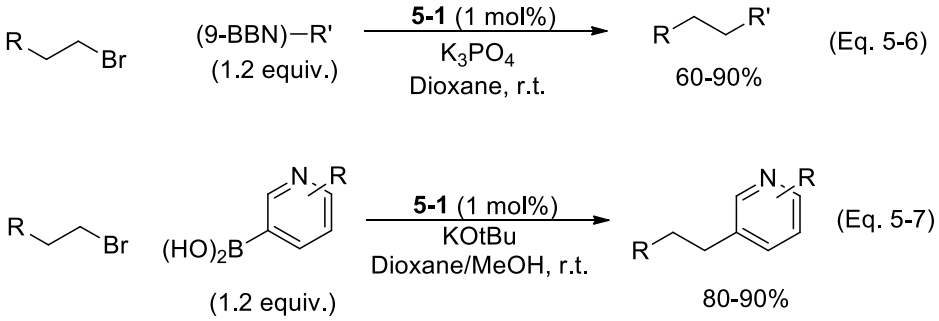


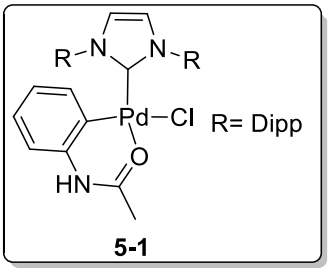


Additionally, Organ described the alkyl-alkyl Negishi coupling, catalyzed by Pd-NHC complexes (Eq. 5-5). He further demonstrated that preformed PEPPSI-type complexes resulted in a substantial increase in the rate of the reaction in sp^3 Negishi reactions, when compared to analogous catalysts that are made in-situ from palladium precursors and imidazolium salts.[18] Assuming the active species in the systems were the same, TOF calculations indicate that the in-situ method only generated 0.1 mol% of active catalyst, even when 4 mol% of precatalyst is added. The use of a preformed IPr-PEPPSI

complex as a precatalyst allowed for alkyl iodides, bromides, chlorides, triflates and even mesylates to undergo sp^3-sp^3 Negishi couplings in good yield at room temperature.[18b] Similar activity has been described with the same catalyst in sp^3-sp^3 Suzuki reactions between alkyl bromides with primary alkyl-9-BBN reagents.[19]

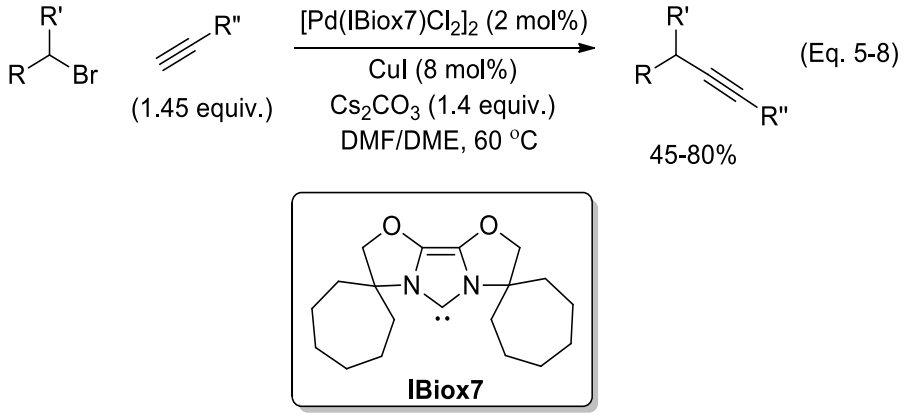
Similar sp^3-sp^3 Suzuki reactions were later reported by Kantchev and coworkers, who demonstrated the effectiveness of **5-1** as a catalyst in Suzuki-Miyaura cross coupling reactions with linear alkyl halides (Eq. 5-6).[20] In contrast to the previous reports however, the authors also described the effectiveness of aryl boronic acids as coupling partners at room temperature (Eq. 5-2). This is an important improvement as phenyl boronic acids are substantially more stable and user friendly than the corresponding 9-BBN adducts. In addition, it gives access to sp^3-sp^2 cross coupled products.





The success of NHCs in alkyl-alkyl cross couplings is likely related to their significant steric bulk, which facilitates product forming reductive elimination, and avoids unwanted β-hydride elimination.[21] This hypothesis is directly in line with results indicating

that larger NHCs generally produce higher activity. Although quite impressive, all of the examples described above only detail the use of primary alkyl halides, and therefore do not carry any stereochemical information. To date, very few examples detailing the Pd-NHC catalyzed cross coupling of secondary alkyl halides have been reported. Glorius reported the racemic Sonogashira coupling of unactivated secondary alkyl bromides, catalyzed by a Pd complex featuring the very large IBiox7 ligand (Eq. 5-8).[22] Attempts at cross coupling enantioenriched secondary bromides resulted in racemic products. Unfortunately, it is a little surprising that although chiral variants of IBiox ligands have been described,[23] no enantioselective variants of this reaction have been reported.

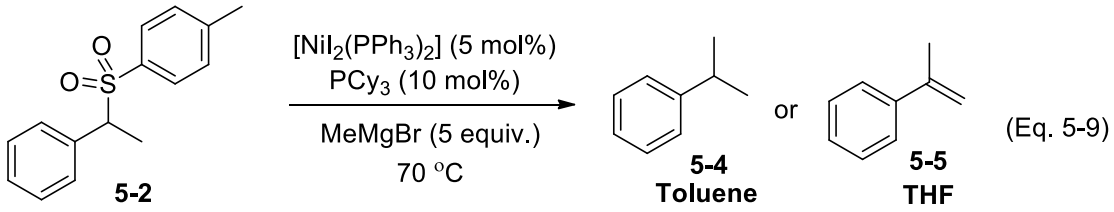


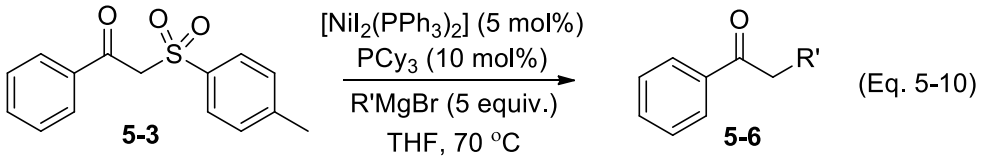
5.1.3 Desulfinative Couplings

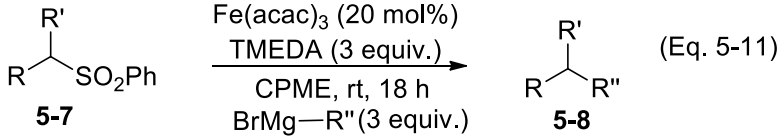
Although all of the alkyl electrophiles for cross coupling mentioned previously have been either halides, or sulfonate esters, a wide variety of alternative electrophiles have also been reported in various forms of cross coupling.[24] In particular, sulfur-derived leaving groups, primarily thioethers,[25] and sulfinic acids[26] have been explored in cross coupling reactions.[27] Recently, there have been some reports detailing alkyl sulfones as effective electrophiles in cross coupling reactions. These substrates are exciting as they typically

display high bench stability, and can be readily synthesized upon oxidation from their corresponding thioethers.

Stemming from the Julia olefination,[28] aromatic[29] and vinyl[30] sulfones have been previously investigated in palladium and nickel catalyzed Kumada type couplings. In 2012, Li and coworkers, demonstrated that benzylic sulfones (**5-2**), and 1-aryl-2-tosylethanones (**5-3**) could also be coupled with alkyl Grignard reagents under nickel catalysis (Eqs. 5-9 and 5-10).[31] Interestingly, the choice of solvent had a dramatic effect on the product of the reaction forming **5-4** in THF, and **5-5** in cyclohexane.



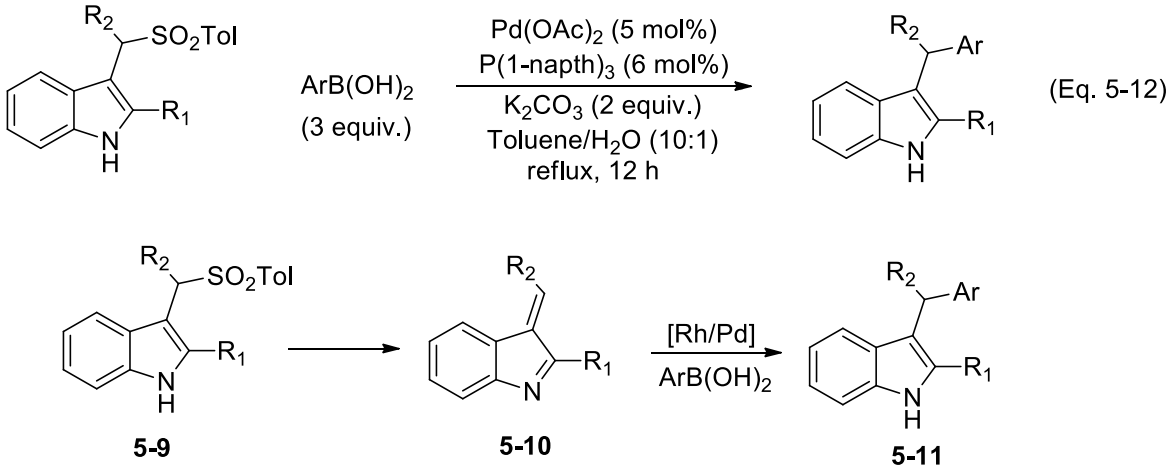




Impressively, Denmark demonstrated that unactived secondary alkyl phenyl sulfones undergo iron catalyzed Kumada type coupling reactions with aryl Grignard reagents (Eq. 5-11).[32] It was hypothesized that the mechanism for this transformation involved an outer sphere electron transfer with the loss of $PhSO_2^-$ as a leaving group.

Jiang and coworkers reported the rhodium catalyzed arylation of sulfonyl indoles with boronic acids.[33] The same group later reported the palladium catalyzed cross coupling

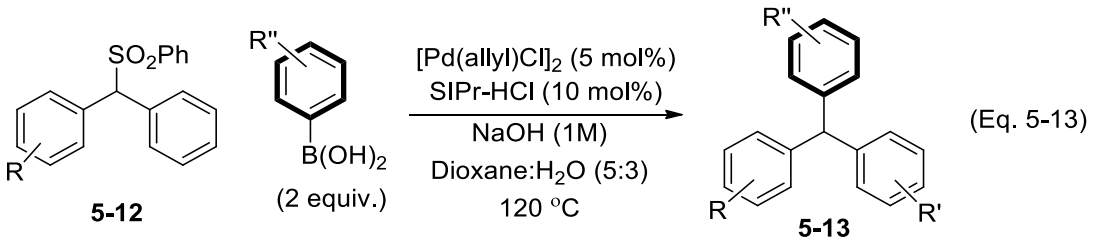
of the same substrates (eq. 5-12).[34] These transformations were proposed to go by a mechanism depicted in Scheme 5-2. Base induced loss of SO_2Tol resulted in **5-10**, followed by 1,4 conjugate addition of the boronic acid to generate **5-11**.



Scheme 5-2: Proposed mechanism for the desulfinative cross coupling of 5-9.

In 2013, Crudden and Nambo, reported the Pd catalyzed synthesis of triaryl methanes from dibenzylic phenyl sulfones **5-13** (Eq. 5-13).[35] This system utilized a Pd-NHC catalyst which was formed in-situ from the carbene salt and $[Pd(allyl)Cl]_2$ in the presence of NaOH. This report was the first example of a Pd-NHC complex catalyzing a Suzuki-Miyaura cross coupling of a secondary alkyl electrophile. Using this method, a wide variety of triaryl methanes could be synthesized. Screening results indicated that NHCs out performed even the most electron rich phosphines. In particular, the larger, more electron rich SIPr was reported to be the most active ligand, and displayed higher activity than the smaller IMes. The strongly electron donating ligand likely helped to aid in the difficult oxidative addition of the sulfone. Interestingly, the phenyl sulfone was selectively

activated at the sp^3 C-S bond. A similar result was also reported by Nolan who reported the C-S cleavage of aryl sulfoxides.[36]

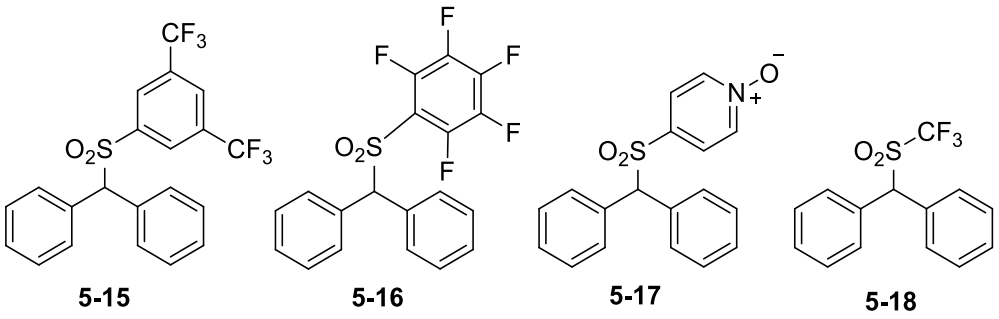


Despite the novelty of this report, the relatively harsh conditions required, namely the high temperatures, and high catalyst loading, limited further development this reaction. In particular, the relatively high temperatures required presented a potential obstacle for the development of enantioselective variants. Additionally, ortho substituted sulfones were poor substrates for this reaction, which severely limited the substrate scope.

We saw great potential from this transformation, and our group was interested in further exploring the nature of the process. We hypothesized that extensive catalyst and substrate development would address some of the limitations listed above, and might lead to the development of an enantioselective variant.

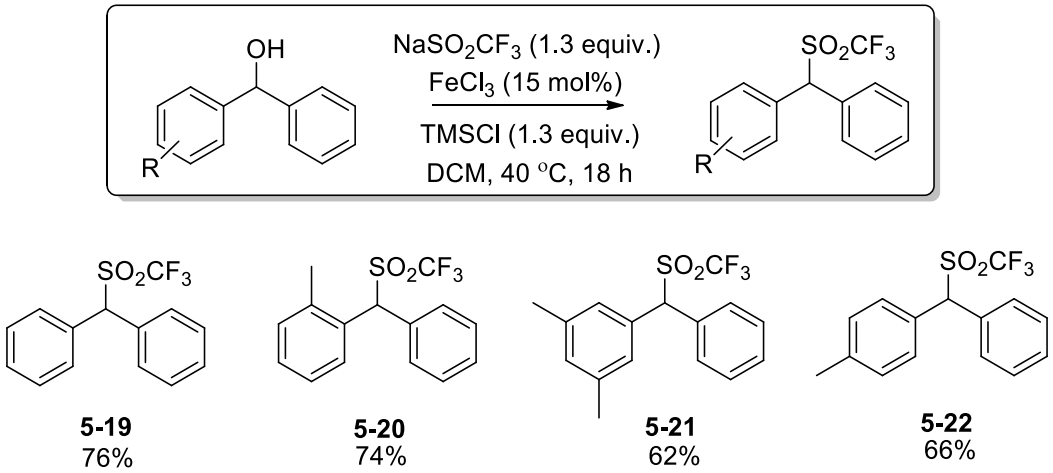
5.2 Results and Discussion

We began by investigating methods to increase the reactivity of the sulfone substrates in order to expand the substrate scope and result in coupling under milder conditions. We hypothesized that electron withdrawing substituents on the sulfone would increase the electrophilicity of the sulfone, which would aid in its activation (Scheme 5-3).



Scheme 5-3: Electron-poor sulfones selected for investigation

Postdoctoral Fellow Cristina Pubil-Ulldemolins preformed preliminary investigations into the activity of different sulfones and identified triflone **5-18** as a highly promising candidate. Conveniently, benzylic sulfones can be synthesized from the corresponding alcohol and sulfinic acid sodium salts in the presence of an iron catalyst.[37] The reaction of benzhydrol derivatives with $NaSO_2CF_3$ and TMSCl with catalytic $FeCl_3$ resulted in the formation of triflones **5-19** to **5-22** in quantitative conversion as determined by ^1H NMR spectroscopy (Scheme 5-4). Unfortunately, the purification of these species proved remarkably difficult. Although **5-19** to **5-22** were bench stable, they displayed remarkable sensitivity to silica gel, and decomposed back to the corresponding alcohol rapidly. Attempts at crystallization, sublimation and distillation were met with failure. Fortunately, purification could be achieved by column chromatography using neutral alumina as the stationary phase. In all cases, compounds **5-19** to **5-22** were isolated as bench stable solids, and were characterized by ^1H, ^{13}C, and ^{19}F NMR spectroscopy.

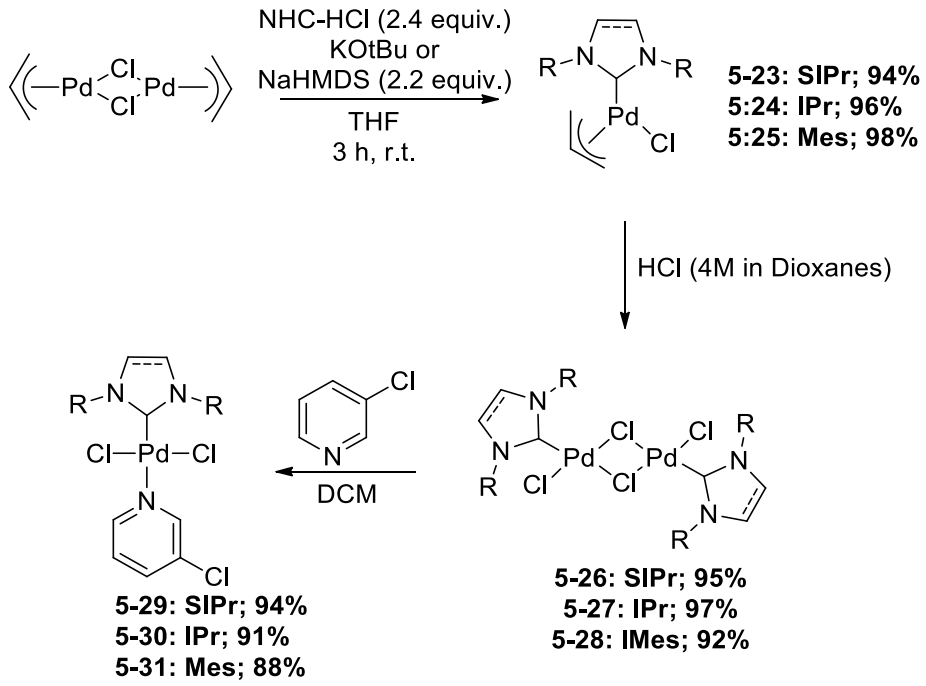


Scheme 5-4: Synthesis of CF_3 sulfones

The ^{1}H NMR spectra are quite diagnostic, as they contain sharp downfield singlets (5.5-6.0 ppm) for the C-H resonance. The ^{13}C NMR spectra of these species have resonances at ~120 ppm, with the characteristic coupling patterns expected for a CF_3 substituent. Additionally, in all cases, a single resonance is observed in the ^{19}F NMR spectrum.

For catalytic studies, several Pd-NHC catalysts were synthesized, rather than forming them in situ (Scheme 5-5). This was done in order to avoid any ambiguity in the nature of the catalyst,[38] as well as hopefully improve catalytic activity.[18a] Several different families of precatalysts were chosen for investigation which have been reported to undergo different mechanisms in their reduction to Pd^0 (*vide infra*). Pd-NHC catalysts were synthesized in high yield by procedures displayed in Scheme 5-5. Conveniently, dimeric Pd-NHC complexes **5-26** to **5-28** can be synthesized from [(NHC)Pd(allyl)Cl] type precursors (**5-23** to **5-25**), which are readily prepared without requiring isolation of the free

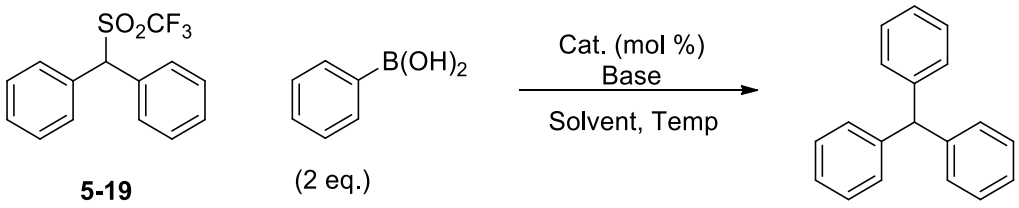
NHC.[39] Compounds **5-26** to **5-28** can then be treated with 3-chloropyridine[39b] resulting in PEPPSI complexes **5-29** to **5-31** or PPh_3[39d] giving compounds **5-32** to **5-34** in high yield.



Scheme 5-5: Synthesis of various Pd-NHC complexes

Initial investigation into the cross coupling of sulfone **5-19**, utilizing conditions inspired from the initial report[35] confirmed that **5-19** has higher reactivity than the phenyl sulfone derivative, since the product could be formed at substantially lower temperatures (Table 5-1). Screening indicated that large bulky NHCs such as SIPr out-performed smaller NHCs such as IMes. This is consistent with the large body of literature on Pd-NHC cross couplings of sp^2 centers.[15a, 15c, 15d, 40] It can further be observed that PEPPSI type complexes, or dimer type **5-27** resulted in substantially lower, if any activity. Pleasingly, the formation of **5-35** could be affected at slightly elevated temperatures (40 °C), using low (2 mol%) catalyst loading of **5-24**.

Table 5-1: Preliminary investigations into catalysis with CF_3 sulfones



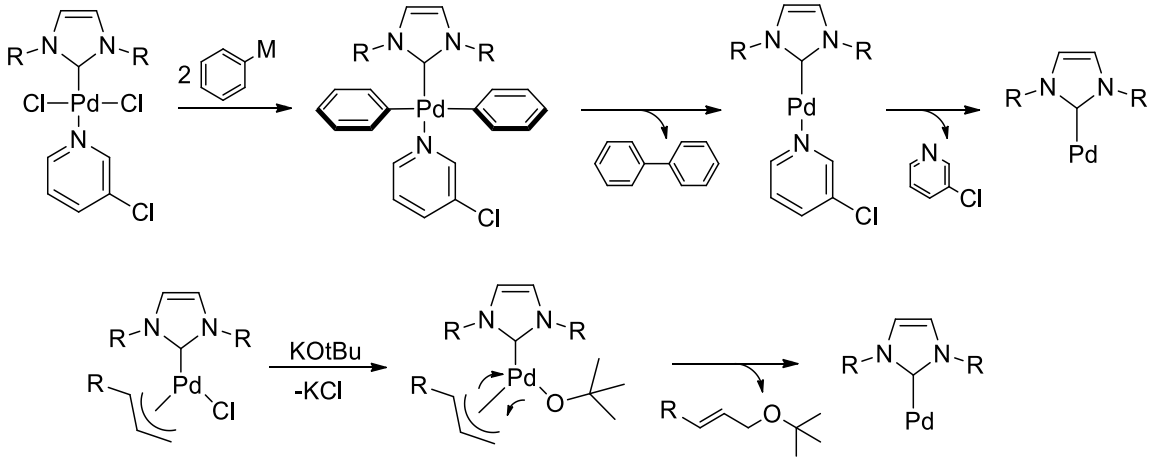
5-19 (2 eq.) **5-32**

Entry	Cat. (mol %)	Temp (°C)	Yield (%)
1	**5-24** (10)	25	79
2	**5-25** (10)	25	NR
3	**5-23** (10)	25	77
4	**5-29** (10)	25	NR
5	**5-30** (10)	25	NR
6	**5-31** (10)	25	NR
7	**5-27** (5)	25	7
8	**5-24** (2)	40	96
9	**5-24** (2)	30	27

General Conditions: 5-19 (0.1 mmol), phenyl boronic acid (0.2 mmol), NaOH (1M) indicated catalyst (from Scheme 5-5), in THF/H_2O (5:3), heated in a one dram sealed vial for 16 hours. Yields determined by ^1H NMR spectroscopy using 1,3,5 trimethoxybenzene as an internal standard.

The higher activity of **5-23** and **5-24** complexes relative to the other precatalysts may be associated with their more efficient reduction to Pd^0. Organ has suggested that reduction of PEPPSI-type complexes may be facilitated by organometallic reagents, followed by the loss of pyridine (Scheme 5-6).[16] This hypothesis was supported by stoichiometric experiments, in which they detected homocoupling of the organometallic reagent.[18a, 41] Although this mechanism may be plausible in some cross coupling reactions, it will be strongly affected by the rate of transmetalation of the organometallic reagent to the palladium centre, which is in turn related to the nature of the base.[4a] Alternatively, Nolan has suggested that [(NHC)Pd(allyl)Cl] type precatalysts undergo reaction with the base itself.[42] For example, attack of KOtBu onto the allyl moiety will generate an active NHC-Pd^0 centre.[43] The rate of this initiation mechanism will also be heavily dictated by

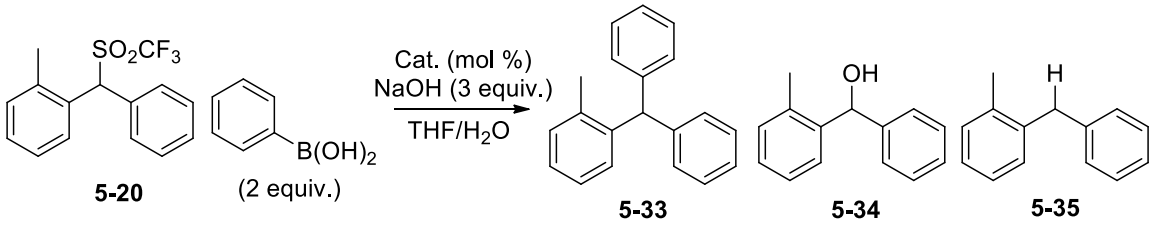
the choice of base, but was found to be applicable with strong alkoxide bases such similar to our study.



Scheme 5-6: Proposed mechanisms for the reduction of Pd^{II}

With conditions in hand, we sought to explore the reactivity towards more highly substituted sulfones. Unfortunately however, substantially lower activity was observed which was attributed to the increased steric bulk around the sulfone (Table 5-2). As a result, higher temperatures were required. Unfortunately, **5-20** displayed very high levels of decomposition to the corresponding alcohol (**5-37**) under these conditions. Control studies indicated that the decomposition occurred in the absence of Pd, and was likely occurring by hydrolysis (Entry 4). As a result, we abandoned these conditions, and pursued anhydrous cross coupling of **5-19** in hopes that this would circumvent this problem.

Table 5-2: Catalysis with *o*-Tol triflone



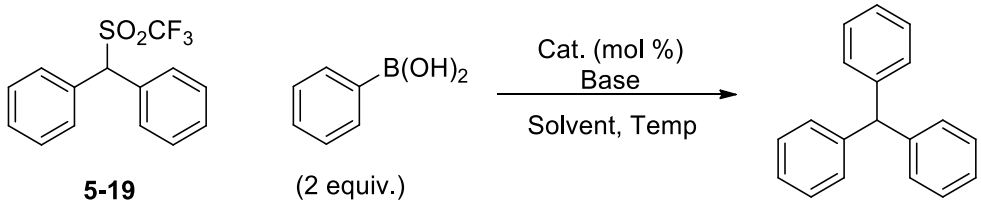
5-20 5-33 5-34 5-35

Entry	Catalyst (mol%)	Temp (°C)	Yield (%) (5-20/5-33/5-34/5-45)
1	**5-24** (2)	40	58/6/25/0
2	**5-24** (2)	60	0/29/30/24
3	**5-24** (5)	60	0/46/35/10
4	-	60	64/0/33/0

General Conditions: **5-20** (0.1 mmol), phenyl boronic acid (0.2 mmol), NaOH (1M, 0.3 mmol), indicated catalyst, in THF/H_2O (5:3), heated in a one dram sealed vial for 16 hours. Yield was obtained by ^{1}H NMR spectroscopy using 1,3,5 trimethoxy benzene as an internal standard

Using **5-23** as a precatalyst, several bases were screened for activity for the coupling of **5-19** with $PhB(OH)_2$ in anhydrous THF, at low temperature (Table 5-3). Moderate yields were obtained using 1.5 equiv. of KOtBu, while other bases such as NaOEt, K_3PO_4, CsF and NaHMDS resulted in much lower activity. This may be in part associated with the generation of Pd^0 (vide supra). While higher temperatures provided the desired product in high yield (Entry 8), a small screening of solvents revealed that toluene provided comparable yields at lower temperatures (Entry 9). Once again precatalyst **5-23** displayed higher activity than other Pd-NHC complexes. Smaller NHCs, while moderately effective (Entry 12), gave lower yields in comparison, while SIPr-PEPPSI was completely ineffective (Entry 13).

Table 5-3: Anhydrous coupling of sulfone **5-19**



5-19 (2 equiv.) **5-32**

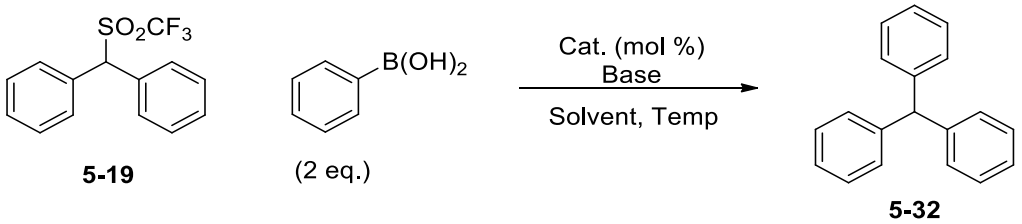
Entry	Catalyst (mol%)	Base (eq.)	Solvent	Temp (°C)	Yield (%)
1	**5-23** (5)	KOtBu (1.5)	THF	40	55
2	**5-23** (10)	KOtBu (1.5)	THF	40	50
3	**5-23** (5)	Cs_2CO_3 (1.5)	THF	40	NR
4	**5-23** (5)	K_3PO_4 (3)	THF	40	15
5	**5-23** (5)	CsF (3)	THF	40	13
6	**5-23** (5)	NaHMDS (1.5)	THF	40	10
7	**5-23** (5)	NaOEt (1.5)	THF	40	8
8	**5-23** (5)	KOtBu (1.5)	THF	60	96
9	**5-23** (5)	KOtBu (1.5)	Toluene	40	97
10	**5-23** (5)	KOtBu (1.5)	Dioxanes	40	85
11	**5-23** (5)	KOtBu (1.5)	Toluene	40	84
12	**5-25** (5)	KOtBu (1.5)	Toluene	40	57
13	**5-29** (5)	KOtBu (1.5)	Toluene	40	NR

General Conditions: 5-19 (0.1 mmol), phenyl boronic acid (0.2 mmol), indicated catalyst, in the indicated solvent, heated in a one dram sealed vial for 16 hours. Yield was determined by ^{1}H NMR spectroscopy using 1,3,5 trimethoxy benzene as an internal standard

Several palladium phosphine complexes were also examined (Table 5-4), but in all cases, these were completely ineffective under the conditions tested, and resulted in the return of starting material. These results highlight the effectiveness of NHCs as ligands in this cross coupling reaction, which promote very active metal centers. Several nickel complexes were also investigated. While Ni^{II} precursor $[Ni(PCy_3)_2Cl_2]$ was completely ineffective under the conditions investigated, Ni^0 precursors displayed marginal yield (entries 8-10). As the active species in all these cases is expected to be the same, these results may highlight the difficulty in reducing the Ni^{II} center under these reaction

conditions. In all cases investigated however, nickel and palladium phosphine complexes were consistently out-performed by Pd-NHC complex **5-23**.

Table 5-4: Screening with Pd and Ni phosphine complexes



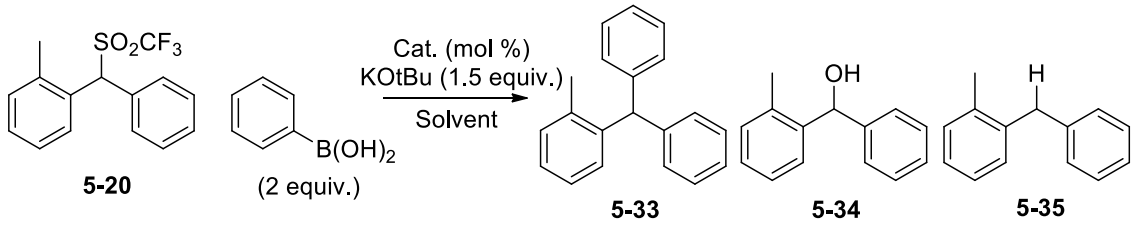
5-19 (2 eq.) **5-32**

Entry	Catalyst (mol%)	Base (eq.)	Solvent	Temp (°C)	Yield (%)
1	$[Pd(OAc)_2]/PCy_3$ (10/20)	KOtBu (1.5)	THF	40	NR
2	$[Pd_2(dba)_3]/PCy_3$ (5/20)	KOtBu (1.5)	THF	40	NR
3	$[Pd(allyl)Cl]_2/PtBu_3$-HBF_4 (2.5/5)	KOtBu (1.5)	Toluene	40	NR
4	$[Pd(allyl)Cl]_2$/SPhos(5/10)	KOtBu (1.5)	Toluene	40	NR
5	$[Pd(QPhos)_2]$ (10)	KOtBu (1.5)	Toluene	40	NR
6	$[Ni(PCy_3)_2Cl_2]$ (10)	K_3PO_4 (3)	THF	40	NR
7	$[Ni(PCy_3)_2Cl_2]$ (10)	KOtBu (1.5)	THF	60	NR
8	$[Ni(COD)_2]/PCy_3$ (10/20)	KOtBu (1.5)	THF	40	17
9	$[Ni(COD)_2]/PCy_3$ (10/20)	KOtBu (1.5)	Toluene	40	10
10	$[Ni(COD)_2]/PCy_3$ (10/20)	Cs_2CO_3 (1.5)	Toluene	40	NR

General Conditions: 5-19 (0.1 mmol), phenyl boronic acid (0.2 mmol), indicated catalyst, in the indicated solvent, heated in a one dram sealed vial for 16 hours. Yield was determined by ^{1}H NMR spectroscopy using 1,3,5 trimethoxy benzene as an internal standard.

With optimized conditions in hand, ortho substituted sulfone **5-20** was examined. While once again, slightly higher temperatures were required to see comparable conversion to product, no hydrolysis was observed (Table 5-5). Consistent with previous results, SIPr appeared to be the most applicable ligand. Interestingly, the use of SIPr-HCl and $[Pd(allyl)Cl]_2$ to form **5-23** in situ resulted in no observable product by ^{1}H NMR spectroscopy (Entries 6 and 7).

Table 5-5: Coupling substituted triflone under anhydrous conditions



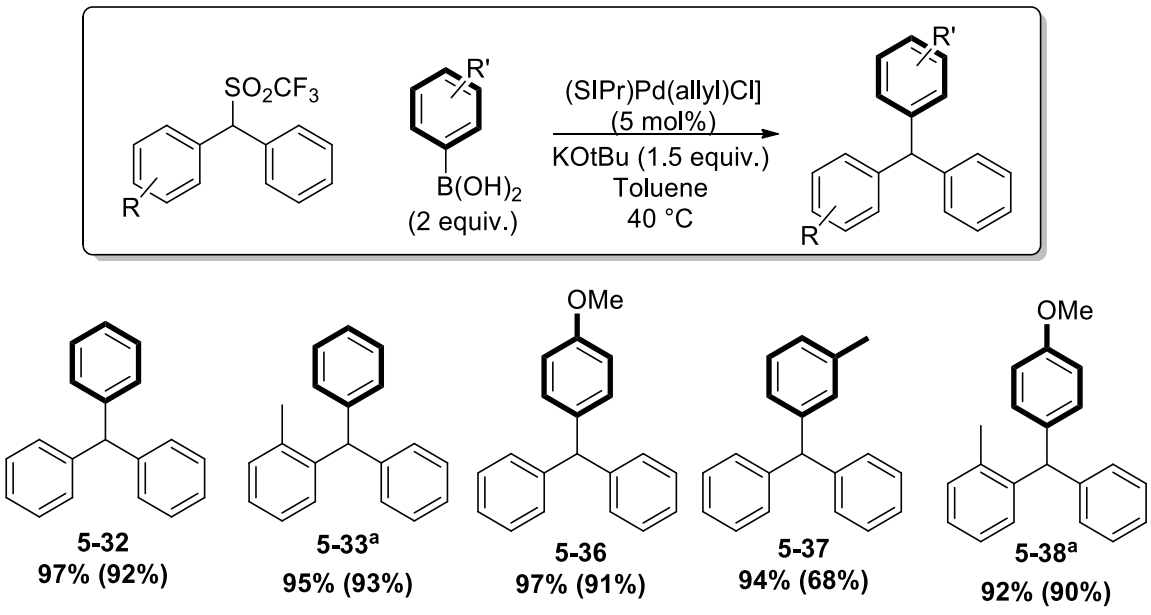
5-20 (2 equiv.) → **5-33**, **5-34**, **5-35**

Entry	Catalyst (mol%)	Solvent	Temp (°C)	Yield (%) (5-20/5-33/5-34/5-45)
1	**5-23** (5)	THF	60	42/33/0/6
2	**5-23** (5)	Toluene	35	86/12/0/0
3	**5-23** (5)	Toluene	50	0/95/0/0
4	**5-24** (5)	Toluene	50	68/30/0/0
5	**5-29** (5)	Toluene	50	96/0/0/0
6	$[Pd(allyl)Cl]_2$/SIPr-HCl (2.5/5)	Toluene	50	93/5/0/0
7	$[Pd_2(dba)_3]$/SIPr-HCl (2.5/5)	Toluene	50	78/0/0/0

General Conditions: 5-20 (0.1 mmol), phenyl boronic acid (0.2 mmol), KOtBu (0.15 mmol), indicated catalyst, in the indicated solvent, heated in a one dram sealed vial for 16 hours. Yield was obtained by ^{1}H NMR spectroscopy using 1,3,5 trimethoxy benzene as an internal standard

The optimized conditions were then applied for the synthesis of the products shown in Table 5-6. In general, comparable yields were obtained with the different phenyl boronic acids investigated, and all products could be purified by column chromatography. The high yield obtained with **5-33** is an important result, as the formation of this compound from the analogous phenyl sulfone required 150 °C, and 10 % catalyst loading.[35]

Table 5-6: Triarylmethanes products



General Conditions: sulfone (0.1 mmol), phenyl boronic acid (0.2 mmol), indicated catalyst, in the indicated solvent, heated in a one dram sealed vial and heated at 40 °C for 16 hours. NMR yields based on 1,3,5 trimethoxybenzene, Isolated yields in parentheses. [a]at 50 °C

5.3 Conclusions and Future Work

In this chapter, the Pd-NHC catalyzed cross coupling of benzylic sp^3 triflones was described. In general, substantially milder conditions are necessary for their successful cross coupling compared to our previous report with phenyl sulfones. Both electron rich and electron deficient boronic acids are acceptable coupling partners. In addition, we demonstrated the importance of anhydrous coupling conditions for the overall transformation to avoid the formation of unwanted by-products. Importantly, we demonstrated the higher reactivity of preformed Pd-NHC complexes compared to in situ generated species. These results were directly in line with results previously reported in the literature which have demonstrated this importance in more traditional cross coupling reactions.

While only a small number of triaryl methanes were reported in Scheme 5-7, we are interested in expanding the scope of this transformation and exploring the reactivity towards a wide variety of other phenyl boronic acids. Both electron rich, deficient phenyl boronic acids will be investigated, as well as more hindered substrates. We are also interested in applying this reaction to substrates which contain heterocycles that are biological interest. Finally, we are also interested in the development of an enantioselective variant, which would give access to enantioenriched triaryl methanes. In order to accomplish this, chiral NHCs are being synthesized, and will then be subjected to the optimized conditions.

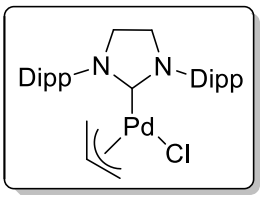
5.4 Experimental

General considerations: All manipulations were carried out under an atmosphere of dry argon in oven dried glassware, or under a nitrogen atmosphere in a glovebox (M. Braun) with oxygen and water levels ≤2 ppm. All solvents were distilled from either CaH_2 (CH_2Cl_2, NEt_3) or Na/benzophenone (THF, C_6H_6, toluene, Et_2O), degassed via three freeze–pump–thaw cycles and stored under N_2 over molecular sieves (4Å) prior to use. $[Pd(allyl)Cl]_2$, was prepared according to previously reported literature procedures.[44] $PdCl_2$, $Pd_2(dba)_3$ and $[Pd(QPhos)_2]$ were generously donated by Johnson-Mattey. IPr-HCl,[45] IMes-HCl,[46] and SIPr-HCl[47] were prepared by previously reported procedures. All other reagents were purchased from commercial suppliers and used without further purification. ^1H NMR spectra were recorded on a Bruker Avance 400 MHz or 500 MHz spectrometer where indicated. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using residual protonated solvent

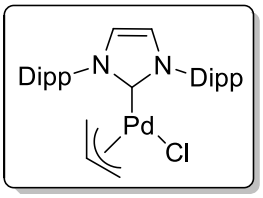
as an internal standard (C_6D_6, 7.15 ppm; $CDCl_3$, 7.26 ppm). ^{13}C NMR spectra were recorded at 100 MHz. Chemical shifts are reported as above using the solvent as an internal standard (C_6D_6, 128.0 ppm; $CDCl_3$, 77.16). Assignments of the ^1H and $^{13}C\{^1H\}$ NMR spectra were made using ^1H-^1H gs-COSY, ^1H-^{13}C-HSQC and ^1H-^{13}C-HMBC NMR experiments.

General procedure for the synthesis of Pd-NHC complexes 5-23 to 5-25:

An over dried 50 mL round bottom flask was charged with $[Pd(allyl)Cl]_2$ (200.0 mg, 0.55 mmol), NHC-HCl (1.15 mmol), and KOtBu (152.3 mg, 1.36 mmol), or NaHMDS (250.1 mg, 1.36 mmol) as solids under argon. Anhydrous THF (10 mL) was added via syringe. The mixture was stirred at room temperature for 3 hours. The mixture was diluted with THF and filtered through Celite™, and all volatiles were removed *in vacuo*. Purification was achieved by silica gel column chromatography eluting with 100% ethyl acetate.

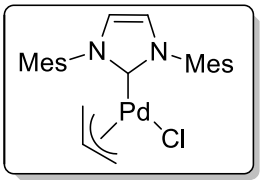


Synthesis of **5-23**: The general procedure was followed using NaHMDS (250.2 mg, 1.36 mmol), $[Pd(allyl)Cl]_2$ (200.0 mg, 0.55 mmol), and SIPr-HCl (488.7 mg, 1.15 mmol), resulting in a lightly yellow solid (592.7 mg, 1.04 mmol) 94 % yield. Spectral data matched those previously reported.[48]



Synthesis of **5-24**: The general procedure was followed using KOtBu (152.3 mg, 1.36 mmol), $[Pd(allyl)Cl]_2$ (200.0 mg, 0.55 mmol), and IPr-HCl (486.4 mg, 1.15 mmol), resulting in a lightly

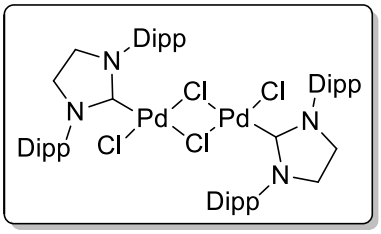
yellow solid (602.3 mg, 1.06 mmol) in 96 % yield. Spectral data matched those previously reported.[48]



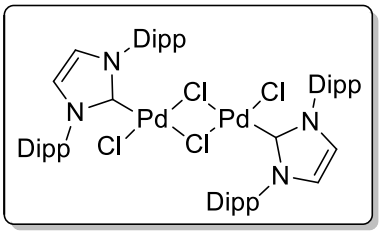
Synthesis of **5-25**: The general procedure was followed using KOtBu (152.5 mg, 1.36 mmol), $[Pd(allyl)Cl]_2$ (200.0 mg, 0.55 mmol), and IMes-HCl (392.1 mg, 1.15 mmol), resulting in a yellow solid (528.2 mg, 1.08 mmol) in 98 % yield. Spectral data matched those previously reported.[48]

General procedure for the synthesis of Pd-NHC complexes 5-26 to 5-28:

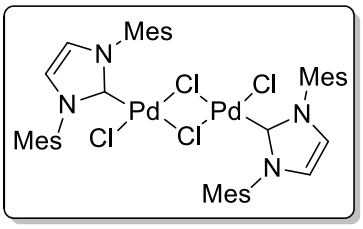
In a procedure modified from Organ,[39b] and Sigman[49] A 4 dram vial sealed with a rubber septum was charged with [(NHC)Pd(allyl)Cl] (0.25 mmol) under argon and 2 mL of HCl (4N in 1,4 dioxane) was added via syringe. The mixture was allowed to stir at room temperature for 18 hours. All volatiles were removed *in vacuo*, and the resulting products were purified by silica gel chromatography using 100 % ethyl acetate as an eluent.



Complex **5-26**: Synthesized by the general procedure from **5-23** (143.2 mg, 0.25 mmol), with 2 mL of HCl (4N in 1,4 dioxane), resulting in an orange solid (270 mg, 0.24 mmol) in 95 % yield. Spectral data matched previously those previously reported.[50]



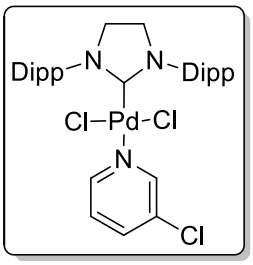
Complex **5-27**: Synthesized by the general procedure from **5-24** (142.7 mg, 0.25 mmol), with 2 mL of HCl (4N in 1,4 dioxane), resulting in an orange solid (274 mg, 0.24 mmol) in 97 % yield. Spectral data matched the previously reported literature.[51]



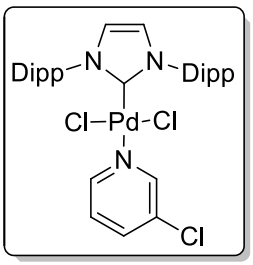
Complex **5-28**: Synthesized by the general procedure from **5-25** (121.1 mg, 0.25 mmol) with 2 mL of HCl (4N in 1,4 dioxanes) resulting in an orange solid (221 mg, 0.23 mmol) 92 % yield. Spectral data matched the previously reported literature.[51]

General procedure for the synthesis of Pd-NHC complexes 5-29 to 5-31:

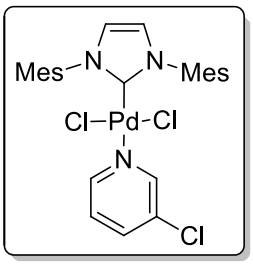
In a procedure modified from Organ,[39b] a 4 dram vial was charged with Pd-NHC complex (**5-25** to **5-27**) (0.2 mmol) and anhydrous CH_2Cl_2 (3 mL) was added. To this solution, 3-chloropyridine (21 µL, 0.22 mmol) was added via syringe, and the solution was stirred at room temperature for 3 hours under argon. The solution was diluted with CH_2Cl_2 (10 mL) and filtered through Celite™. Purification was achieved by silica gel column chromatography eluting with 100% ethyl acetate.



Synthesis of **5-29**: Following the general procedure using **5-25** (113.2 mg, 0.10 mmol), with 3-chloropyridine (21 µL, 0.22 mmol) in CH_2Cl_2 (3 mL), resulting in an off-white solid (127.3 mg, 0.19 mmol) in 94 %. Spectra data matched the previously reported literature.[52]



Synthesis of **5-30**: Following the general procedure using **5-26** (112.8 mg, 0.10 mmol), with 3-chloropyridine (21 µL, 0.22 mmol), in CH_2Cl_2 (3 mL) resulting in a light yellow solid (123.5 mg, 0.18 mmol) in 91 % yield. Spectral data matched the previously reported literature.[18a]

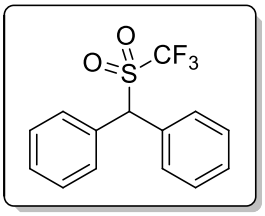


Synthesis of **5-31**: Following the general procedure from **5-27** (80.1 mg, 0.1 mmol), with 3-chloropyridine (21 µL, 0.22 mmol), resulting in a yellow solid (104.3 mg, 0.17 mmol) in 88 %. Spectral data matched the previously reported literature.[18a]

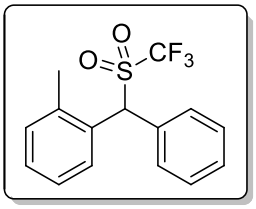
General Procedure for the synthesis of sulfones (5-19 to 5-22):

A 50 mL Schlenk flask was charged with benzhydrol (3.0 mmol), $NaSO_2CF_3$ (3.9 mmol), and $FeCl_3$ (0.45 mmol) under argon. Anhydrous CH_2Cl_2 (20 mL) was added, and TMSCl (0.5 mL, 3.9 mmol) was added via syringe. The mixture was stirred at reflux for 16 hours resulting in a deep red heterogeneous solution. The solution was filtered through Celite™,

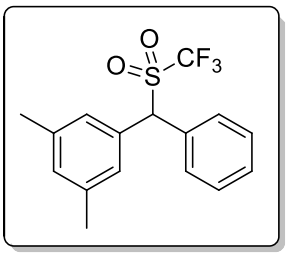
and all volatiles were removed *in vacuo*. Compounds **5-19** to **5-22** were purified by column chromatography on neutral alumina eluting with CH_2Cl_2/hexanes (1:1).



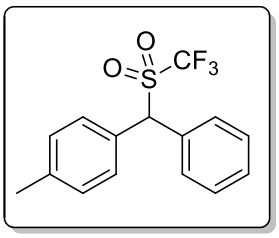
Synthesis of 5-19. The general procedure was followed using diphenylmethanol (552 mg, 3.00 mmol), $NaSO_2CF_3$ (608.4 mg, 3.90 mmol), and $FeCl_3$ (77.8 mg, 0.48 mmol), in CH_2Cl_2 (20 mL) resulting in a yellow solid (685.3 mg, 2.28 mmol) in 76 % yield. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.69-7.67 (m, 4H, Ar*H*), 7.47-7.44 (m, 6H, Ar*H*), 5.66 (s, 1H, Ph_2CH-SO_2). **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ = 130.0, 129.8, 129.6, 129.2, 120.0 (q, $^1J_{C\text{-}F}$ = 330.8 Hz), 72.1. **^{19}F NMR** ($CDCl_3$, 376 MHz): δ = -73.8. **HRMS** (EI-TOF): calculated for [$C_{14}H_{11}F_3O_2S$] (M+Na)= 323.0330, found 323.0335.



Synthesis of 5-20. The general procedure was followed using 2-methylbenzhydrol (594.0 mg, 3.00 mmol), $NaSO_2CF_3$ (608.2 mg, 3.90 mmol), and $FeCl_3$ (77.2 mg, 0.48 mmol), in CH_2Cl_2 (20 mL) resulting in a yellow solid (697.2 mg, 2.22 mmol) in 74 % yield. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.08-8.06 (m, 1H, Ar*H*), 7.67-7.66 (m, 2H, Ar*H*), 7.44-7.46 (m, 3H, Ar*H*), 7.33-7.37 (m, 2H, Ar*H*), 7.27-7.28 (m, 1H, Ar*H*), 6.00 (s, 1H, Ph_2CH-SO_2), 2.45 (s, 3H, -CH_3). **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ = 137.1, 131.4, 130.4, 129.7, 129.5, 129.2, 129.2 128.9, 128.5, 126.8, 120.1 (q, $^1J_{C\text{-}F}$ = 330.7 Hz), 67.2, 19.8. **^{19}F NMR** ($CDCl_3$, 376 MHz): δ = -74.1. Despite our efforts, we were unable to obtain HRMS data for this compound.



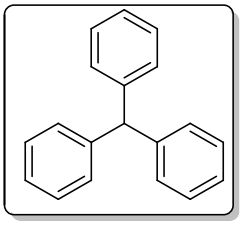
Synthesis of 5-21: The general procedure was followed using 3,5-dimethylbenzhydrol (636.0 mg, 3.00 mmol), $NaSO_2CF_3$ (609.0 mg, 3.91 mmol), and $FeCl_3$ (77.3 mg, 0.48 mmol), in CH_2Cl_2 (20 mL) resulting in a yellow solid (609.9 mg, 1.86 mmol) in 62 % yield. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.65-7.63 (m, 2H, Ar*H*), 7.44-7.42 (m, 3H, Ar*H*), 7.24 (s, 2H, Ar*H*), 7.04 (s, 1H, Ar*H*), 5.53 (s, 1H, Ph_2CH-SO_2), 2.34 (s, 6H, -CH_3). **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ = 139.0, 131.5, 130.0, 129.9, 129.7, 129.4, 129.2 127.7, 120.2 (q, $^1J_{C\text{-}F}$ = 330.8 Hz), 72.1, 21.3. **^{19}F NMR** ($CDCl_3$, 376 MHz): δ = -73.9. **HRMS** (EI-TOF, m/z) calculated for [$C_{16}H_{17}F_3O_2S$] (M+Na): 351.06371, found 351.06517.



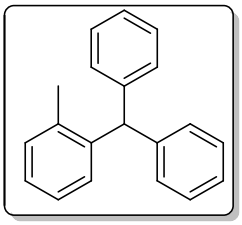
Synthesis of **5-21**: The general procedure was followed using 4-methylbenzhydrol (594.3 mg, 3.00 mmol), $NaSO_2CF_3$ (607.8 mg, 3.89 mmol), and $FeCl_3$ (78.1 mg, 0.49 mmol), in CH_2Cl_2 (20 mL) resulting in an orange solid (620 mg, 1.97 mmol) in 66 % yield. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.70 (m, 2H, Ar*H*), 7.59 (d, 2H, $J_{H\text{-}H}$ = 8.1 Hz, Ar*H*), 7.47 (m, 3H, Ar*H*), 7.29 (d, 2H, $J_{H\text{-}H}$ = 8.1 Hz, Ar*H*), 5.65 (s, 1H, -C*H*SO_2CF_3), 2.40 (s, 3H, -CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 140.0, 130.0, 130.0, 129.9, 129.8, 129.7, 129.2, 126.4, 120.13 (q, $^1J_{C\text{-}F}$ = 330.9 Hz), 71.9, 21.2. **^{19}F NMR** ($CDCl_3$, 376 MHz): 73.8. Despite our efforts, we were unable to obtain HRMS data for this compound.

General procedure for the synthesis of triaryl methanes:

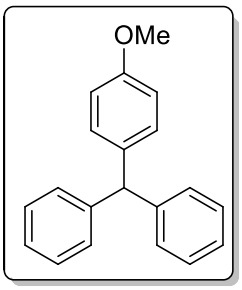
In a nitrogen-filled glovebox, a one dram vial was charged with KOtBu (50.4 mg, 0.45 mmol), **5-23** (8.61 mg, 0.015 mmol), boronic acid (0.6 mmol), and sulfone (0.3 mmol) as solids, and toluene (1.5 mL) was added. The inside lining of the vial was wrapped in Teflon tape, and sealed with a Teflon lined cap, then wrapped in electrical tape. The vial was then removed from the glovebox, and heated in an oil bath to the indicated temperature for 16 hours. Upon completion of the reaction, the reaction mixture was diluted with Et_2O and filtered through a short plug of silica gel. Purification was achieved by silica gel column chromatography eluting with hexanes/ethyl acetate mixtures.



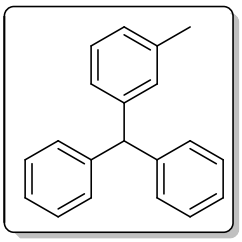
Synthesis of 5-32: Synthesized by the general procedure using **5-19** (90.0 mg, 0.3 mmol), phenyl boronic acid (72.6 mg, 0.6 mmol), KOtBu (50.4 mg, 0.45 mmol) and **5-23** (8.6 mg, 0.015 mmol) in toluene (1.5 mL) at 40 °C resulting in a white solid (67.4 mg, 0.27 mmol) in 92 % yield. Spectra data matched the previously reported literature.[35]



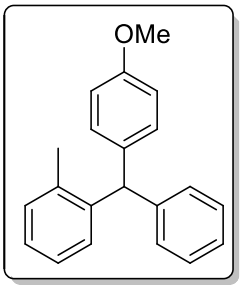
Synthesis of 5-33: Synthesized by the general procedure using **5-20** (94.2 mg, 0.3 mmol), phenyl boronic acid (72.6 mg, 0.6 mmol), KOtBu (50.4 mg, 0.45 mmol) and **5-23** (8.6 mg, 0.015 mmol) in toluene (1.5 mL) at 50 °C resulting in a white solid (72.0 mg, 0.28 mmol) in 93 % yield. Spectra data matched the previously reported literature.[35]



Synthesis of 5-36: Synthesized by the general procedure using **5-19** (0.3 mmol), 4-methoxyphenyl-boronic acid (91.2 mg, 0.6 mmol), KOtBu (50.4 mg, 0.45 mmol) and **5-23** (8.6 mg, 0.015 mmol) in toluene (1.5 mL) at 40 °C resulting in a light yellow solid (74.8 mg, 0.27 mmol) in 91 %. Spectra data matched the previously reported literature.[35]



Synthesis of 5-37: Synthesized by the general procedure using **5-19** (90.0 mg, 0.3 mmol), and 3-methyl phenyl boronic acid (81.0 mg, 0.6 mmol), KOtBu (50.4 mg, 0.45 mmol), and **5-23** (8.61 mg, 0.015 mmol) in toluene (1.5 mL) at 40 °C resulting in a white solid (52.3 mg, 0.20 mmol) in 68 % yield. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.37-7.33 (m, 4H, Ar*H*), 7.29-7.22 (m, 3H, Ar*H*), 7.21-7.19 (m, 4H, Ar*H*), 7.11 (d, 1H, $J_{H\text{-}H}$ = 7.5 Hz, Ar*H*), 7.03 (br s, 1H, $J_{H\text{-}H}$ = 7.5 Hz, Ar*H*), 5.59 (s, C*H*), 2.36 (s, CH_3). **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ = 144.1, 143.9, 137.9, 130.3, 129.5, 128.3, 128.2, 127.1, 126.6, 126.3, 56.9, 21.5. **HRMS** (EI-TOF): calculated for [$C_{20}H_{18}$] = 258.1408, found 258.1407.



Synthesis of 5-38: Synthesized by the general procedure using **5-20** (94.2 mg, 0.3 mmol), 4-methoxyphenyl boronic acid (91.2 mg, 0.6 mmol), KOtBu (50.3 mg, 0.45 mmol) and **5-23** (8.7 mg, 0.015 mmol) in toluene (1.5 mL) at 50 °C resulting (78.0 mg, 0.27 mmol) in **5-38** in 90 % as a yellow solid. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.34-7.23 (m, 3H, Ar*H*), 7.22-7.15 (m, 3H, Ar*H*), 7.12 (d, 2H, $J_{H\text{-}H}$ = 7.4 Hz, Ar*H*), 7.03 (d, 2H,

$J_{H\text{-}H}$ = 8.6 Hz, Ar*H*), 6.88 (d, 3H, $J_{H\text{-}H}$ = 8.4 Hz, Ar*H*), 5.67 (s, C*H*, 1H), 3.83 (s, 3H, OCH_3), 2.26 (s, 3H, CH_3). **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ = 158.0, 143.8, 142.7, 136.6, 135.5, 130.6, 130.4, 129.6, 129.4, 128.3, 126.3, 126.2, 125.8, 113.7, 55.2, 52.7, 19.9. **HRMS** (EI-TOF, m/z) calculated for [$C_{21}H_{20}O$]: 288.1514, found 288.1513.

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Chapter 6

Conclusions and Future Work

In Chapter 2, the synthesis of a variety of Rh^{I}-NHC complexes was presented. Dimeric Rh-NHC olefin complexes $[Rh(NHC)(C_2H_4)Cl]_2$ (**2-37** to **2-40**) were demonstrated to be effective precursors for the formation of heteroleptic Rh-NHC complexes upon treatment with additional ligands. Specifically, complexes **2-37** to **2-40** were reacted with PPh_3 to form tetraheteroleptic $[Rh(NHC)(PPh_3)(C_2H_4)Cl]$ (**2-34** to **2-48**) complexes in high yield. In addition, **2-40** was further reacted with chelating nitrogen donors bipy and phen resulting **2-50** and **2-51** respectively. In comparison, treatment of [Rh(IPr)(COD)Cl] under comparable conditions failed to produce **2-50**, illustrating the higher reactivity of **2-40**.

The reactivity of several of these complexes towards O_2 was also investigated. While $[Rh(NHC)(PPh_3)(C_2H_4)Cl]$ (**2-34** to **2-48**) resulted in intractable mixtures, in part due to the oxidation of the phosphine ligand, bipy and Phen derivatives **2-50** and **2-51** resulted in the formation of O_2 adducts **2-58**, and **2-59** respectively. The coordination of O_2 was confirmed by IR spectroscopy, by comparing $^{16}O_2$ spectra to $^{18}O_2$ labeled species. In contrast to rhodium bis(NHC) complexes such as **2-18** which was previously reported in our group, **2-58** and **2-59** appear to be Rh^{III} peroxo complexes. Similarly, cationic complexes **2-27** and **2-62**, synthesized by previous members of our group, display similar coordination peroxide coordination modes of O_2. These results suggest that the coordination number of Rh-NHC complexes greatly affects the reducing potential of the

metal complex, and therefore dictates the mode in which O_2 binds. This was further confirmed by extensive DFT studies performed by our collaborators.

Finally, the single crystal-to-single crystal transformations of small molecule adducts of rhodium bis(NHC) complexes was investigated. Single crystals of **2-63** were found to react with O_2 resulting in single crystals of **2-29**, which were further treated with CO resulting in single crystals of **2-64**. To our knowledge this was the first reported demonstration of a back to back single crystal-to-single crystal transformation. Key to this transformation was that **2-63**, **2-29**, and **2-64** all crystallize in the same crystal system, and in the space group, with nearly identical unit cells. This suggests that minimal rearrangement is necessary within the crystal during these transformations.

In chapter 3, [Rh(IPr)(C_2H_4)Cl] (**3-7**) was demonstrated to be an effective catalyst for the C-H borylation of phenyl pyridine derivatives. Stoichiometric studies demonstrated the ability of **3-7** to C-H activate these substrates, resulting in rhodium hydride species at room temperature which could be observed by ^{1}H NMR spectroscopy. In the presence of a base, **3-7** could be reacted with phenyl pyridine derivatives and HBPin at room temperature resulting in C-H borylated products in high yield at room temperature. The reaction occurred regioselectively, producing only mono-borylated products with few exceptions. The mono-borylated products were subjected to Suzuki-Miyaura coupling conditions resulting in complete selectivity for overall C-H mono-arylation.

Future work on this project involves further catalyst development in order to expand the substrate scope for a wider variety of directing groups. In particular, the use of rhodium NHC complexes coordinated to anionic ligands is of particular interest, as these would obviate the requirement for external bases. As such, we are interested in exploring

dimeric complexes such as $[Rh(NHC)(C_2H_4)OAc]_2$, or $[Rh(NHC)(C_2H_4)H]_2$. Further optimization will be performed by considering different NHCs as well, varying both in steric and electron parameters. Finally, other electrophiles will also be investigated, such as silanes and thiols, in order to generate other C-H functionalized products that are of high interest. Detailed mechanistic investigations into the mechanism of the C-H borylation would greatly aid in these endeavours, and help to further other catalytic reactions.

In chapter 4, the synthesis of mesoionic carbene ligands, and their coordination to transition metals was described. Various strategies were found to be effective in the metallation of these ligands, and Ag, Rh, and Pd complexes were efficiently synthesized. Efforts to synthesize CCC pincer complexes were also presented, which in all cases instead resulted in bimetallic complexes. The catalytic activity of Pd-MIC complexes in the Mizoroki-Heck reaction were also presented. These species were found to be poor catalysts for this transformation, as they appeared to be unstable, resulting in the formation of Pd nanoparticles. These results likely indicate the significant lability of MICs from the Pd center, which is in sharp contrast to the analogous NHC complexes.

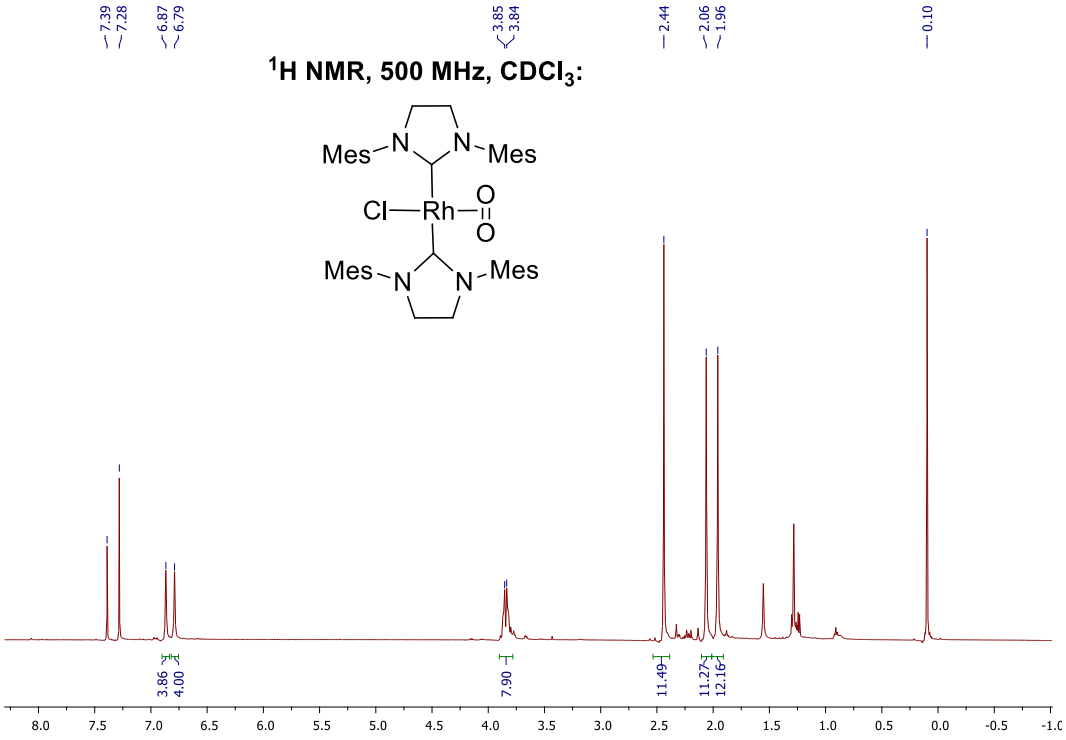
Future work involves the use of smaller MIC ligands which display high levels of flexibility in order to form discrete pincer species. In addition, the use of higher oxidation state metal precursors which possess basic ligands such as $Pd(OAc)_2$ are expected to be highly promising. In addition, our group is further interested in pursuing boron-MIC complexes in catalytic hydrogenations of aldimines, ketimines and various *N*-heterocycles. Preliminary investigations have been highly promising, and our group is currently pursuing enantioselective variants.

Chapter 5 detailed efforts towards the Pd-NHC catalyzed cross coupling of benzylic sulfones with phenyl boronic acids. Preliminary investigations have demonstrated that trifluoromethylsulfones are highly reactive, and can be coupled under very mild conditions resulting in triaryl methanes in high yield. These products are of high interest as they are very difficult to synthesize using other methods. The nature of the Pd-NHC precursor was found to be remarkably important. Specifically, [(NHC)Pd(allyl)Cl] complexes were found to be the most efficient, which is likely associated with the more facile generation of Pd^0. In comparison, all other Pd-NHC precursors investigated, as well as methods for *in situ* generation were completely ineffective. In addition, larger, more basic NHCs such as SIPr were found to result in higher yields than smaller ones.

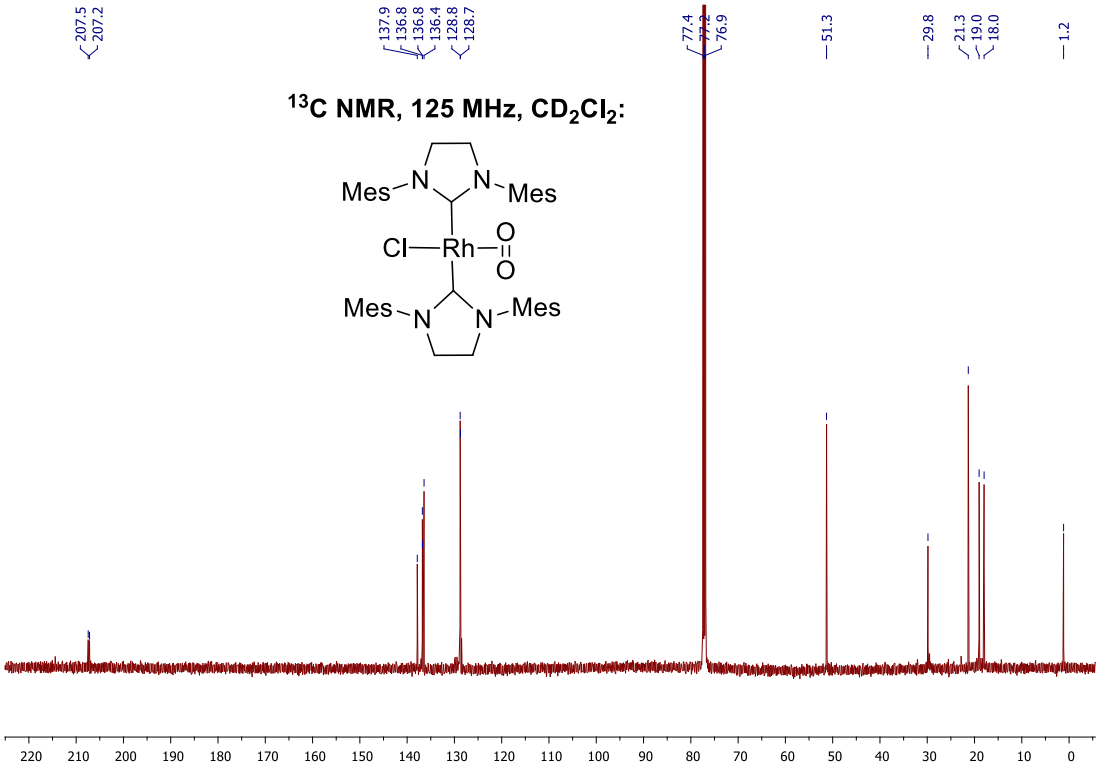
While only a small number of triaryl methanes have been reported, we are interested in expanding the scope of this transformation and exploring the reactivity towards a more wide variety of other phenyl boronic acids. In particular, we are particularly interested in applying this reaction to substrates which contain heterocycles that are biological interest. Future work will also involve the development of an enantioselective variant, giving access to enantioenriched triaryl methanes. In order to accomplish this, chiral NHCs are being synthesized in our lab, and will be subjected to the optimized conditions.

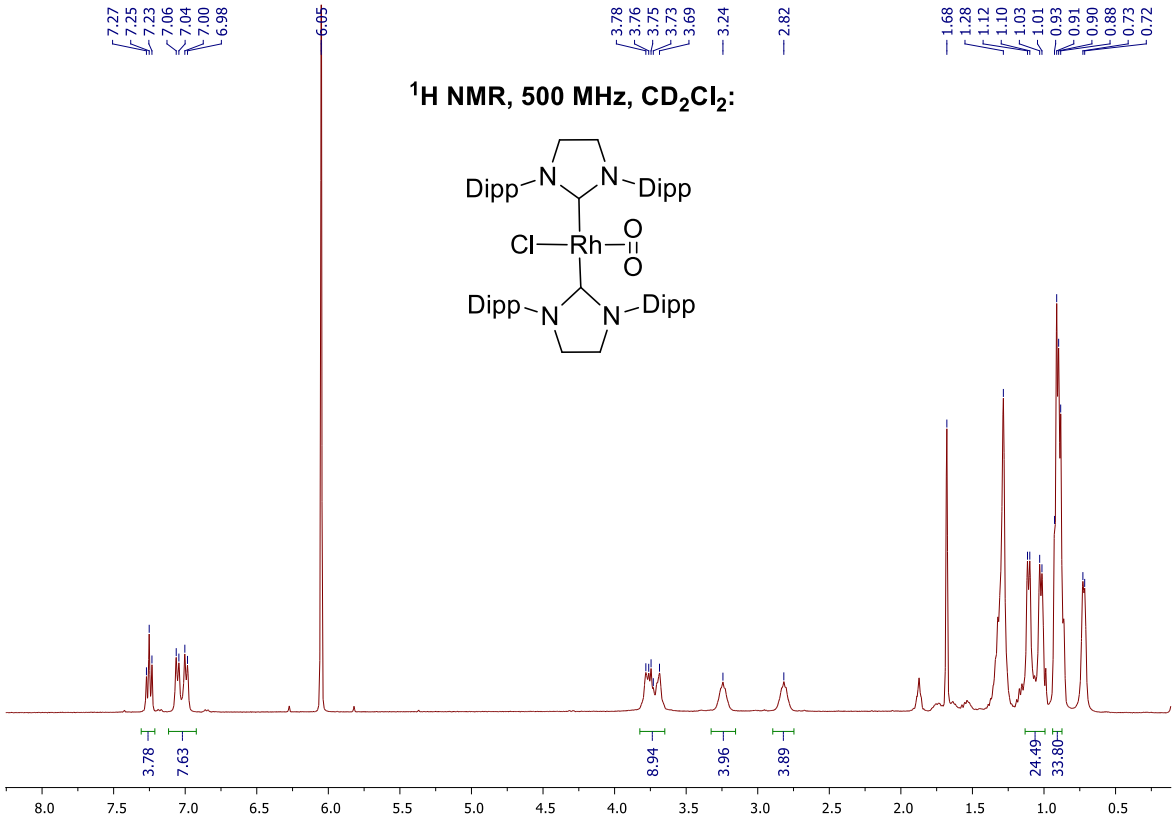
Appendix A: Representative NMR Spectra

^{1}H NMR, 500 MHz, $CDCl_3$:

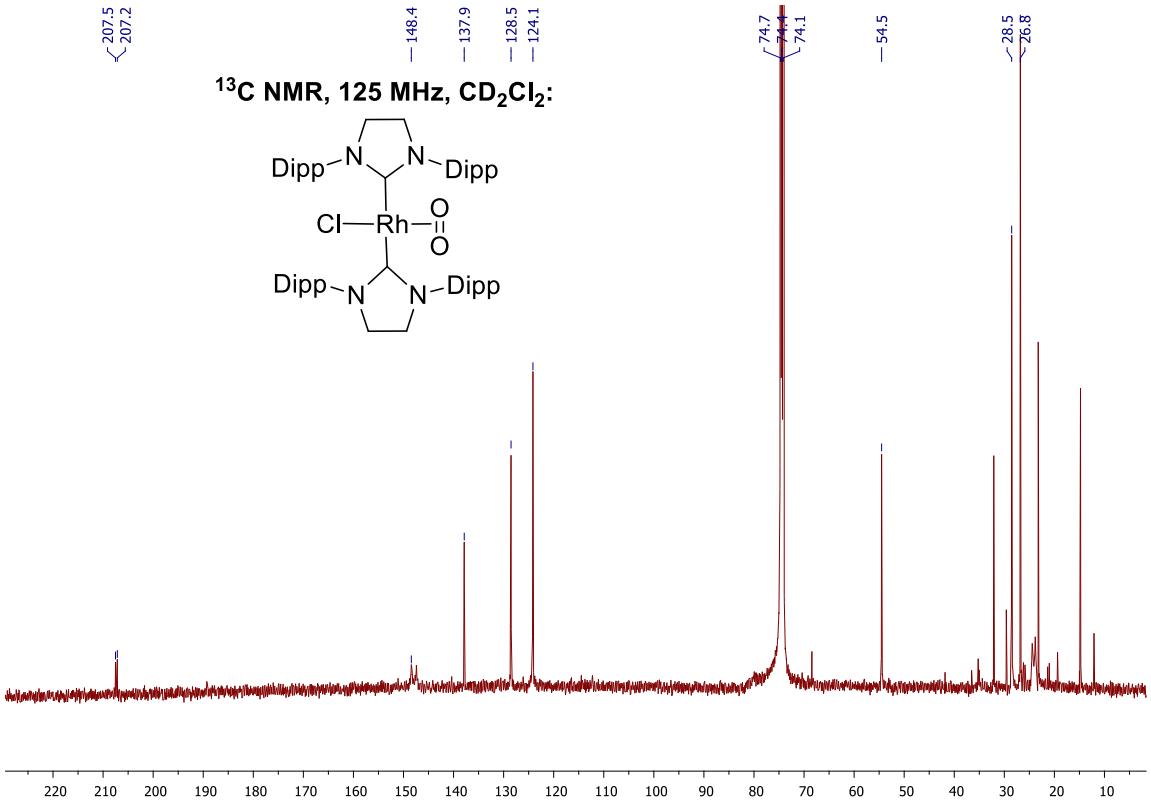


^{13}C NMR, 125 MHz, CD_2Cl_2:



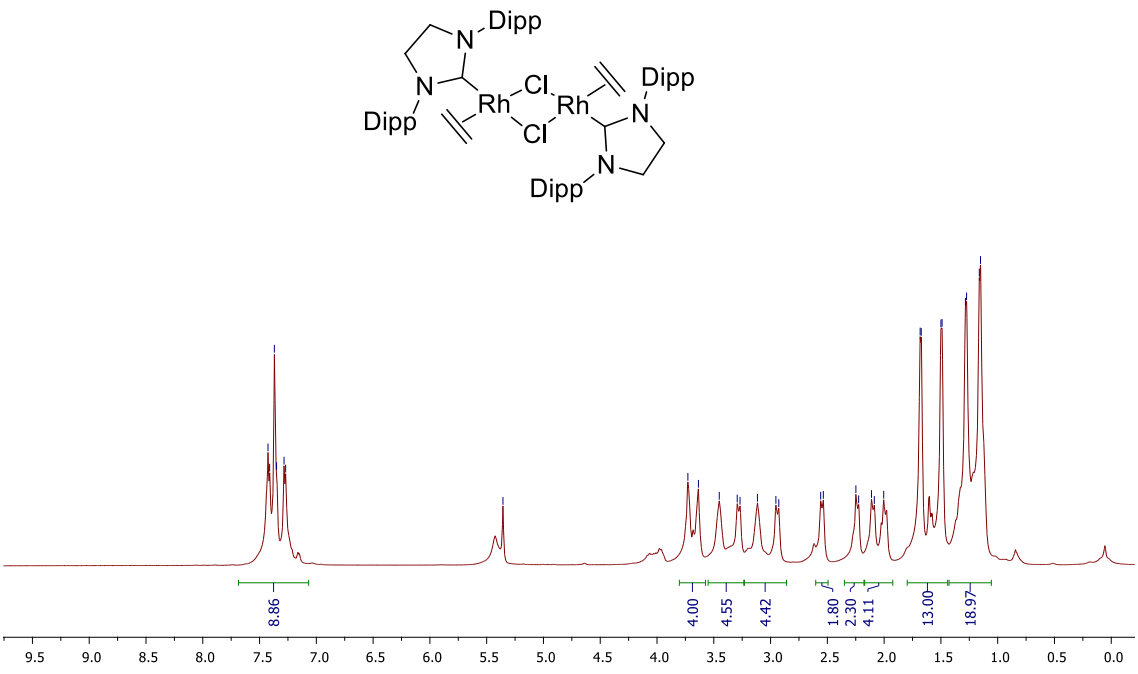


^{1}H NMR, 500 MHz, CD_2Cl_2:

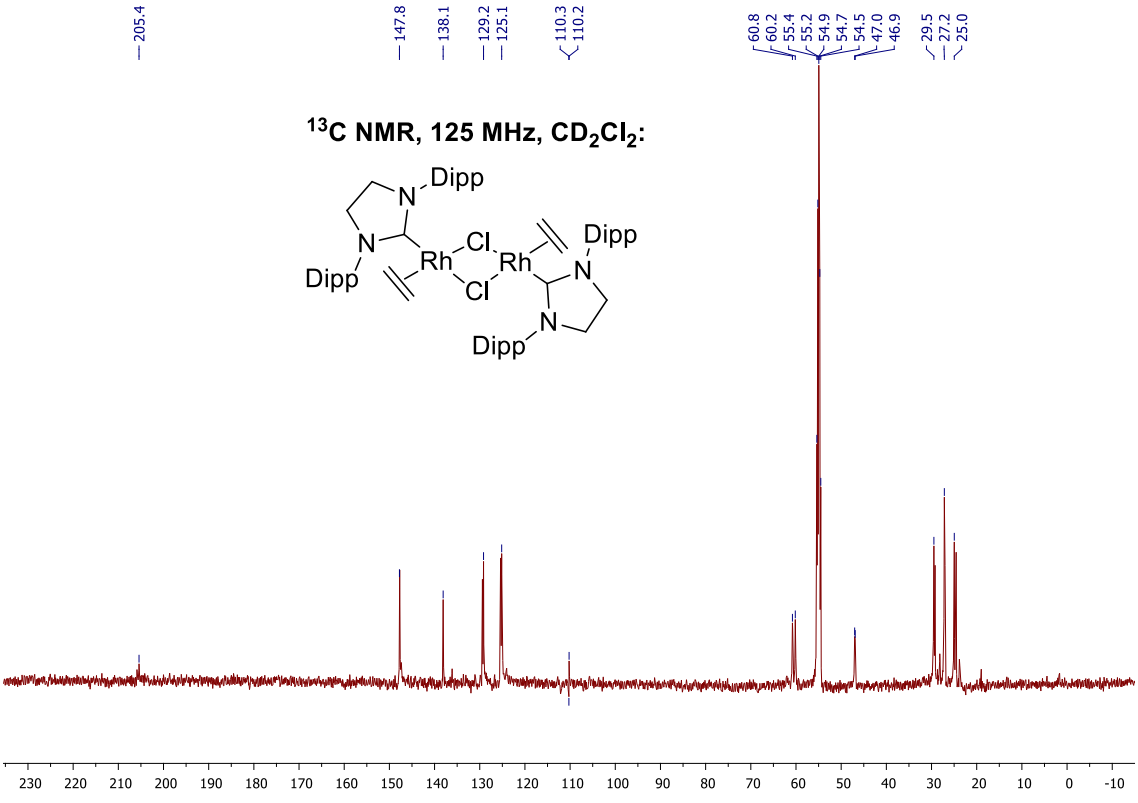


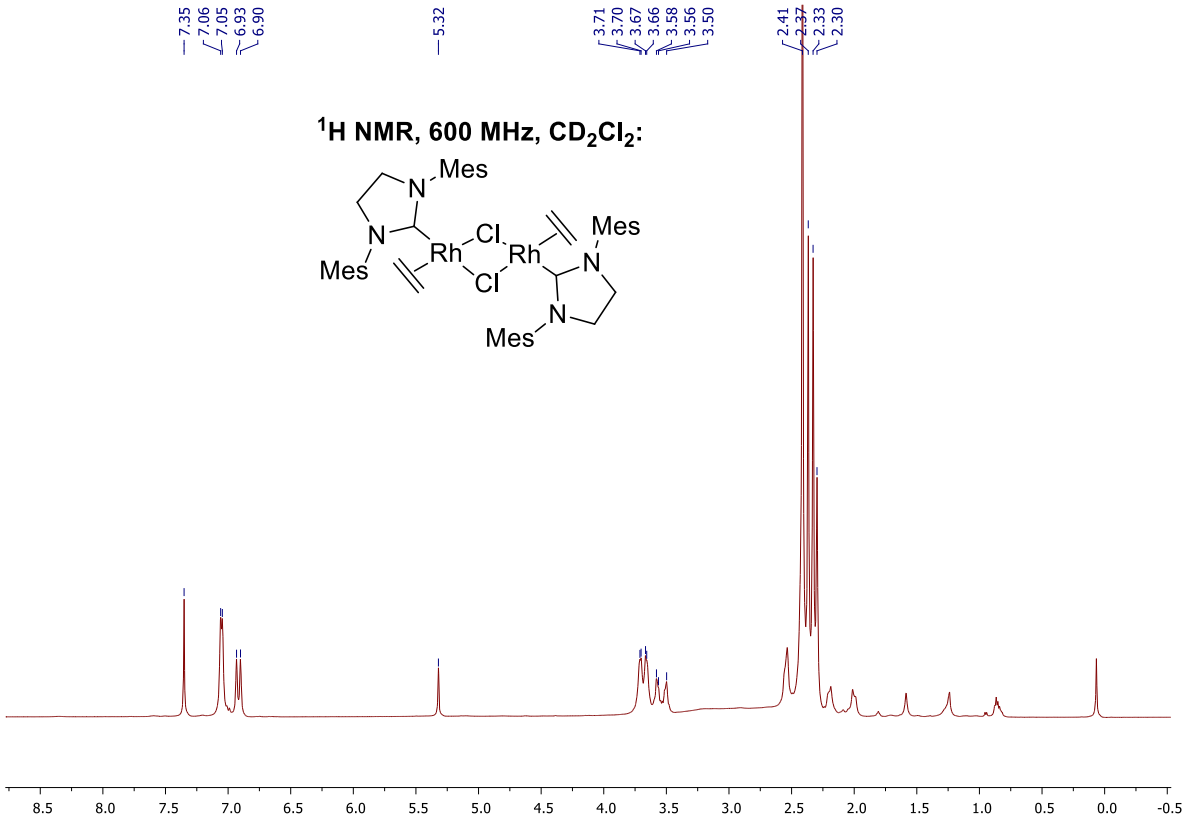
^{13}C NMR, 125 MHz, CD_2Cl_2:

^{1}H NMR, 500 MHz, CD_2Cl_2:

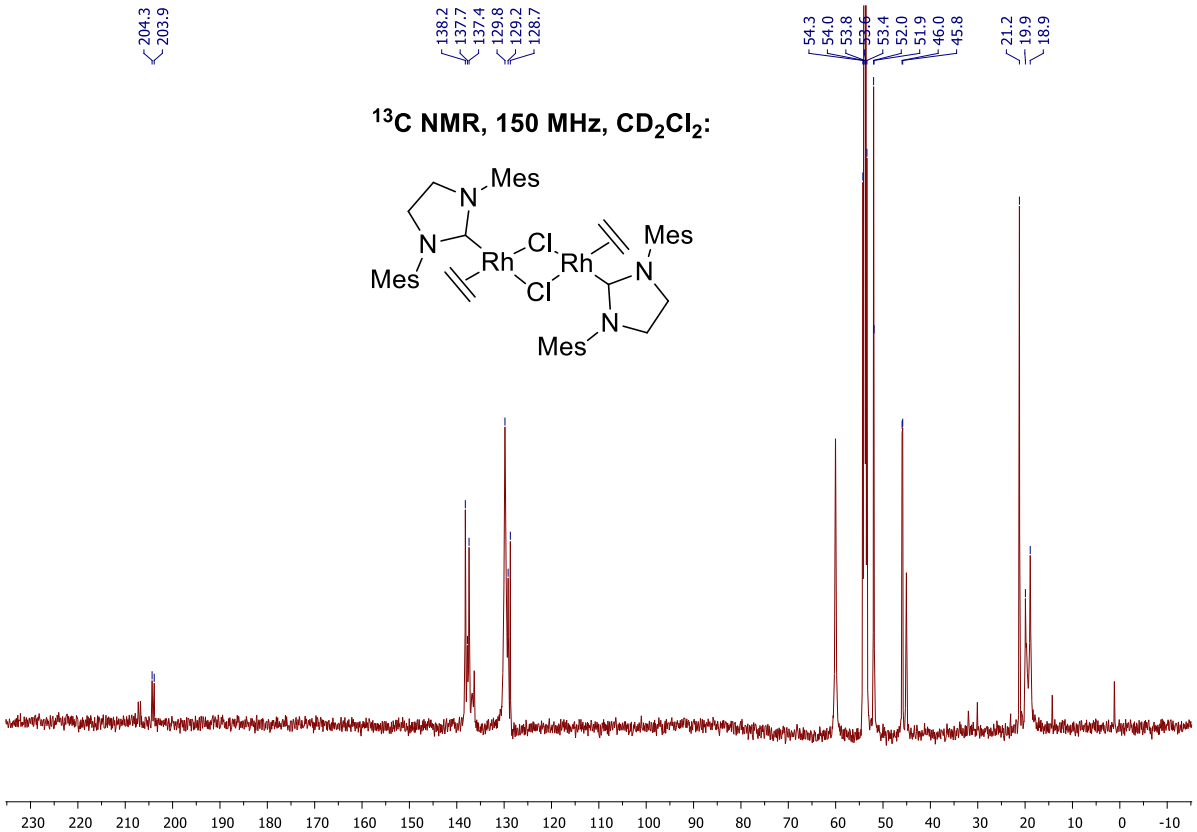


^{13}C NMR, 125 MHz, CD_2Cl_2:



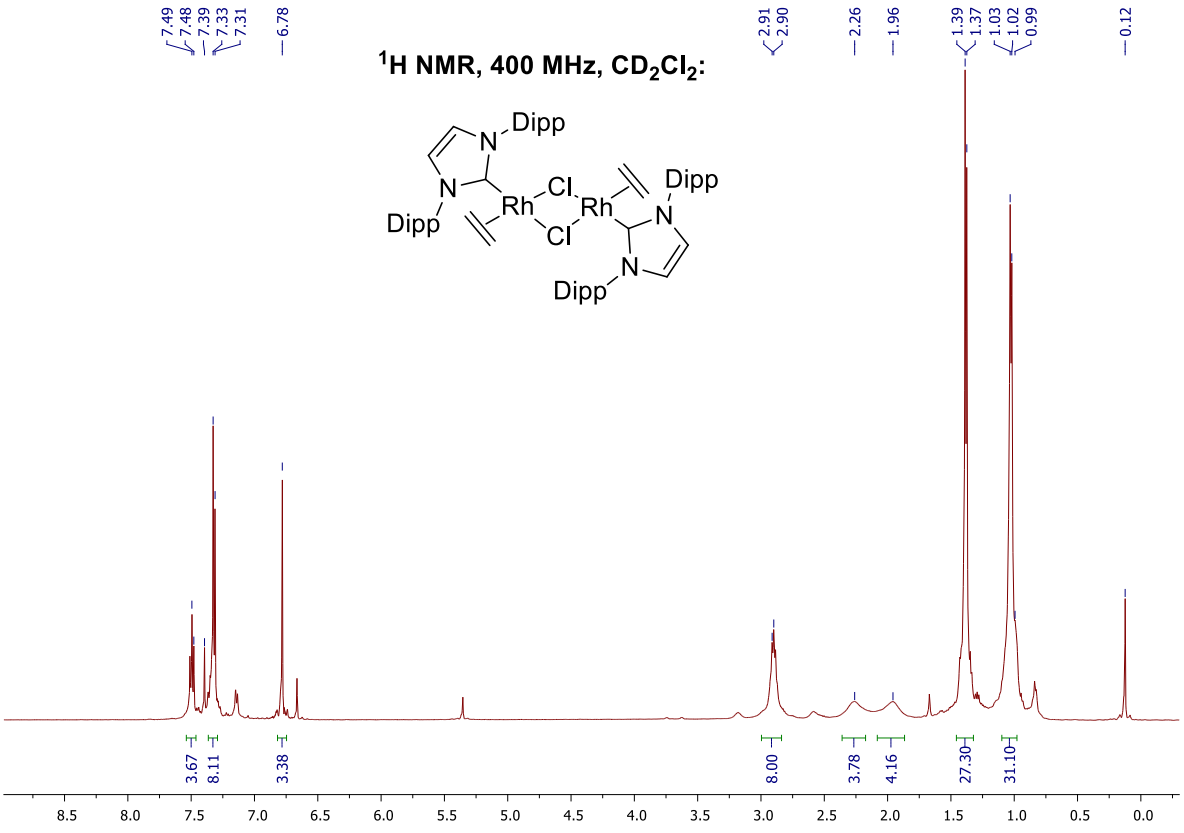


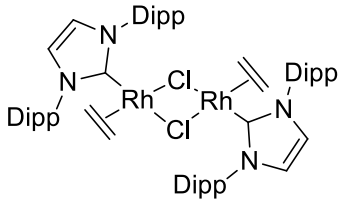
^{1}H NMR, 600 MHz, CD_2Cl_2:



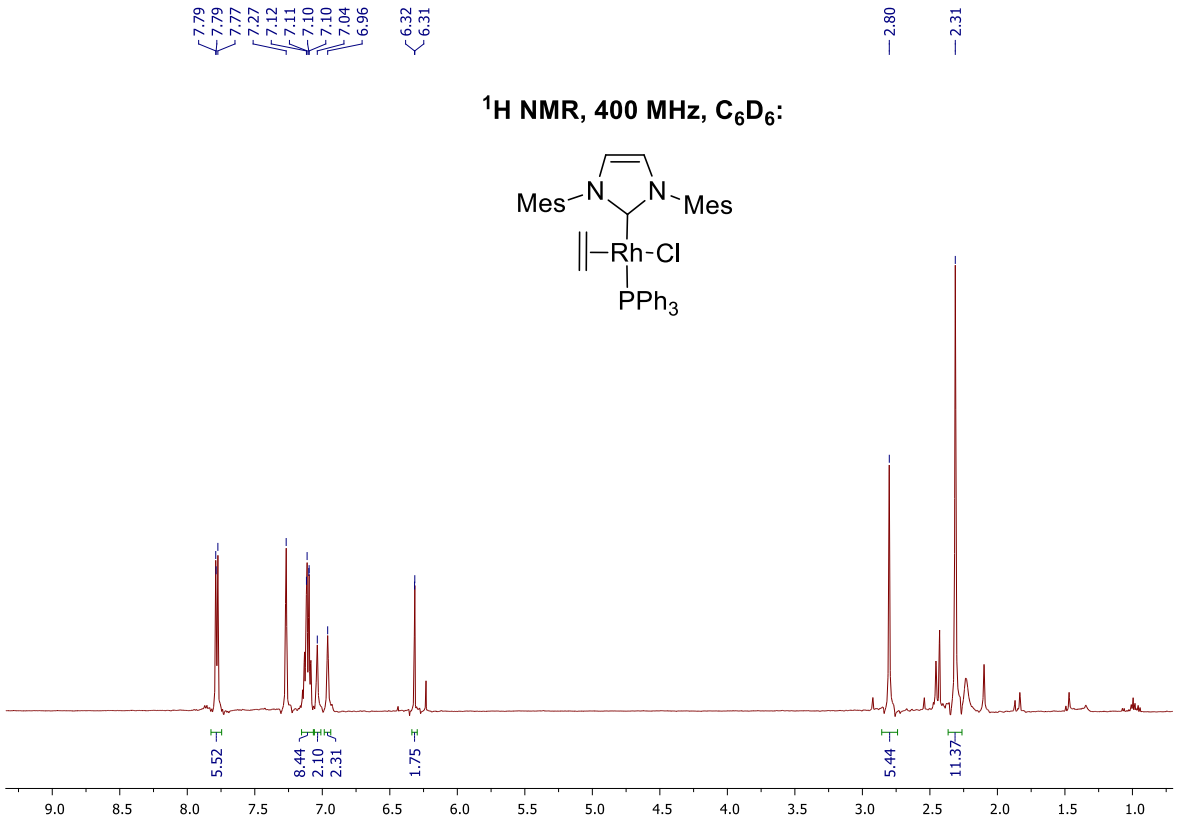
^{13}C NMR, 150 MHz, CD_2Cl_2:

^{1}H NMR, 400 MHz, CD_2Cl_2:

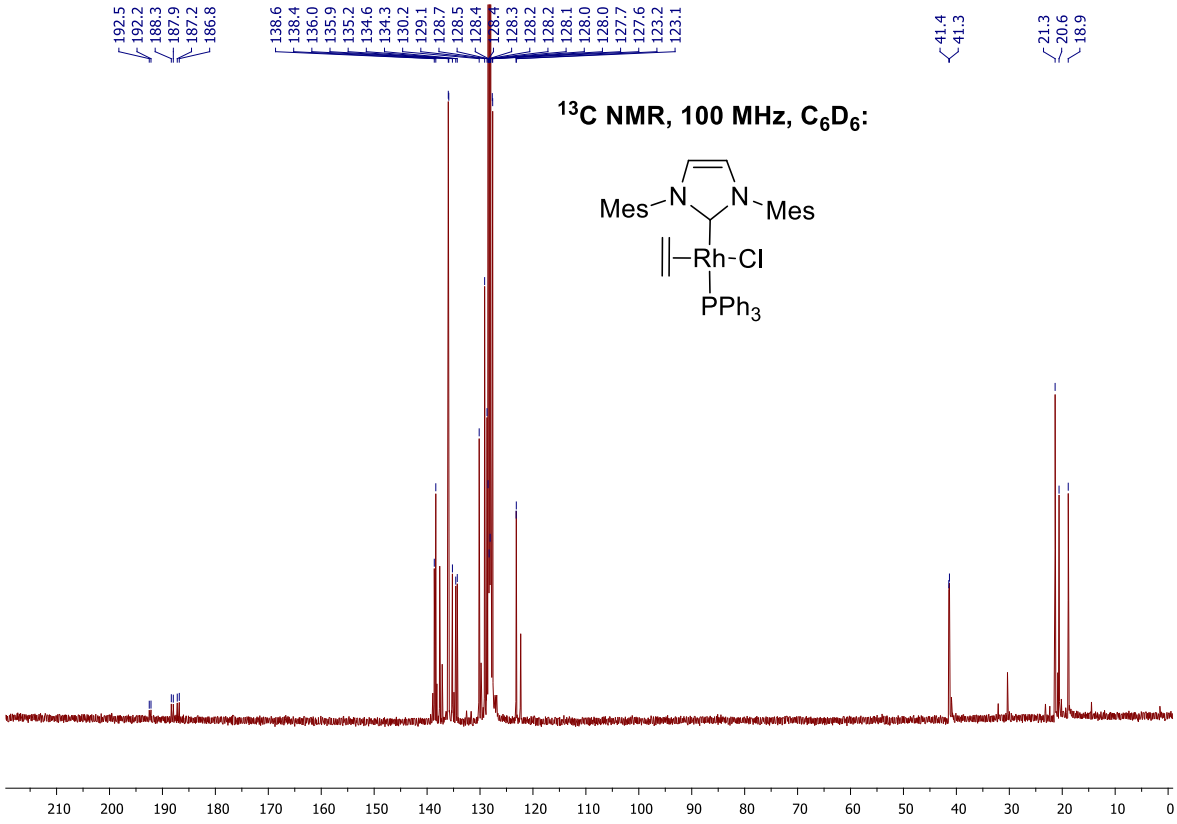




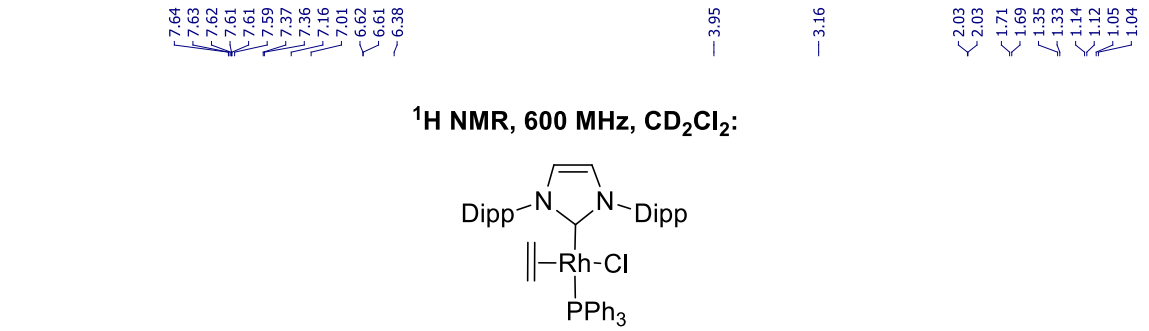
^{13}C NMR, 125 MHz, CD_2Cl_2:



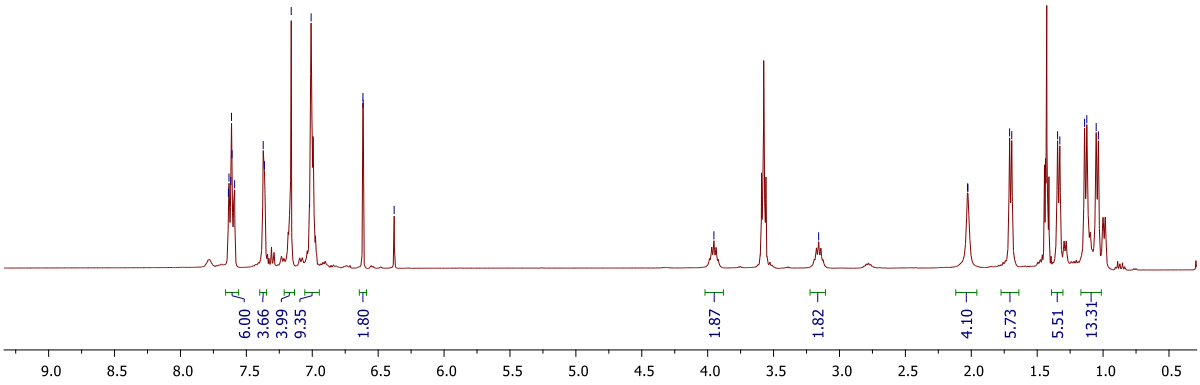
^{1}H NMR, 400 MHz, C_6D_6:

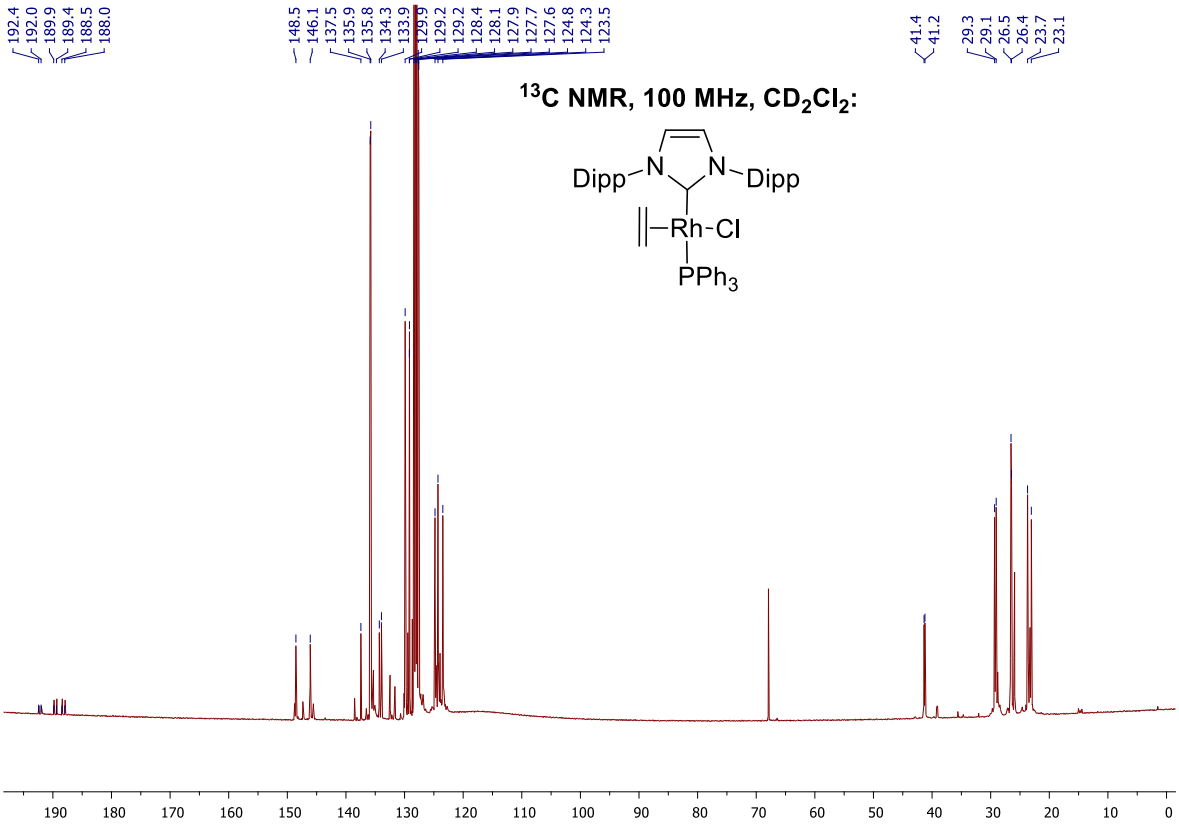


^{13}C NMR, 100 MHz, C_6D_6:



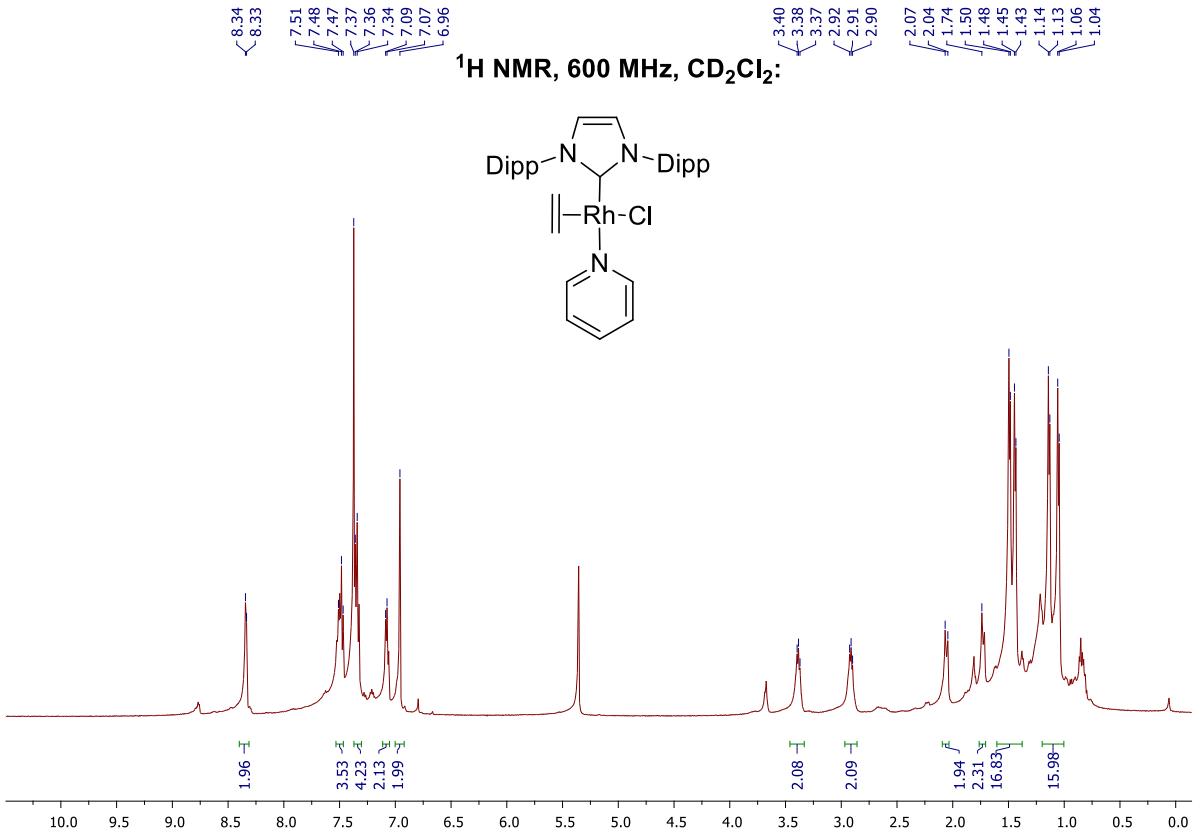
^{1}H NMR, 600 MHz, CD_2Cl_2:



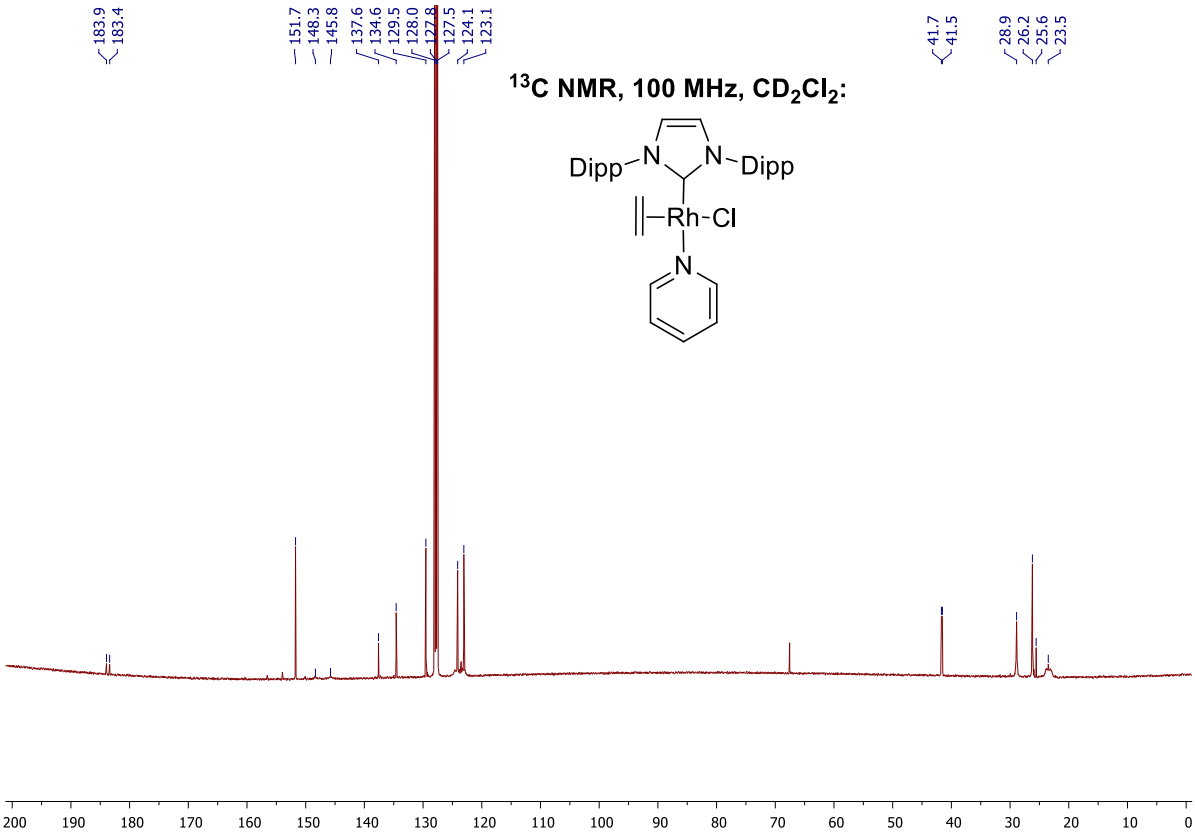


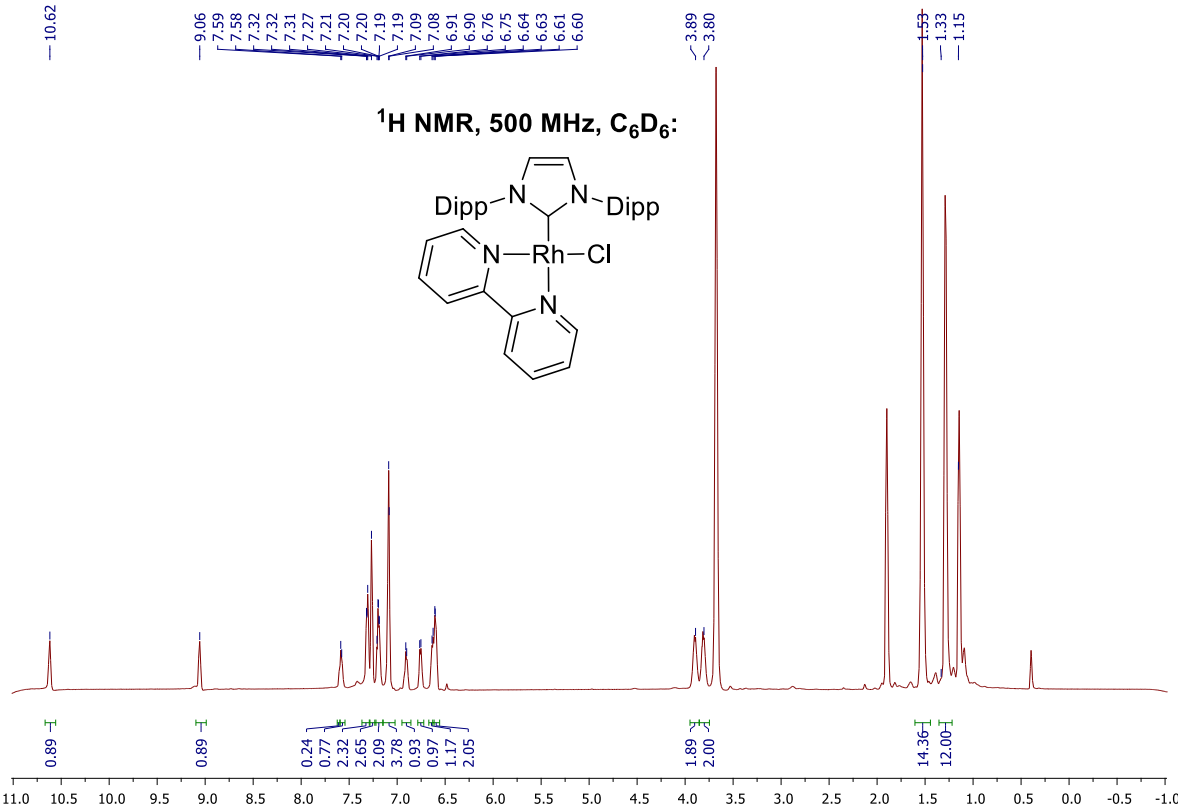
^{13}C NMR, 100 MHz, CD_2Cl_2:

^{1}H NMR, 600 MHz, CD_2Cl_2:

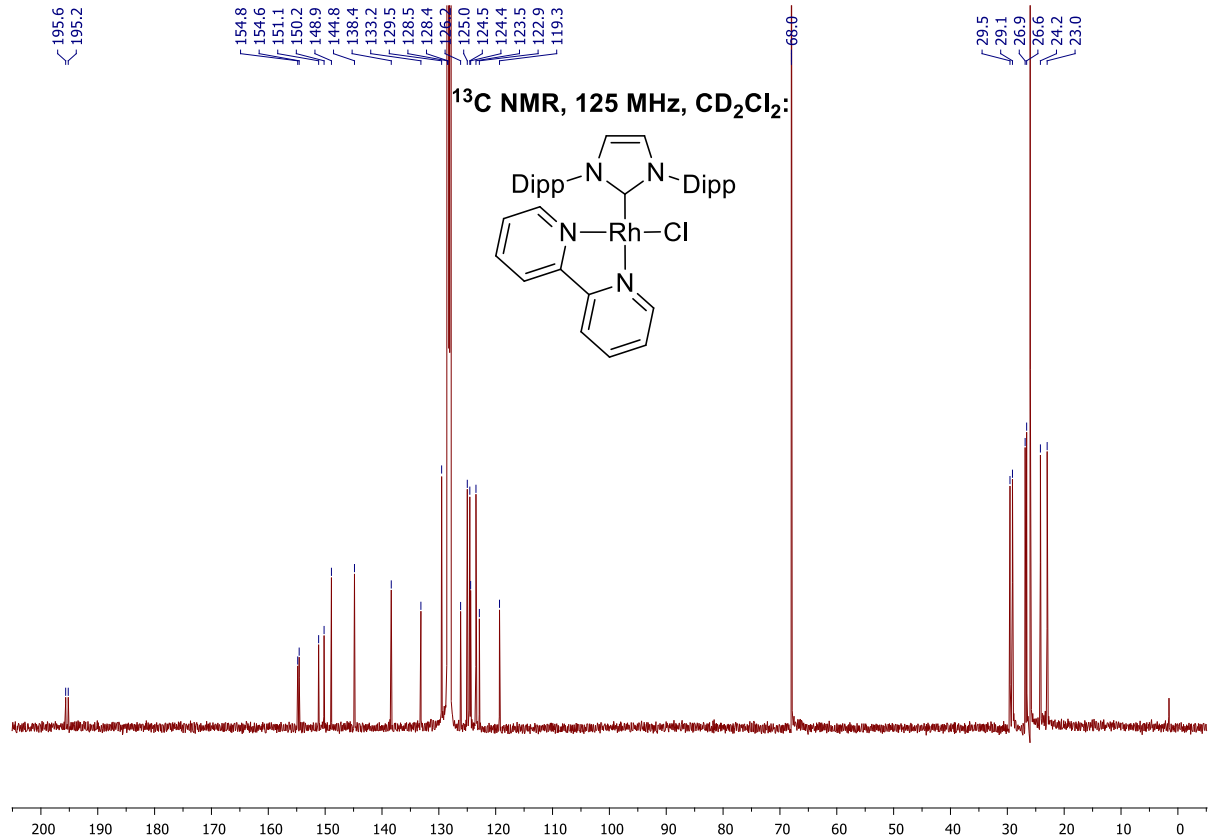


^{13}C NMR, 100 MHz, CD_2Cl_2:

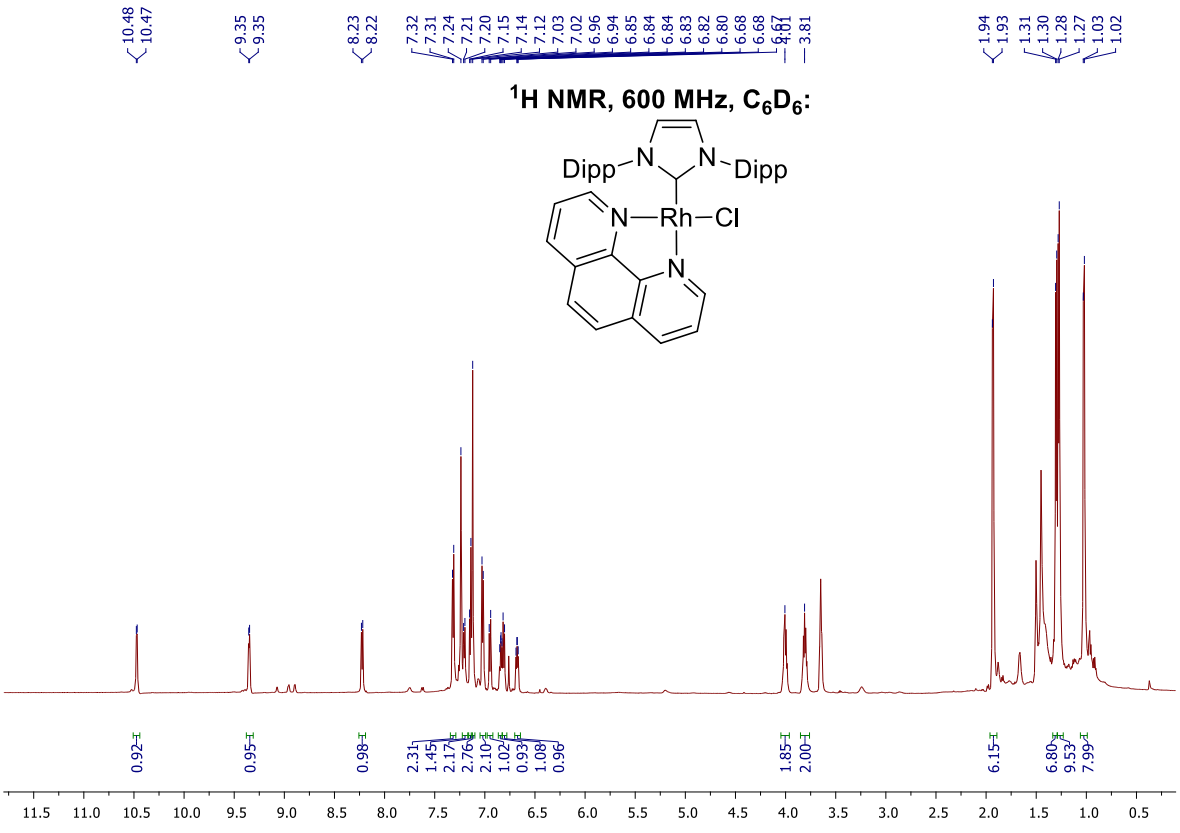




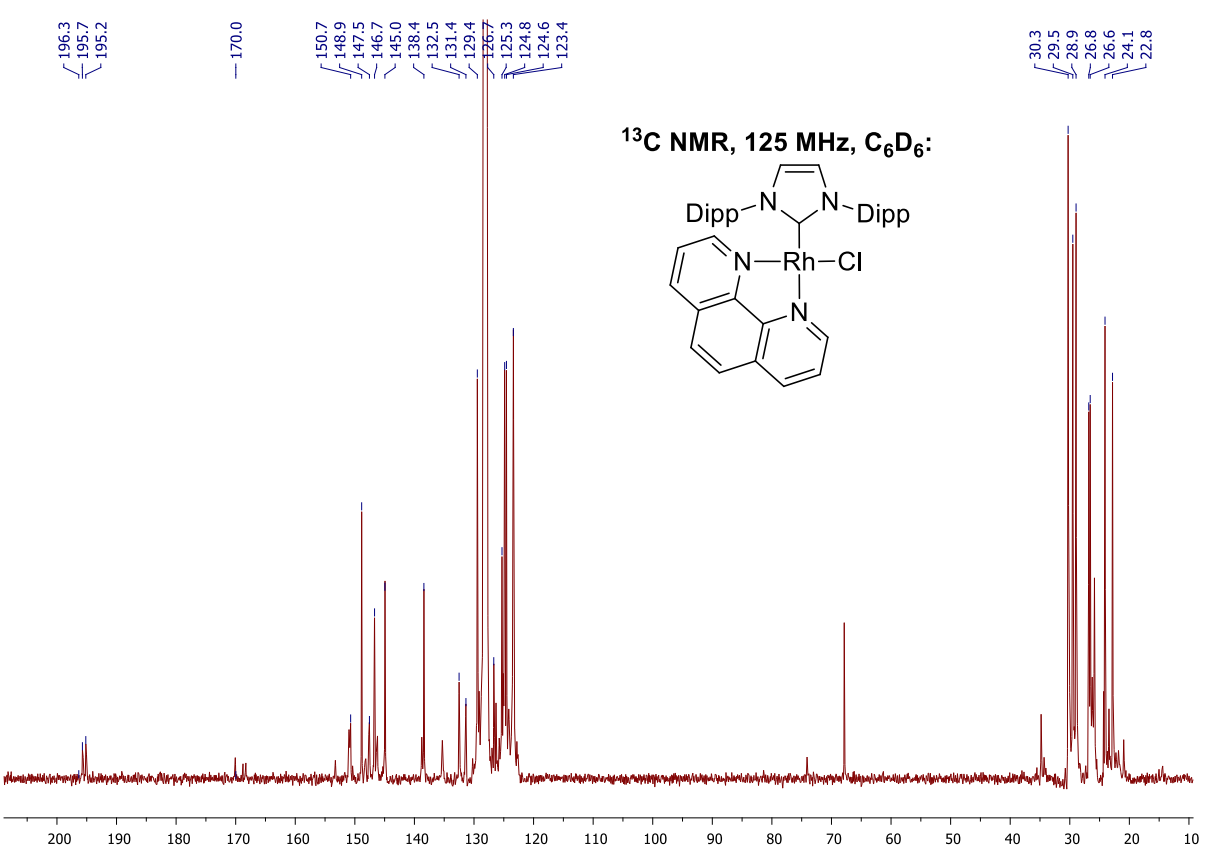
^{1}H NMR, 500 MHz, C_6D_6:



^{13}C NMR, 125 MHz, CD_2Cl_2:

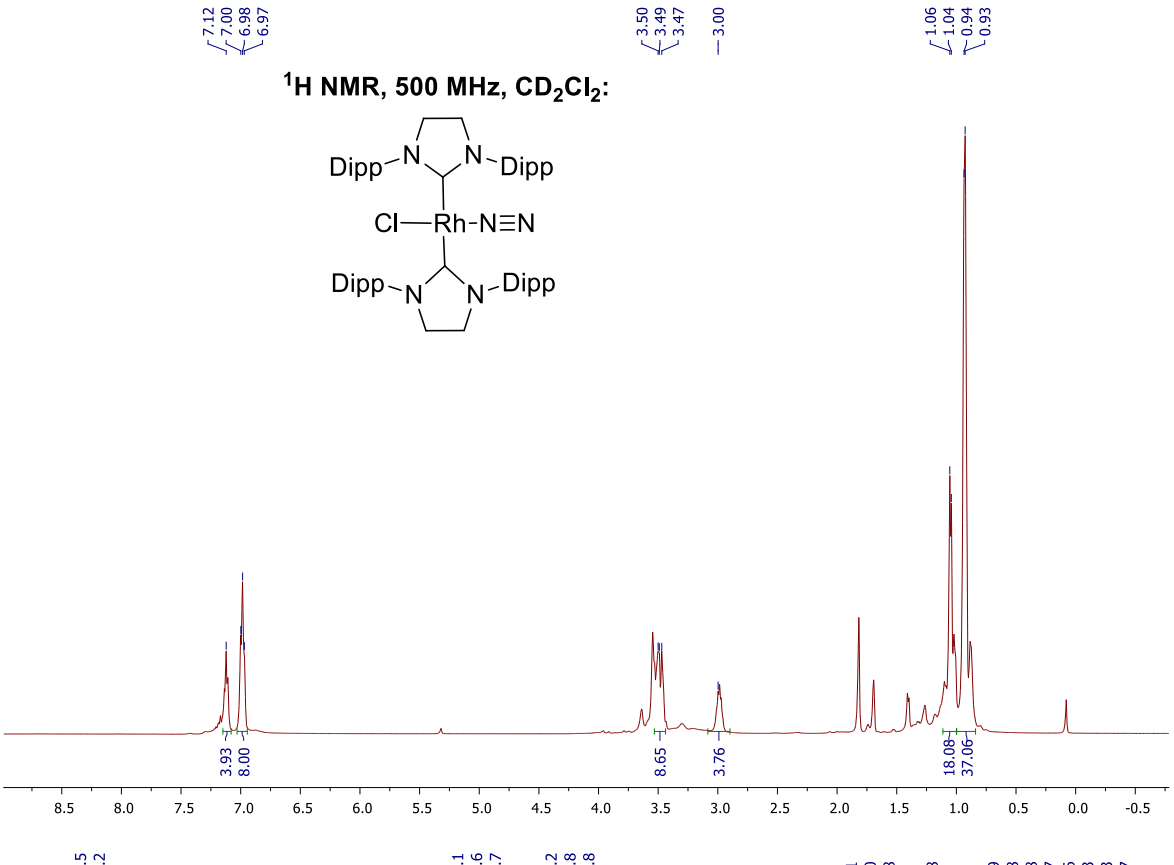


^{1}H NMR, 600 MHz, C_6D_6:



^{13}C NMR, 125 MHz, C_6D_6:

^{1}H NMR, 500 MHz, CD_2Cl_2:



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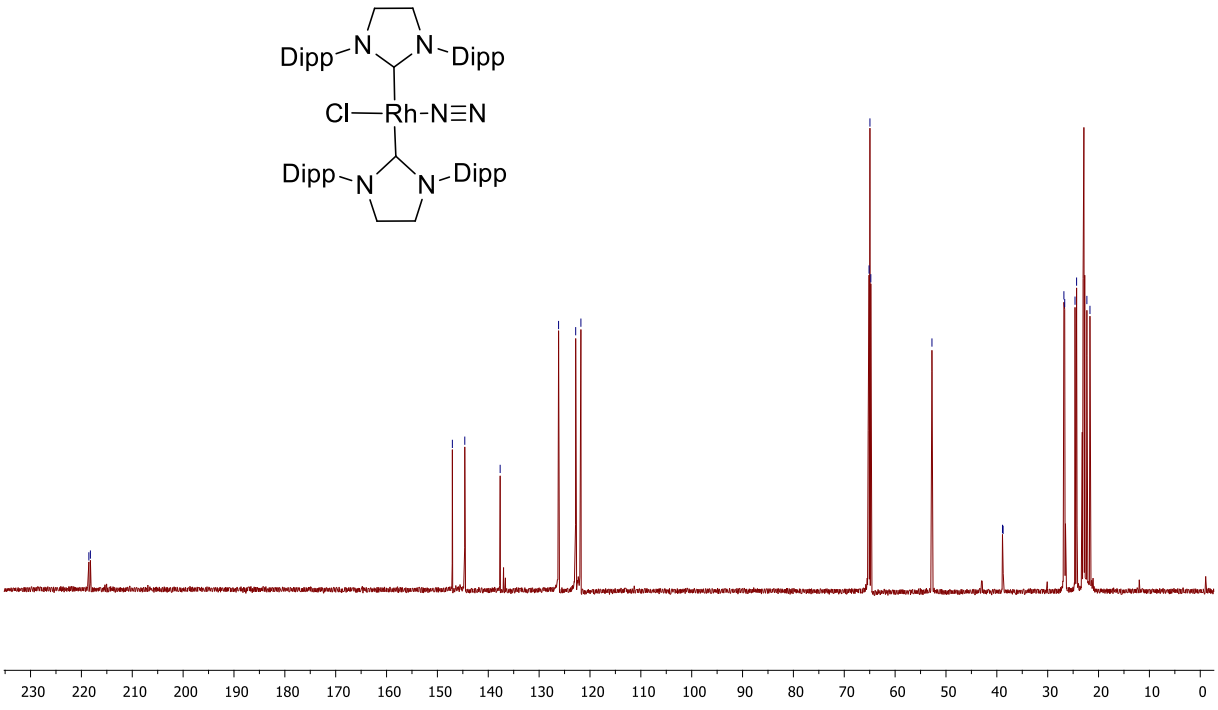
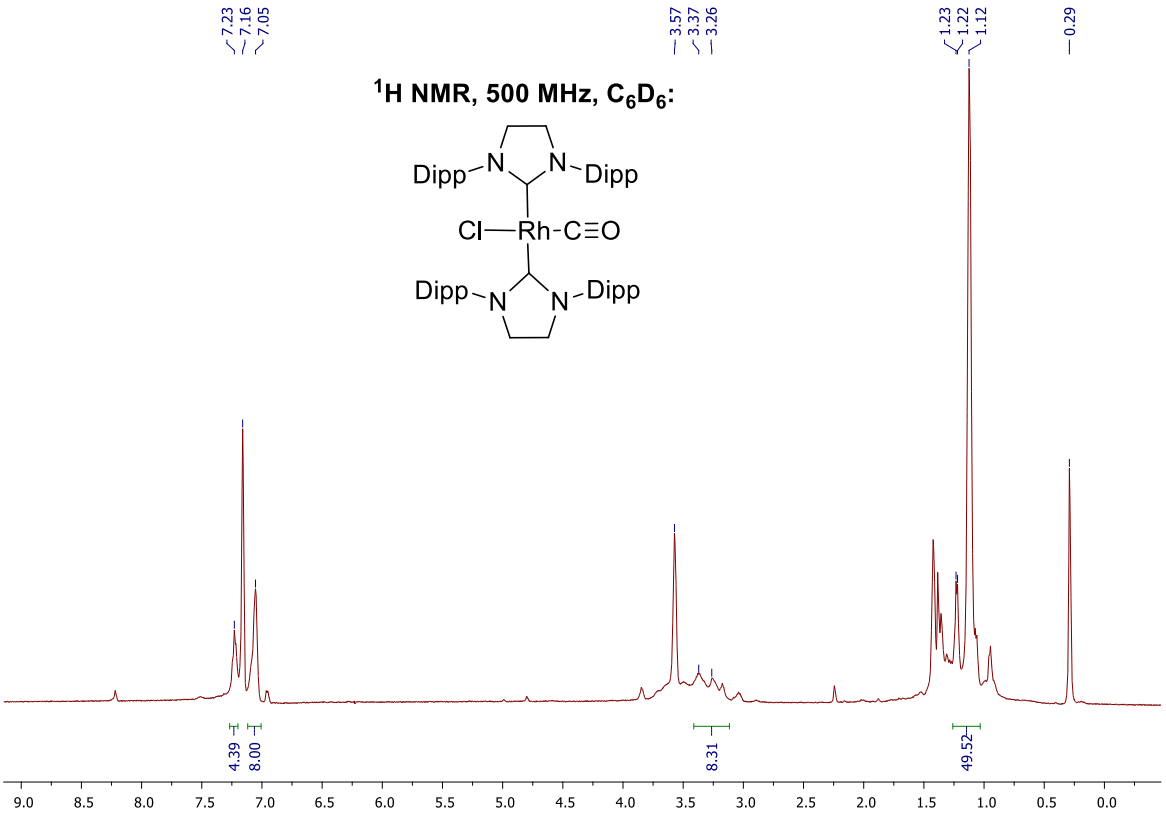
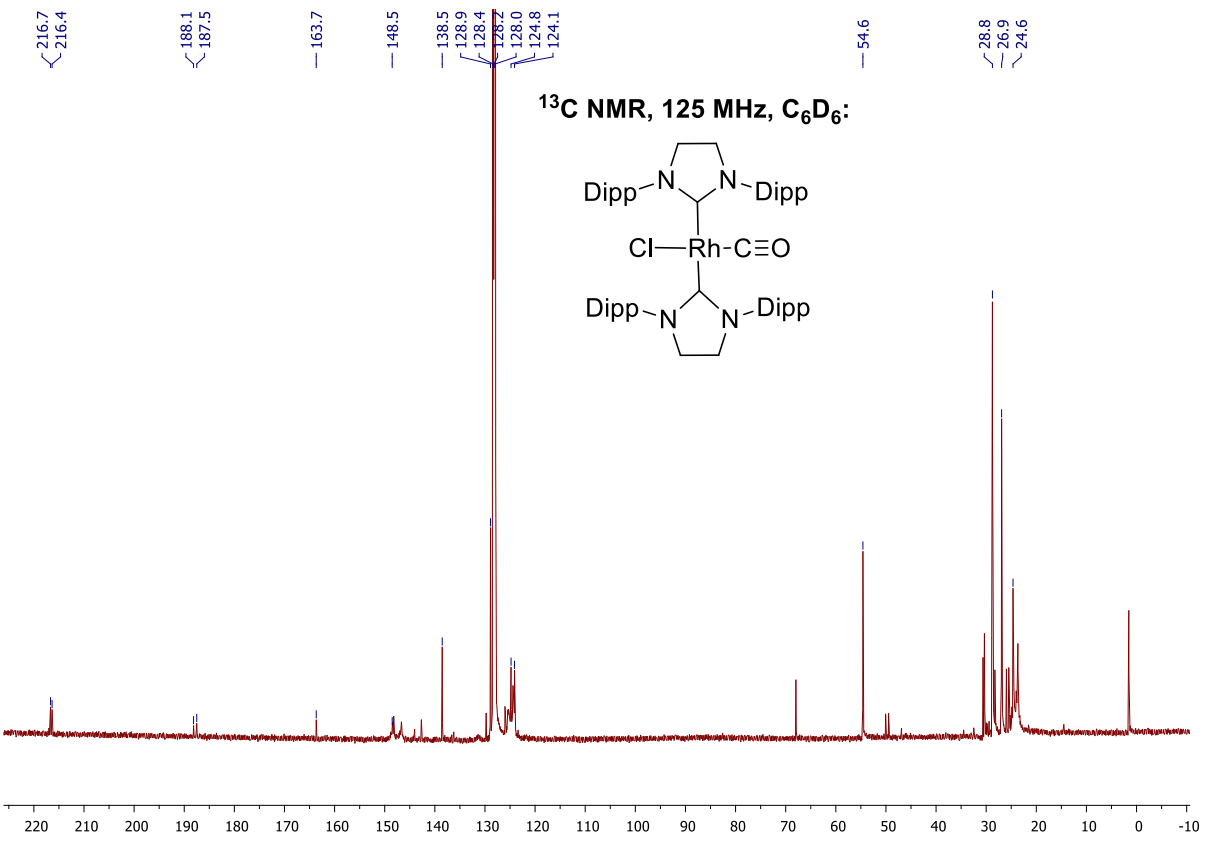



7.23
7.16
7.05
3.57
3.37
3.26
1.23
1.22
1.12
0.29
^{1}H NMR, 500 MHz, C_6D_6:
Dipp
N
N
Dipp
Cl—Rh-C≡O
Dipp
N
N
Dipp
4.39
8.00
8.31
49.52
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


216.7
216.4
188.1
187.5
163.7
148.5
138.5
128.9
128.4
128.2
128.0
124.8
124.1
54.6
28.8
26.9
24.6
^{13}C NMR, 125 MHz, C_6D_6:
Dipp
N
N
Dipp
Cl—Rh-C≡O
Dipp
N
N
Dipp
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

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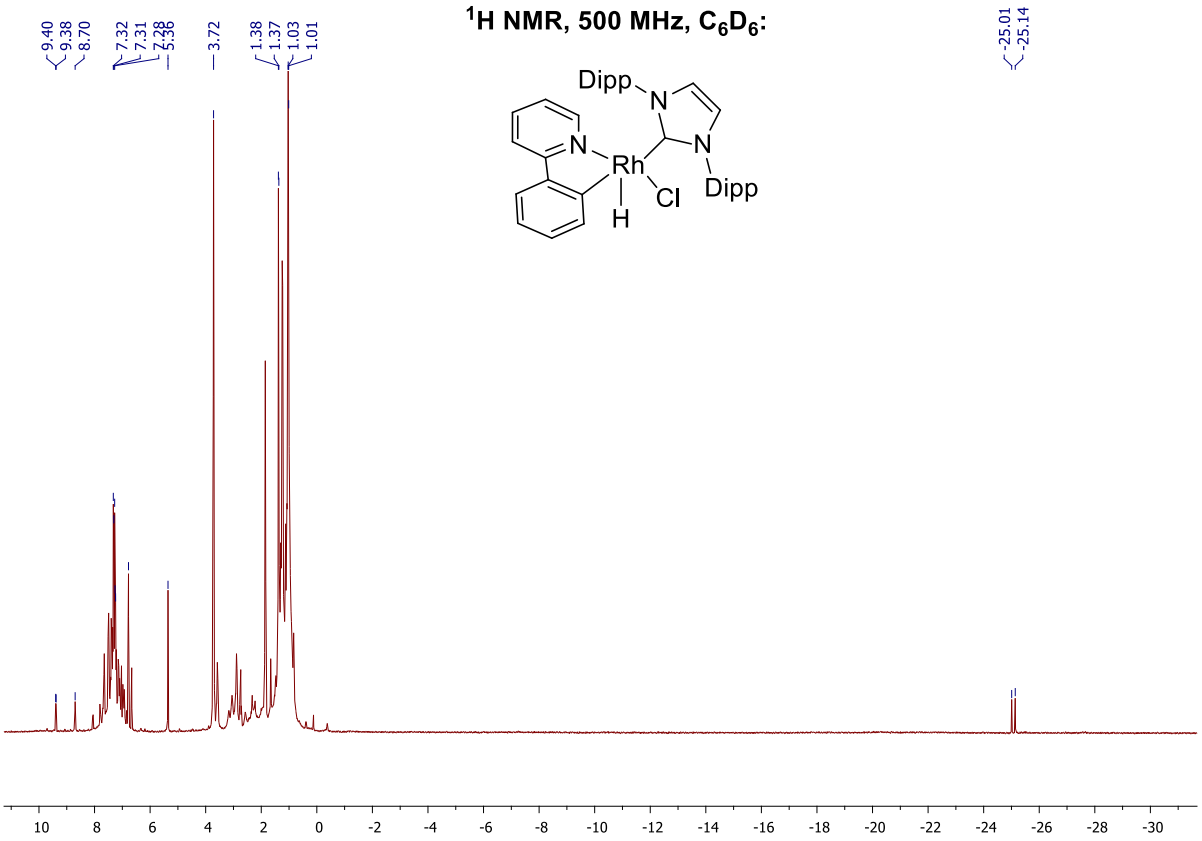

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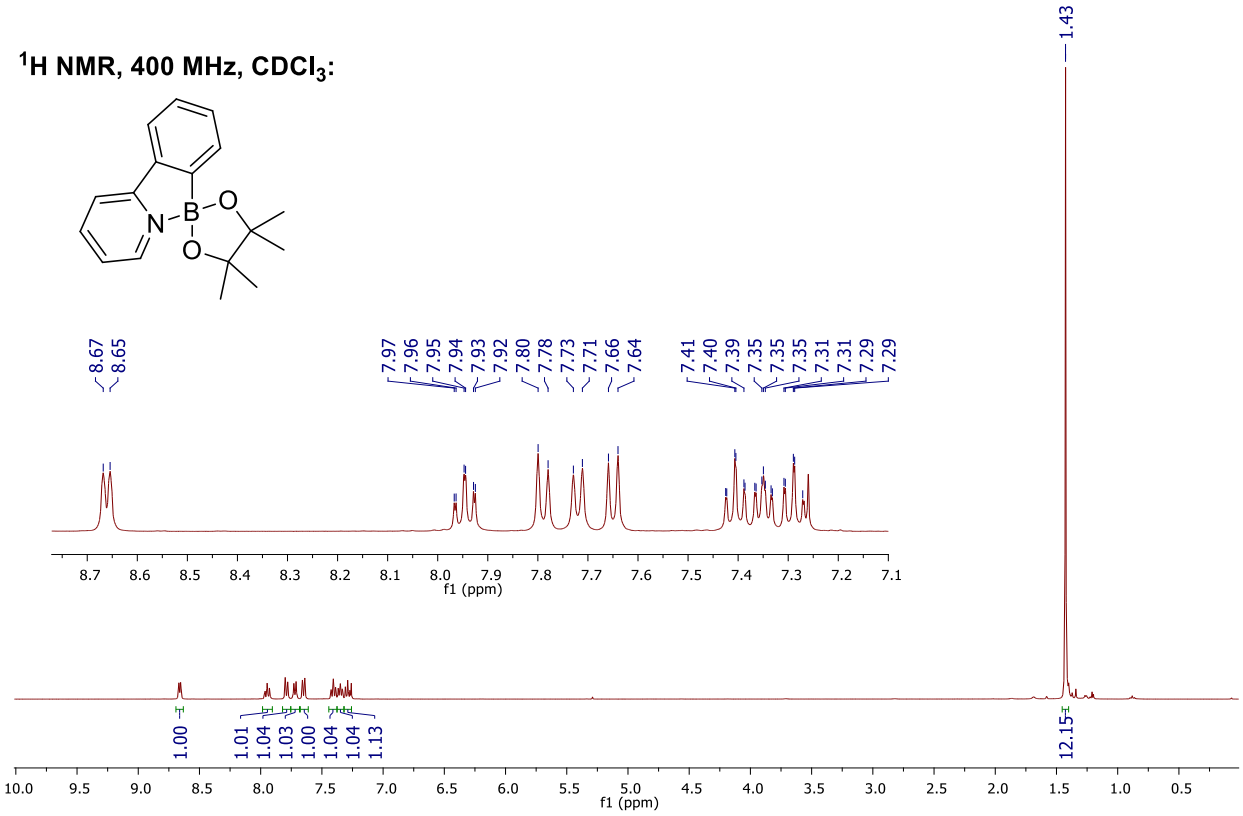
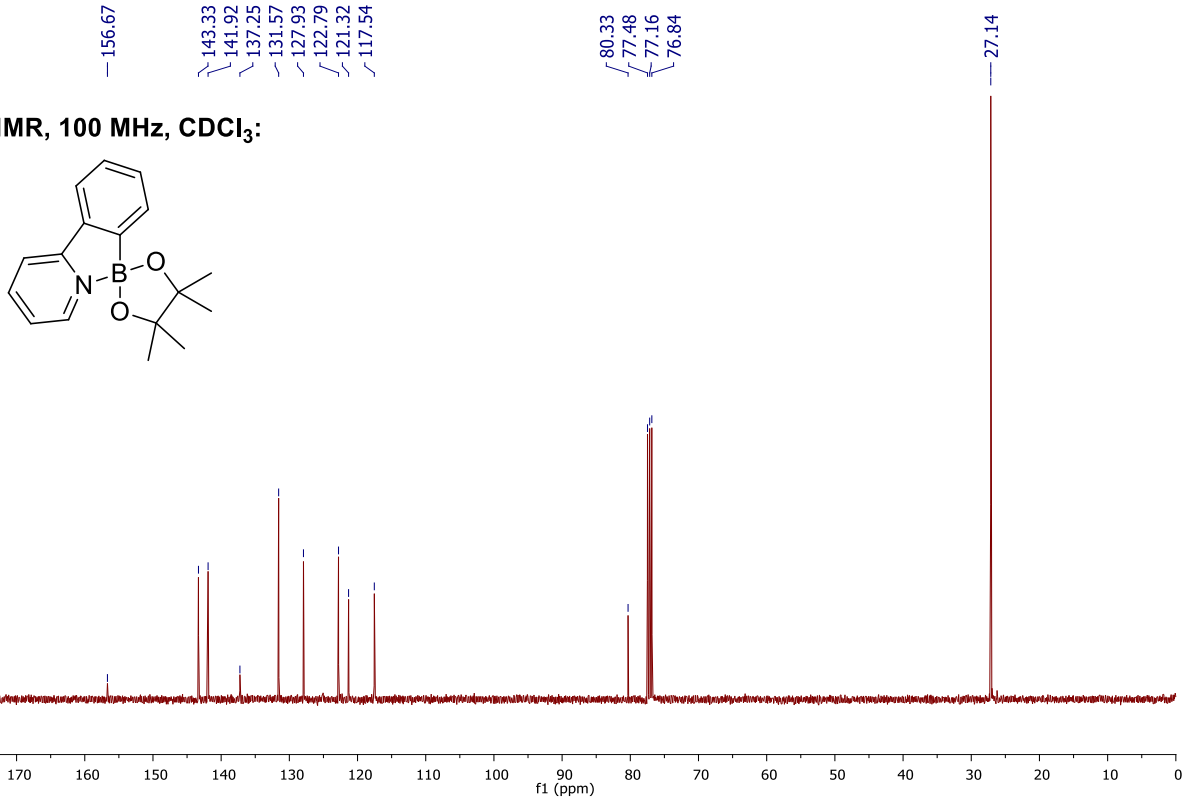
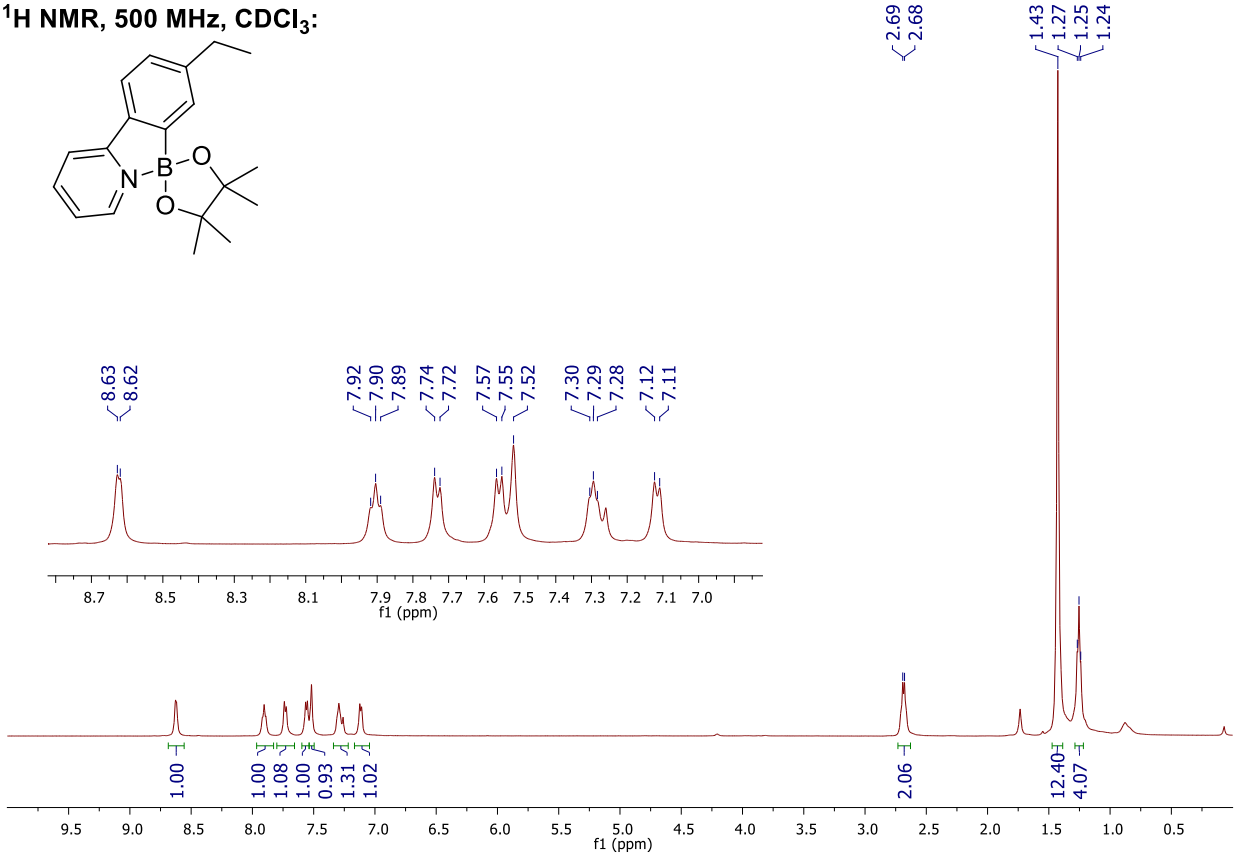


^{13}C NMR, 100 MHz, $CDCl_3$:



^{1}H NMR, 500 MHz, $CDCl_3$:



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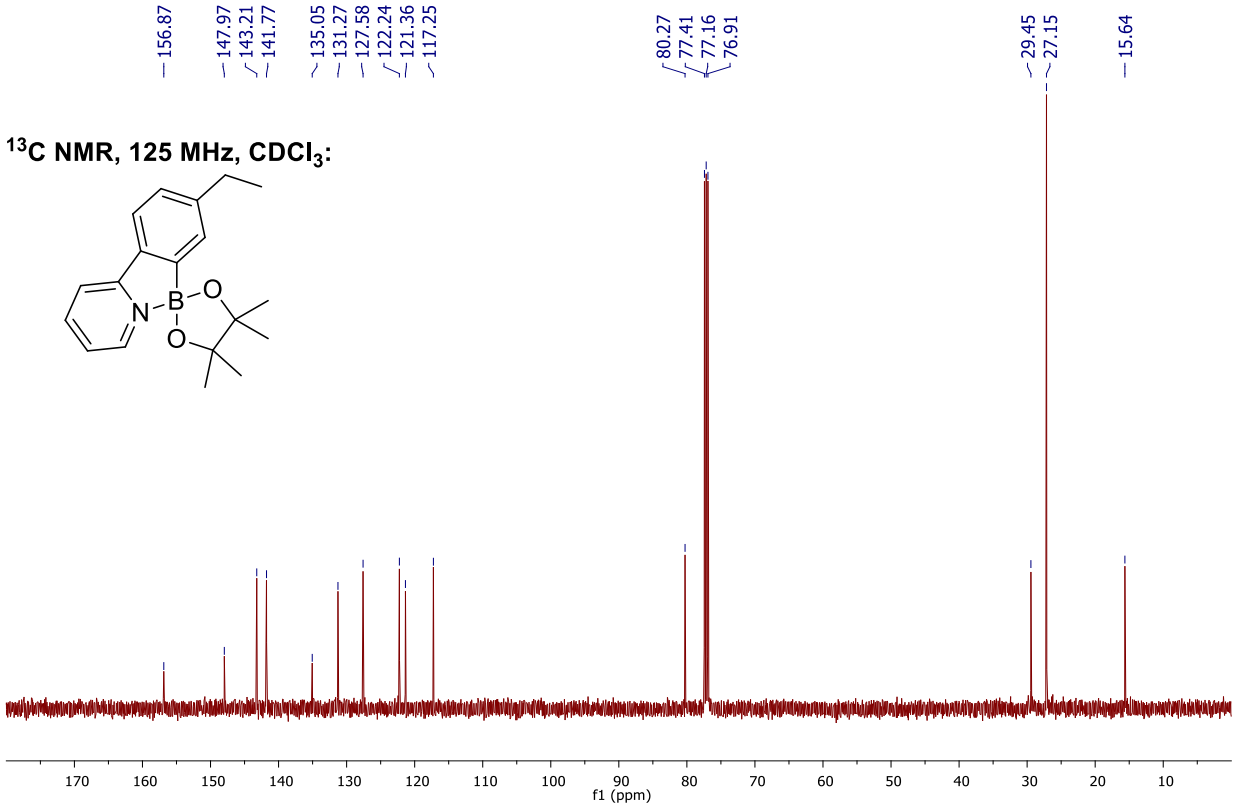
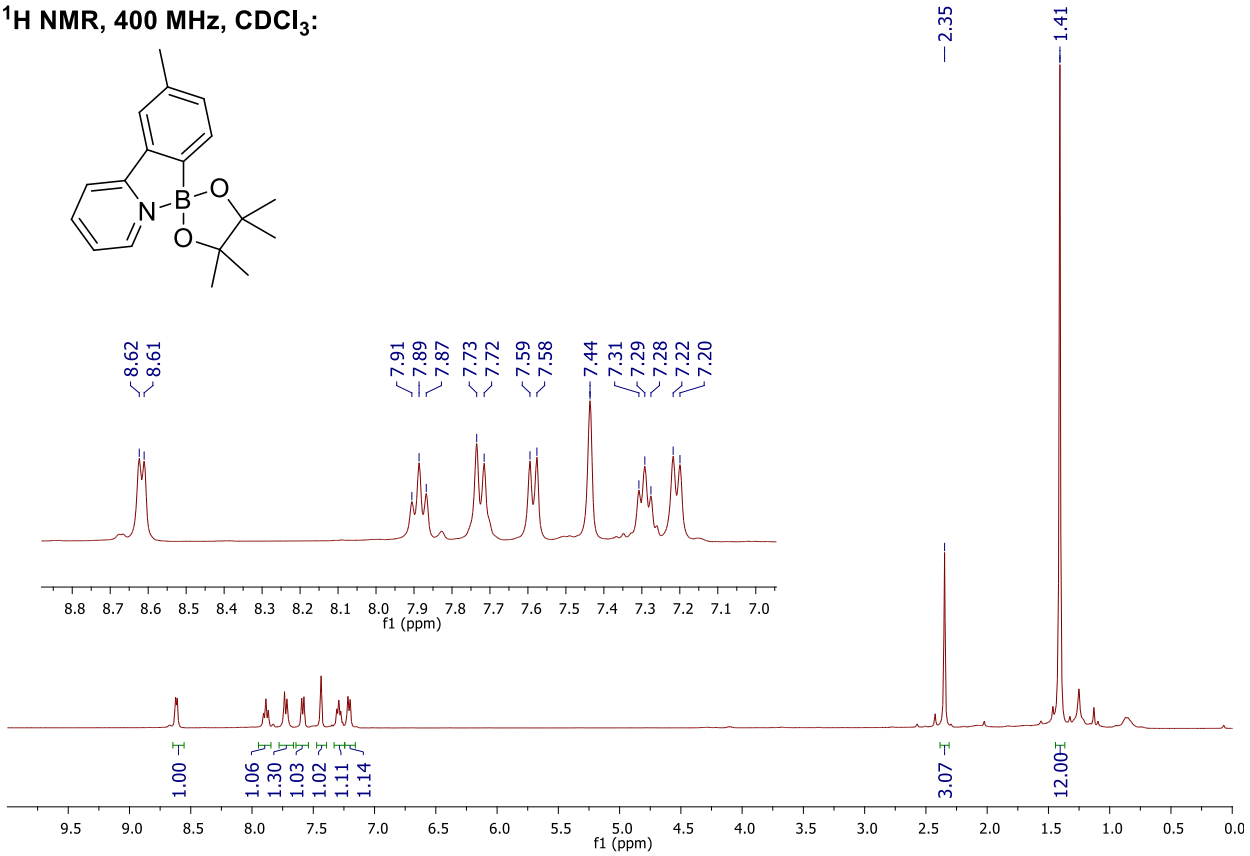
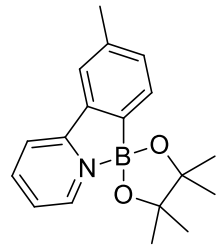


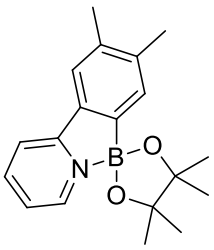
^{1}H NMR, 400 MHz, $CDCl_3$:



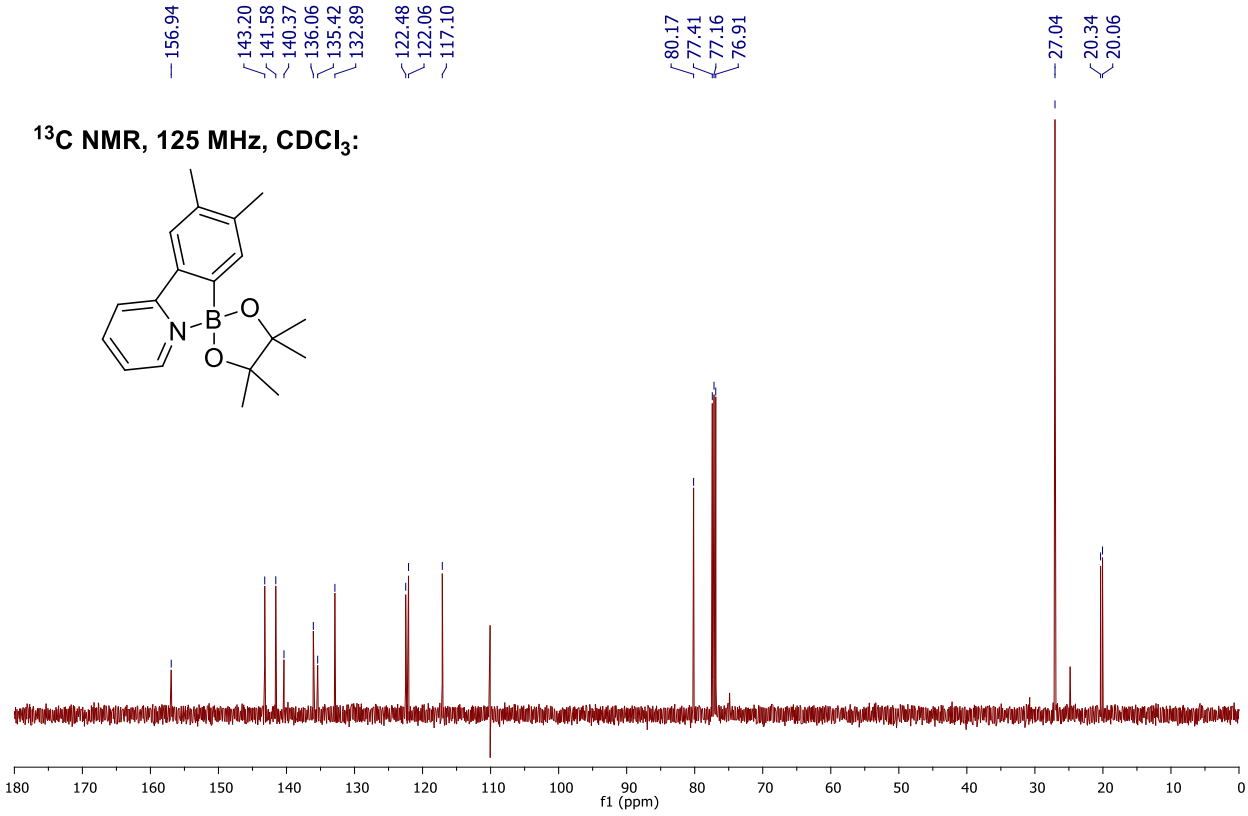
^{13}C NMR, 100 MHz, $CDCl_3$:



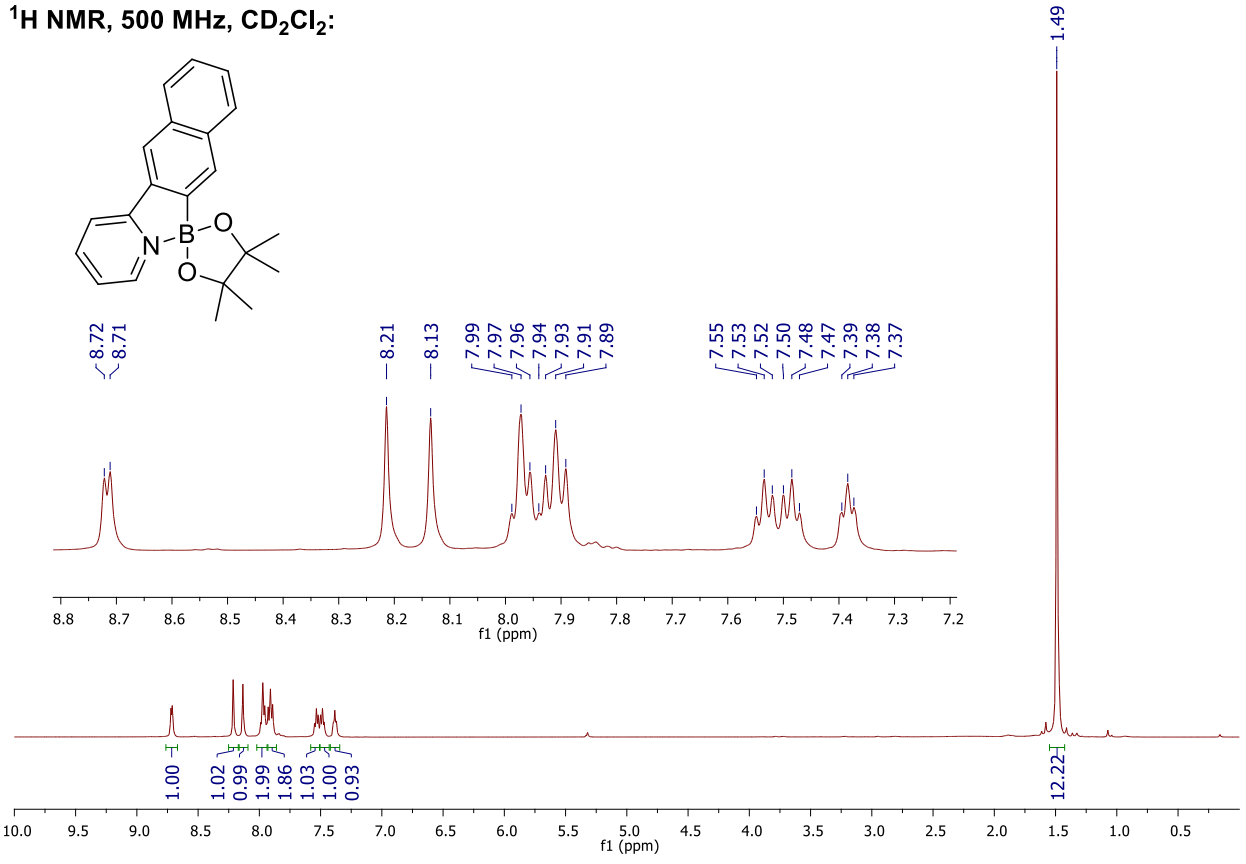
^{1}H NMR, 500 MHz, $CDCl_3$:

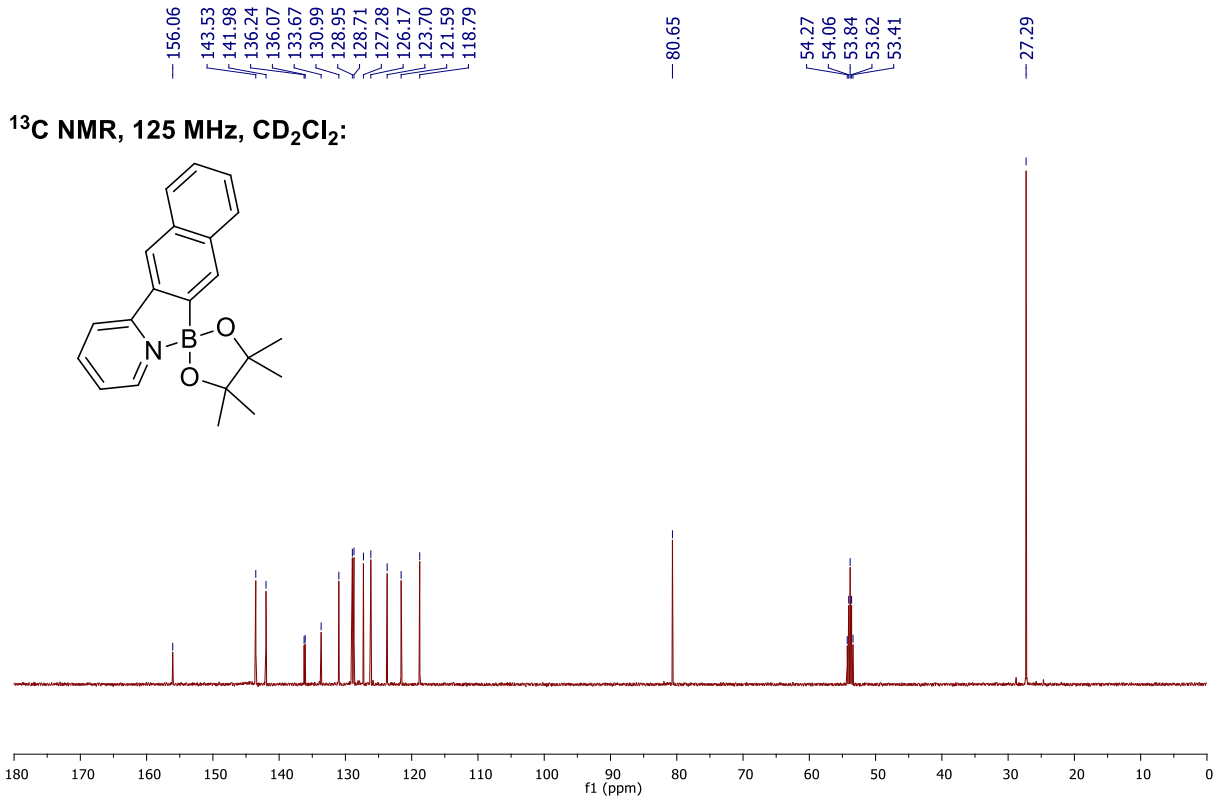


^{13}C NMR, 125 MHz, $CDCl_3$:

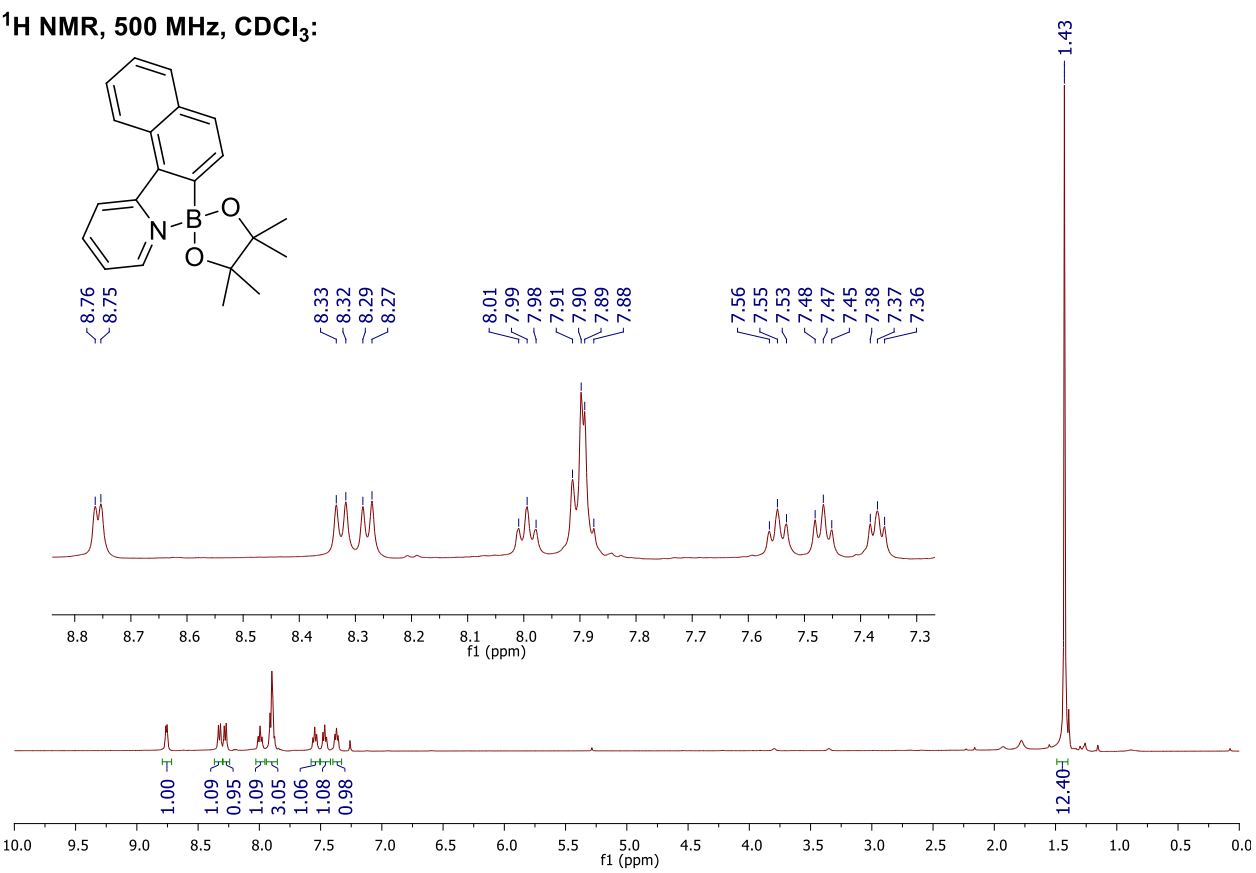


^{1}H NMR, 500 MHz, CD_2Cl_2:



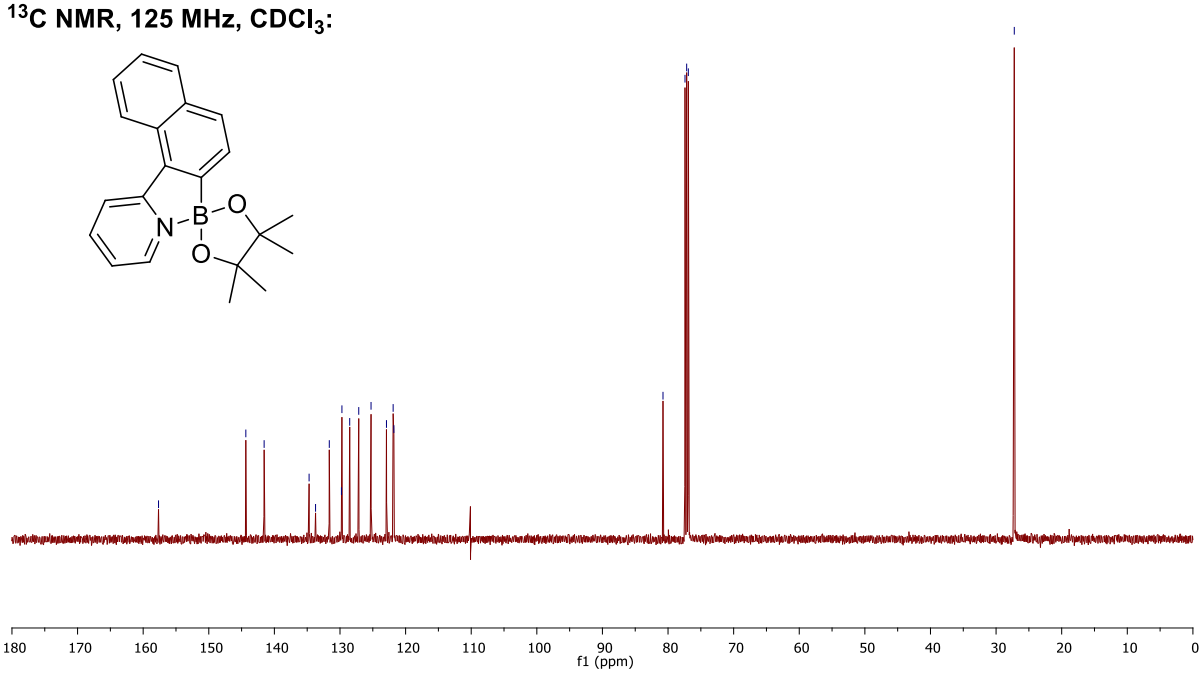


^{13}C NMR, 125 MHz, CD_2Cl_2:

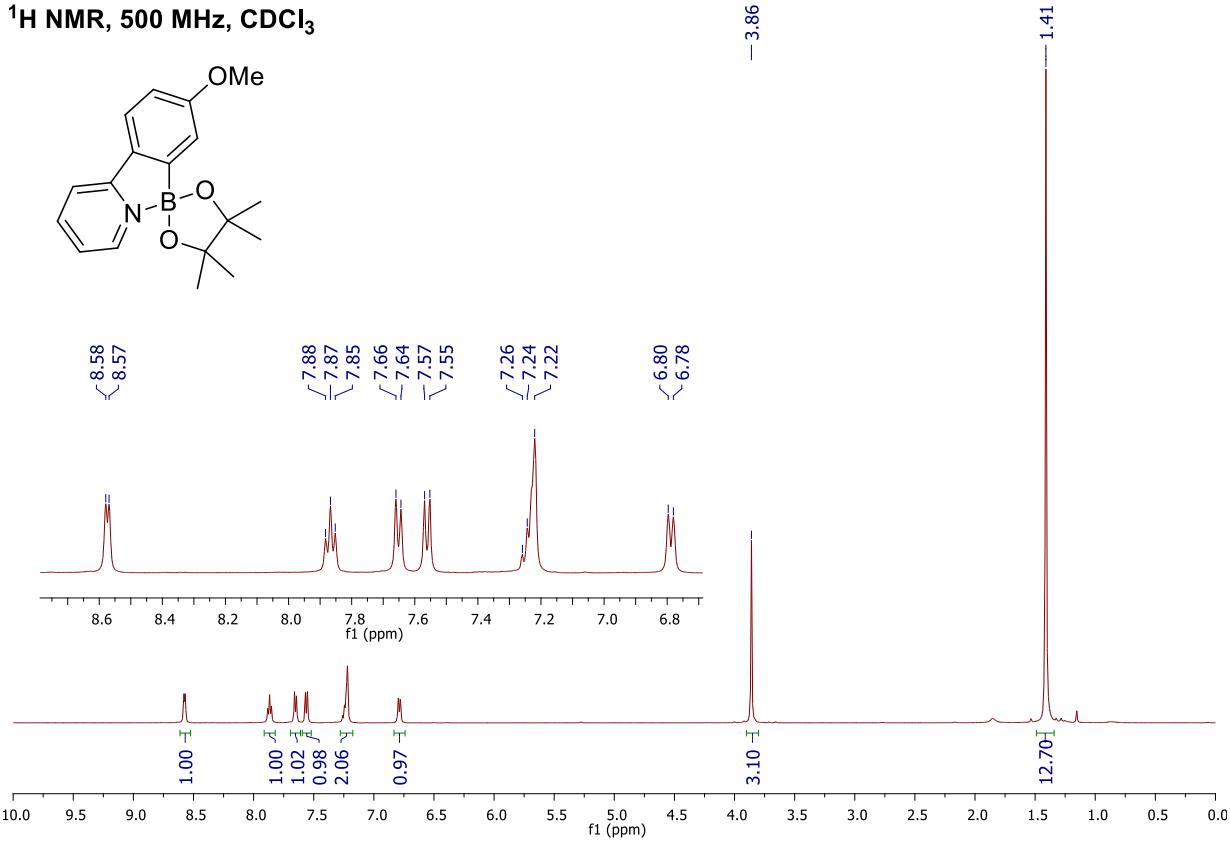


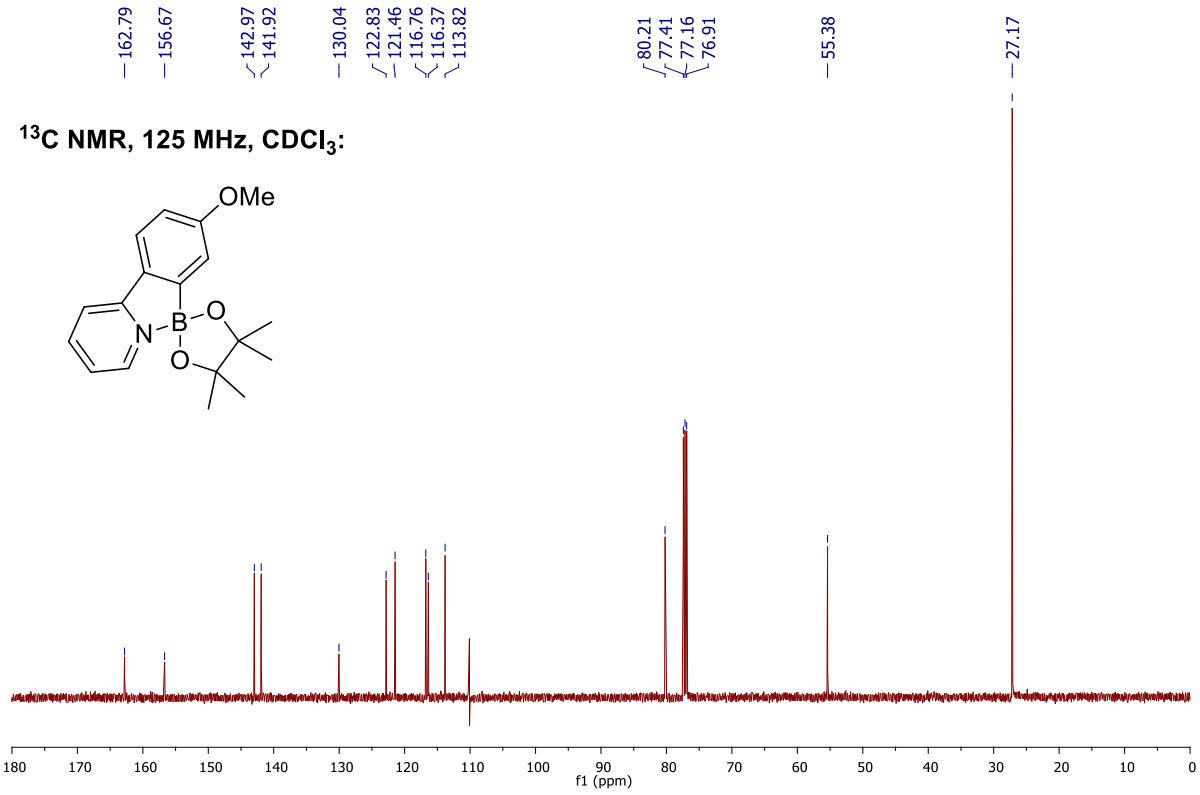
^{1}H NMR, 500 MHz, $CDCl_3$:

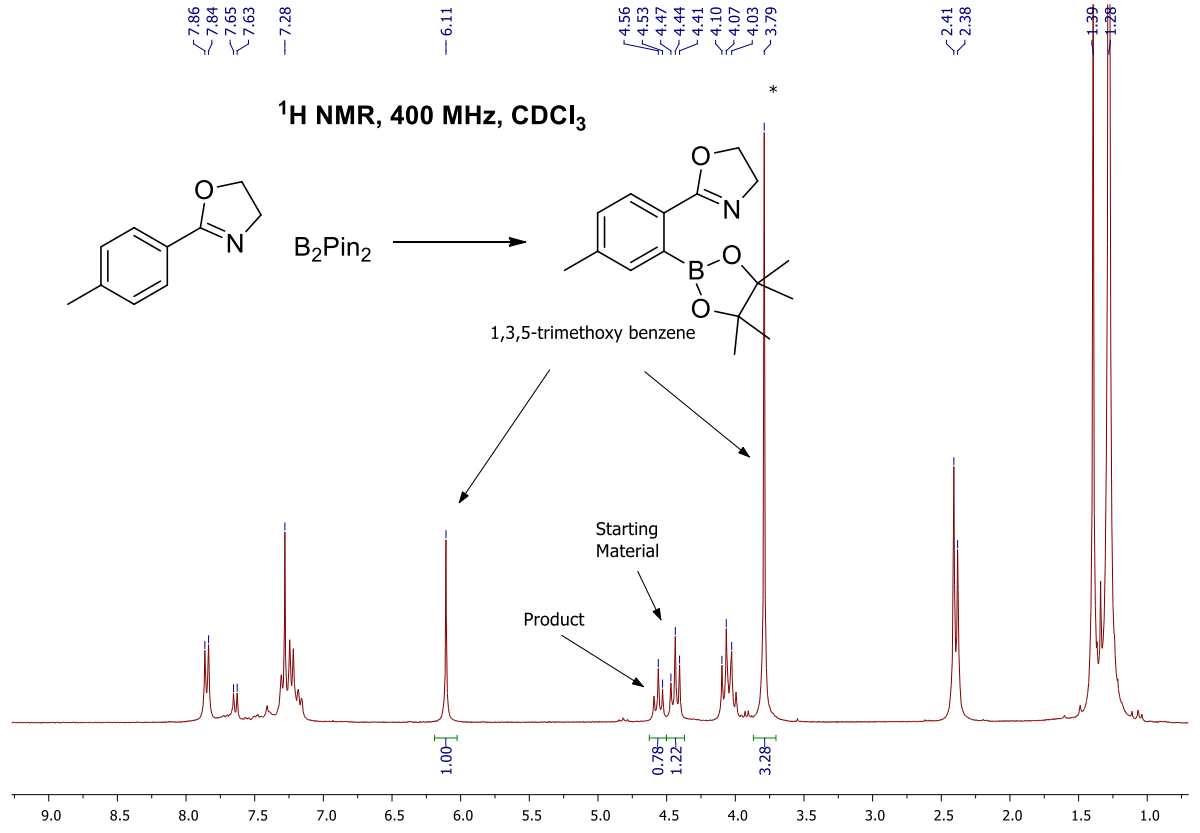
^{13}C NMR, 125 MHz, $CDCl_3$:

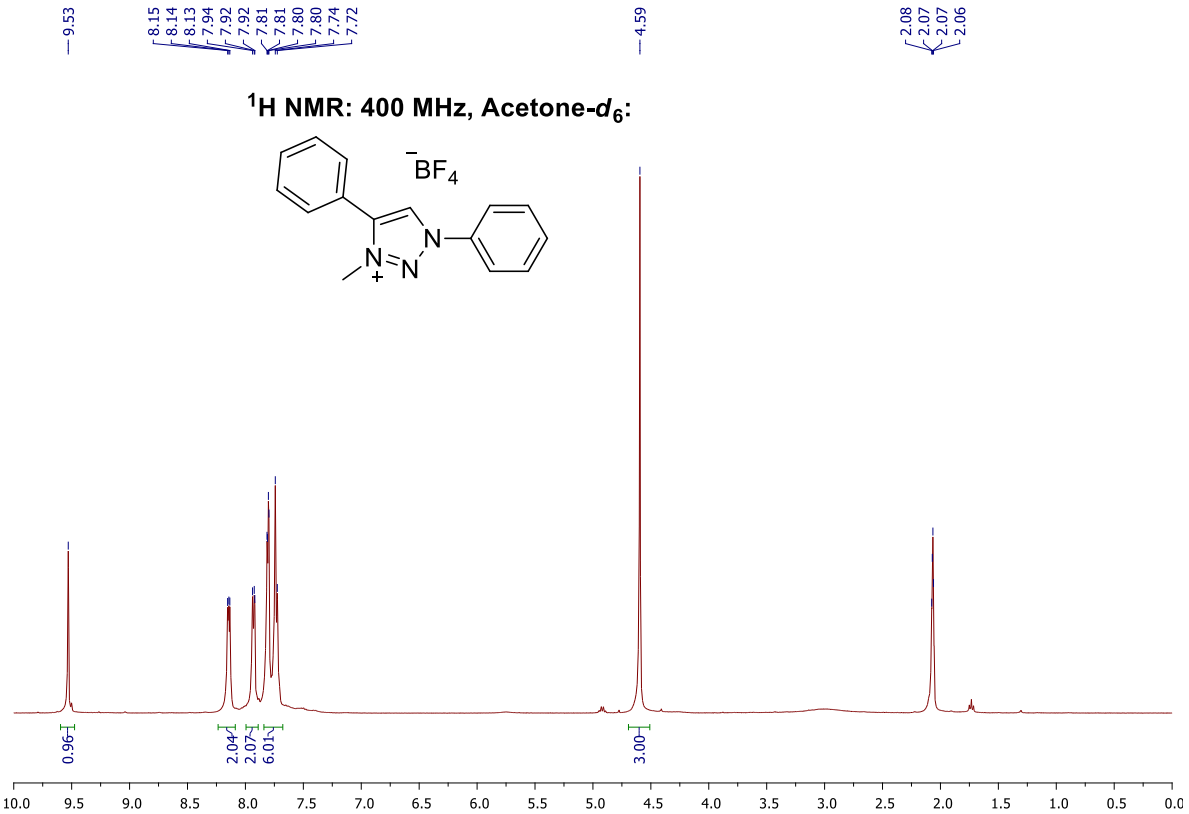


^{1}H NMR, 500 MHz, $CDCl_3$

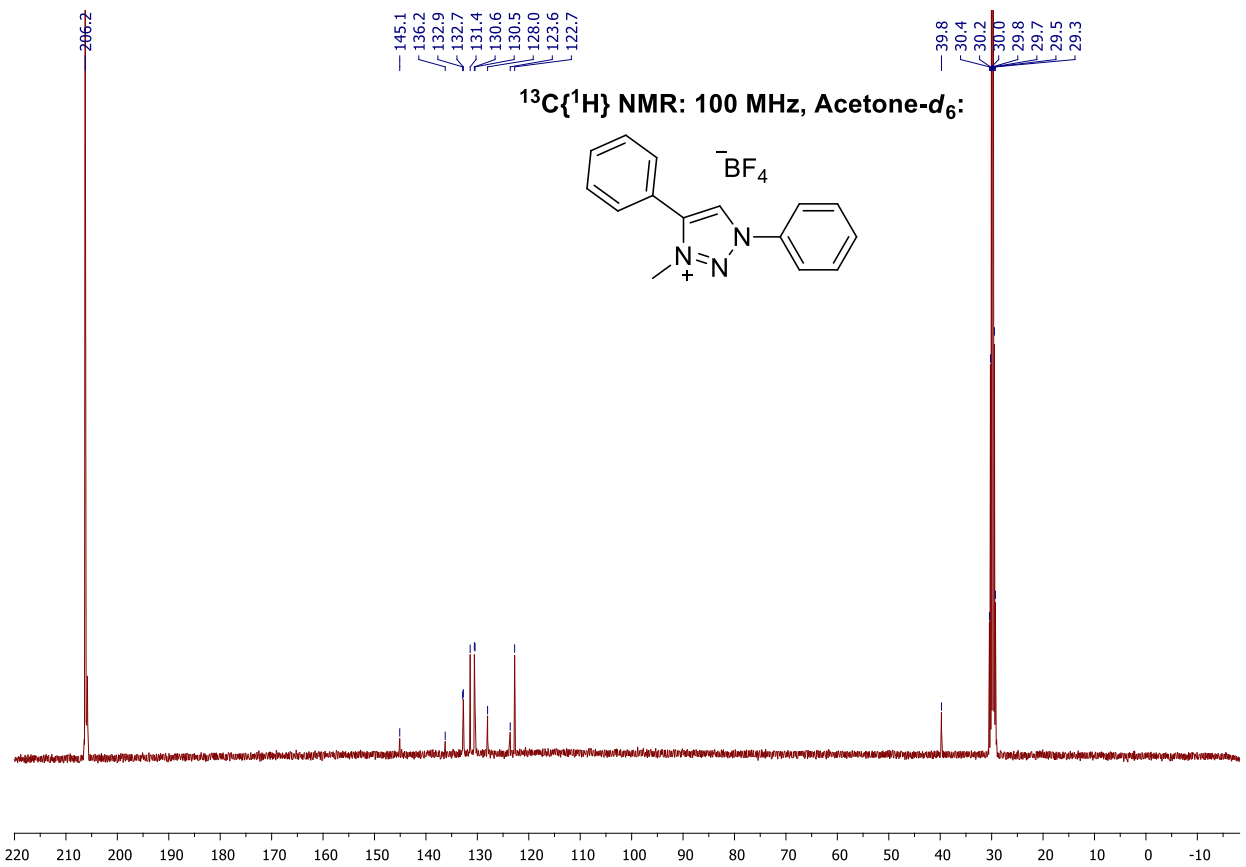



162.79
156.67
142.97
141.92
130.04
122.83
121.46
116.76
116.37
113.82
80.21
77.41
77.16
76.91
55.38
27.17
13C NMR, 125 MHz, CDCl3:
OMe
N
B
O
O
f1 (ppm)


7.86
7.84
7.65
7.63
7.28
6.11
4.56
4.53
4.47
4.44
4.41
4.10
4.07
4.03
3.79
2.41
2.38
1.39
1.28
1H NMR, 400 MHz, CDCl3
B2Pin2
1,3,5-trimethoxy benzene
Starting Material
Product
1.00
0.78
1.22
3.28

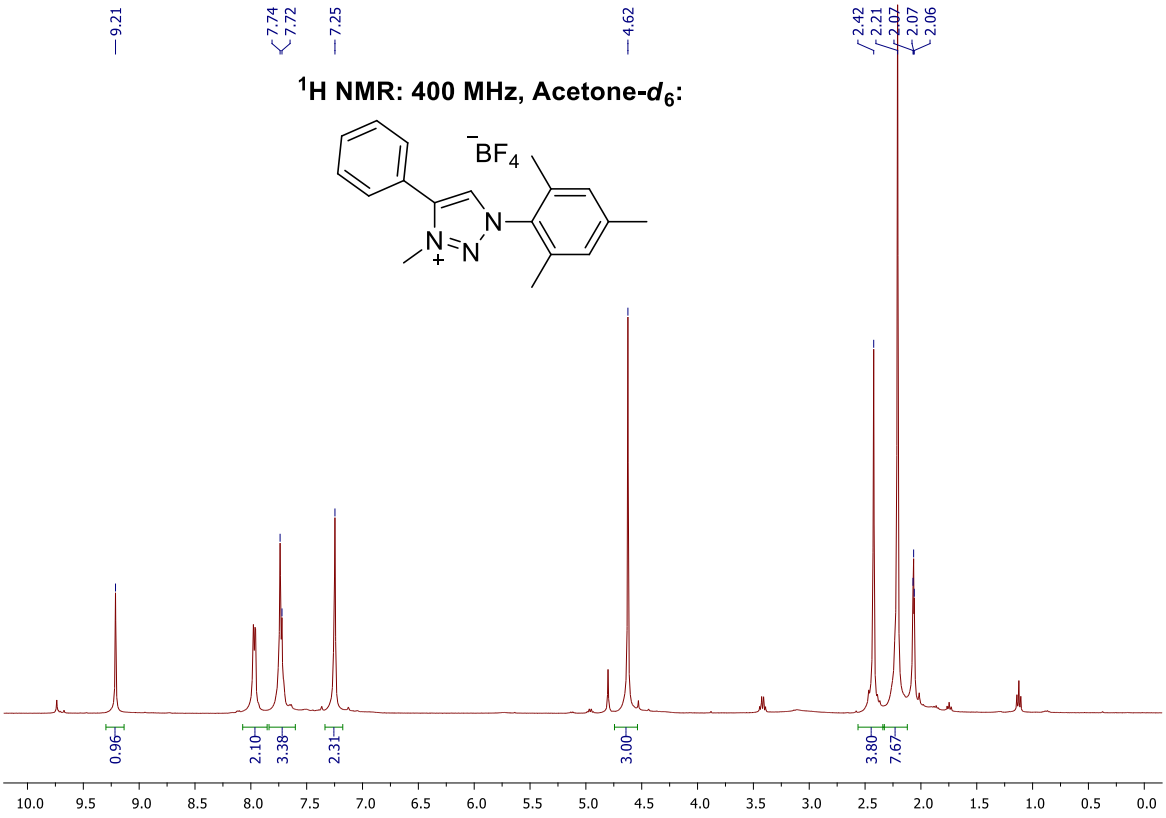


^{1}H NMR: 400 MHz, Acetone-d_6:

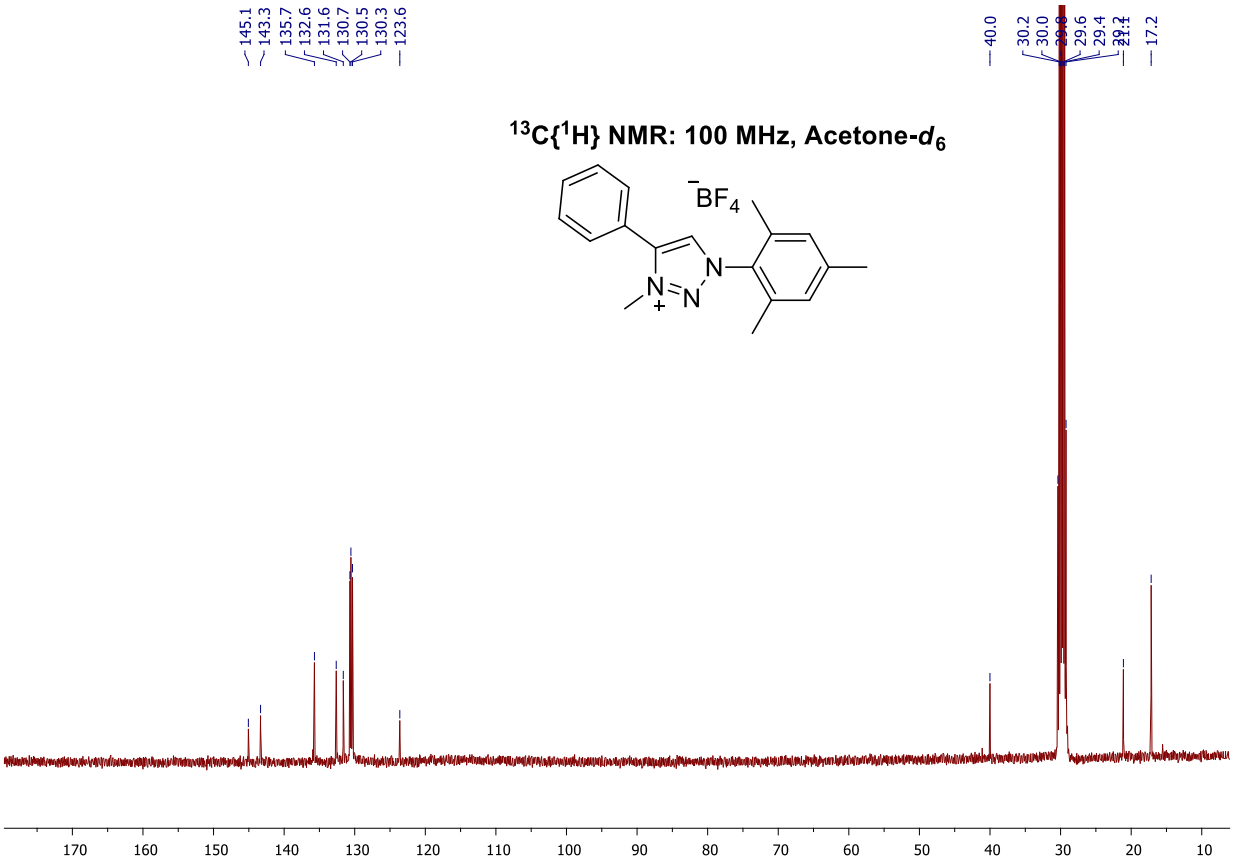


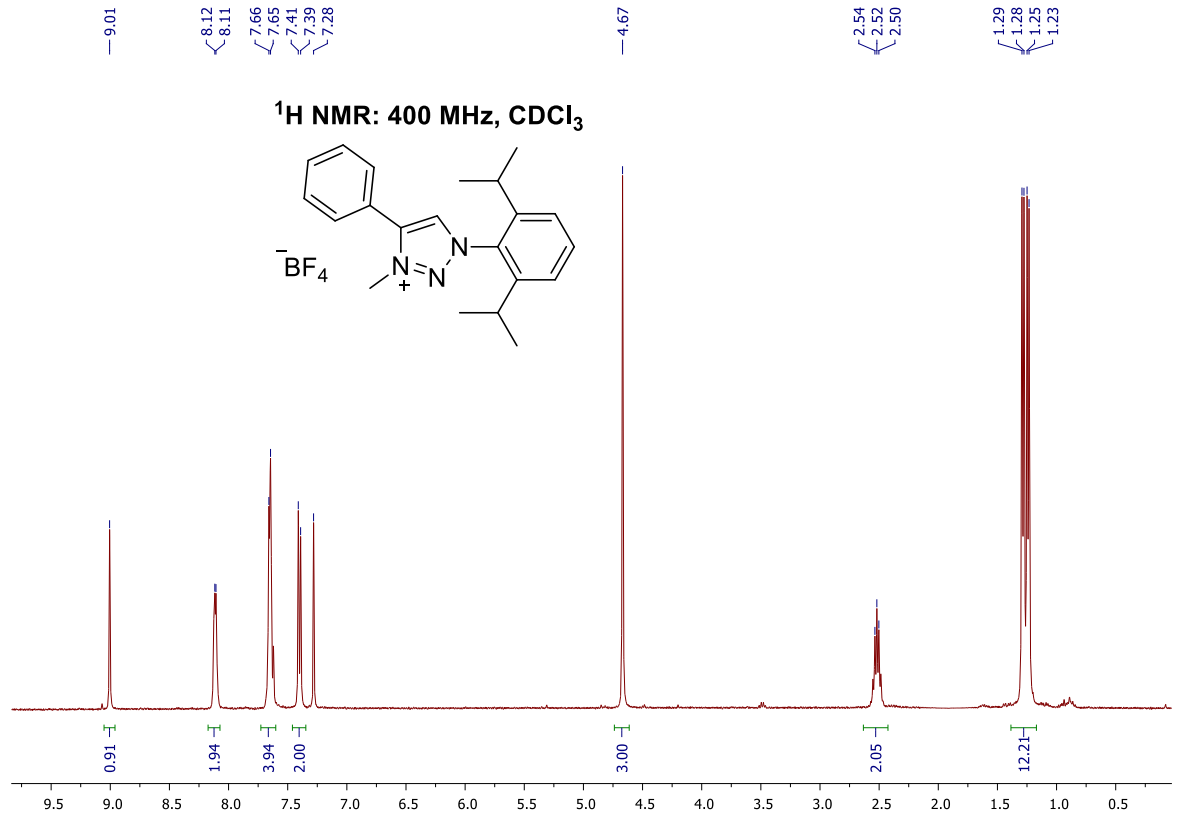
^{13}C{^{1}H} NMR: 100 MHz, Acetone-d_6:

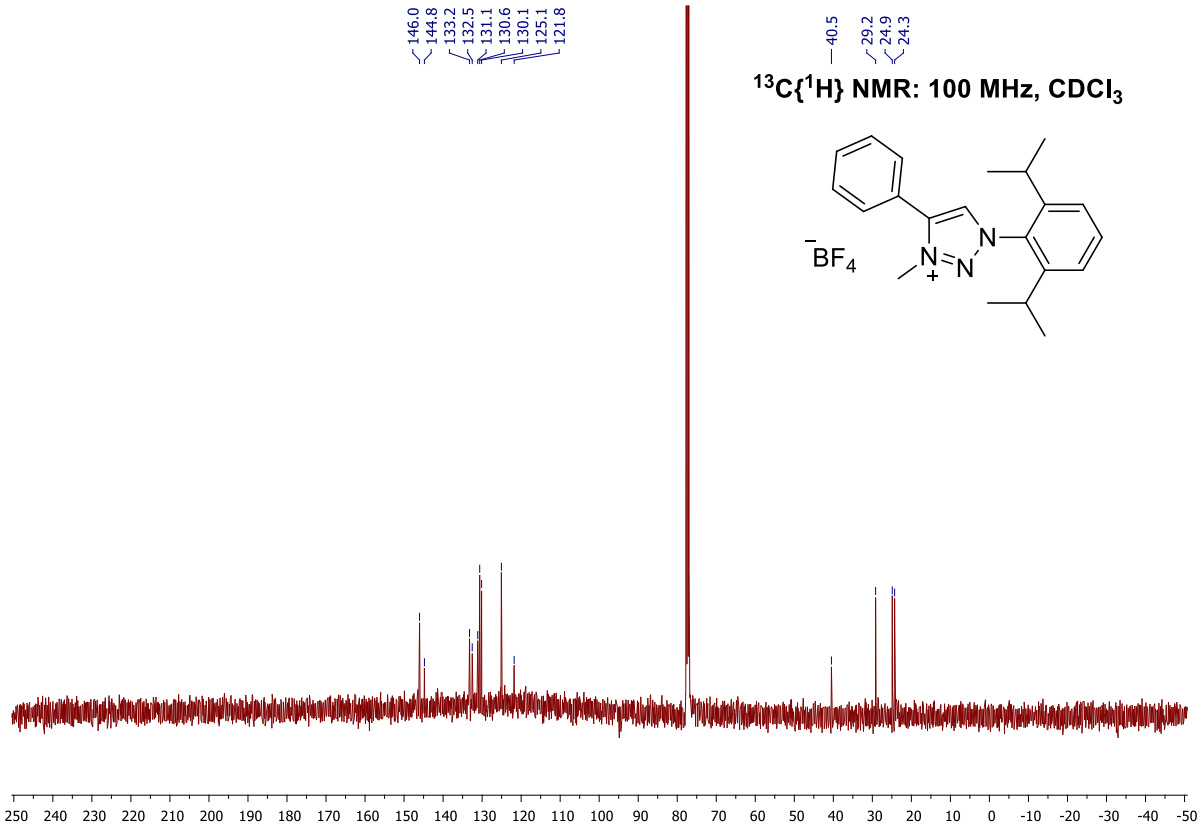
^{1}H NMR: 400 MHz, Acetone-d_6:

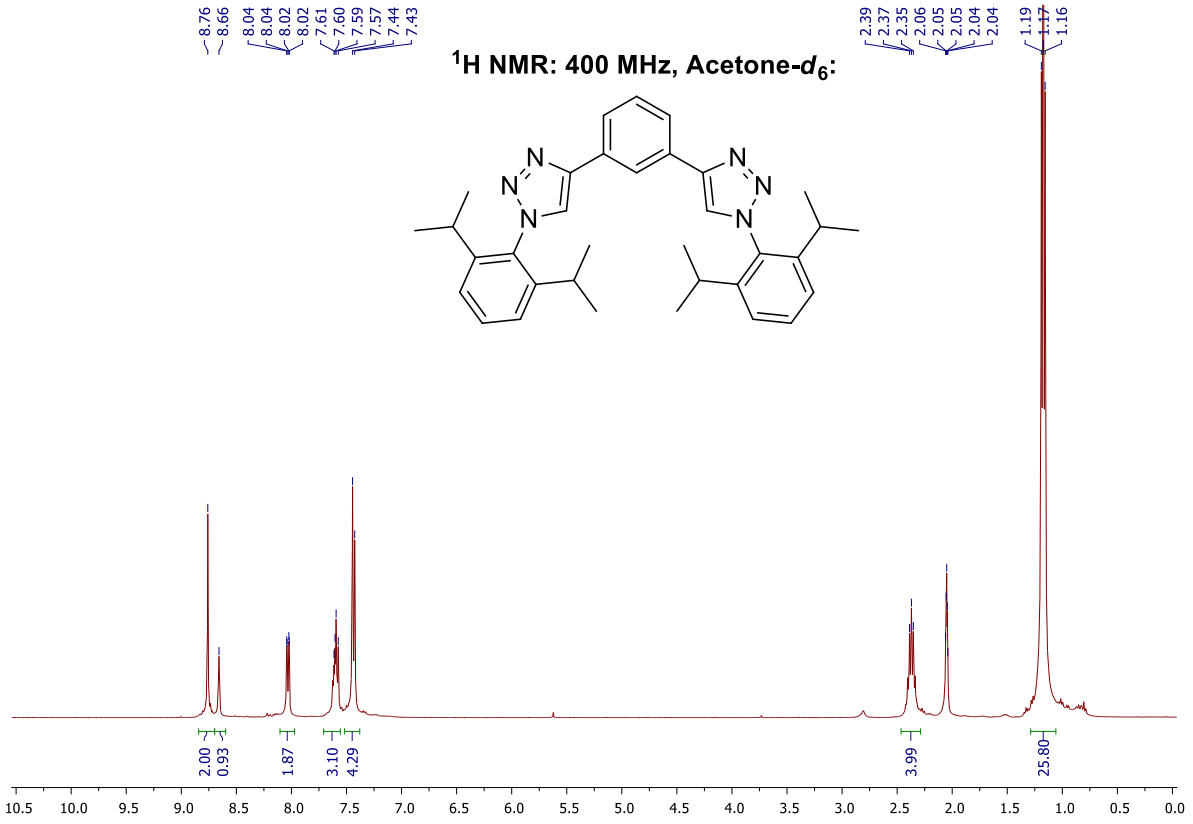


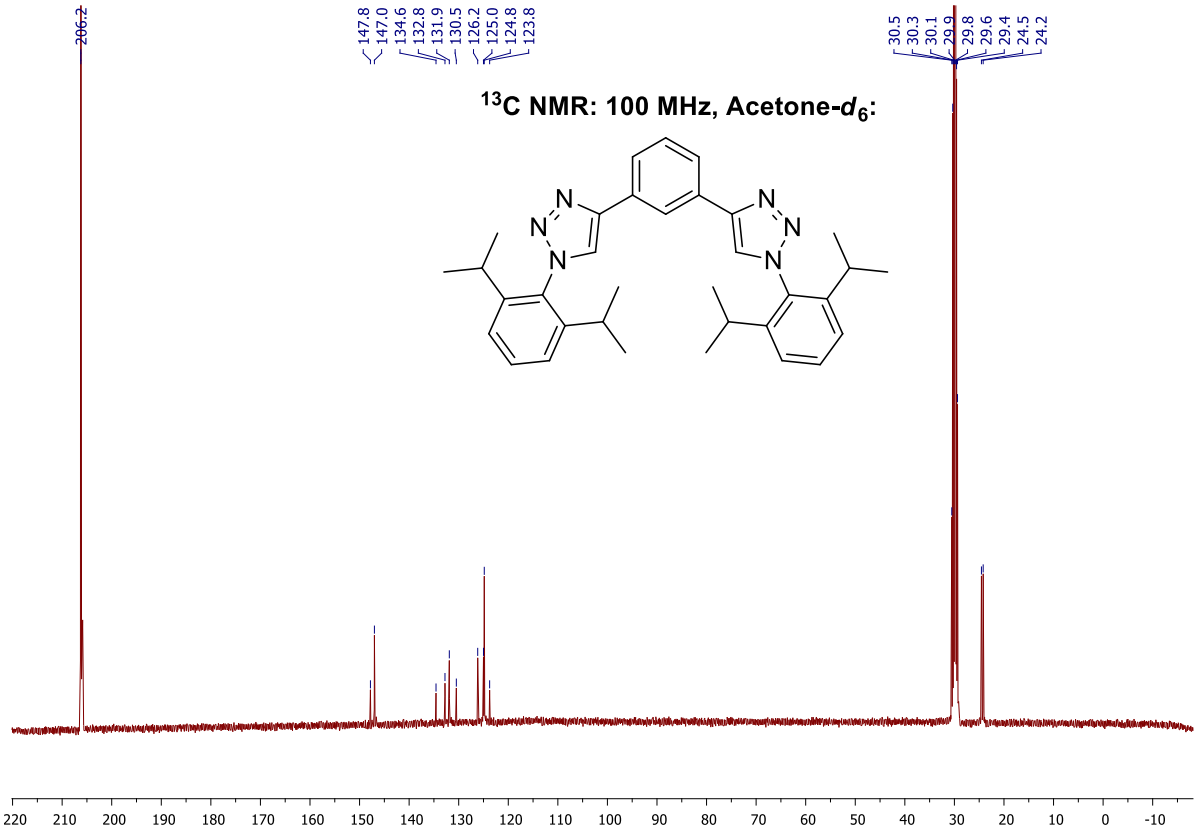
^{13}C{^{1}H} NMR: 100 MHz, Acetone-d_6

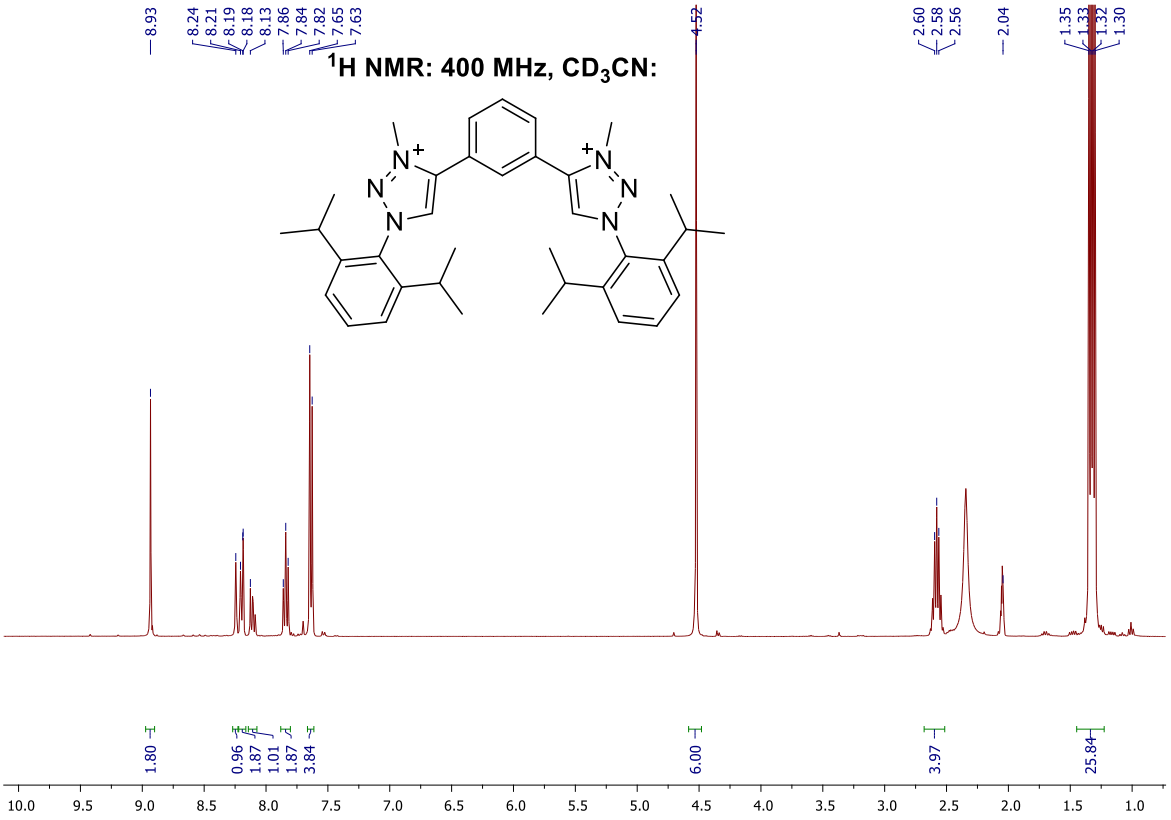


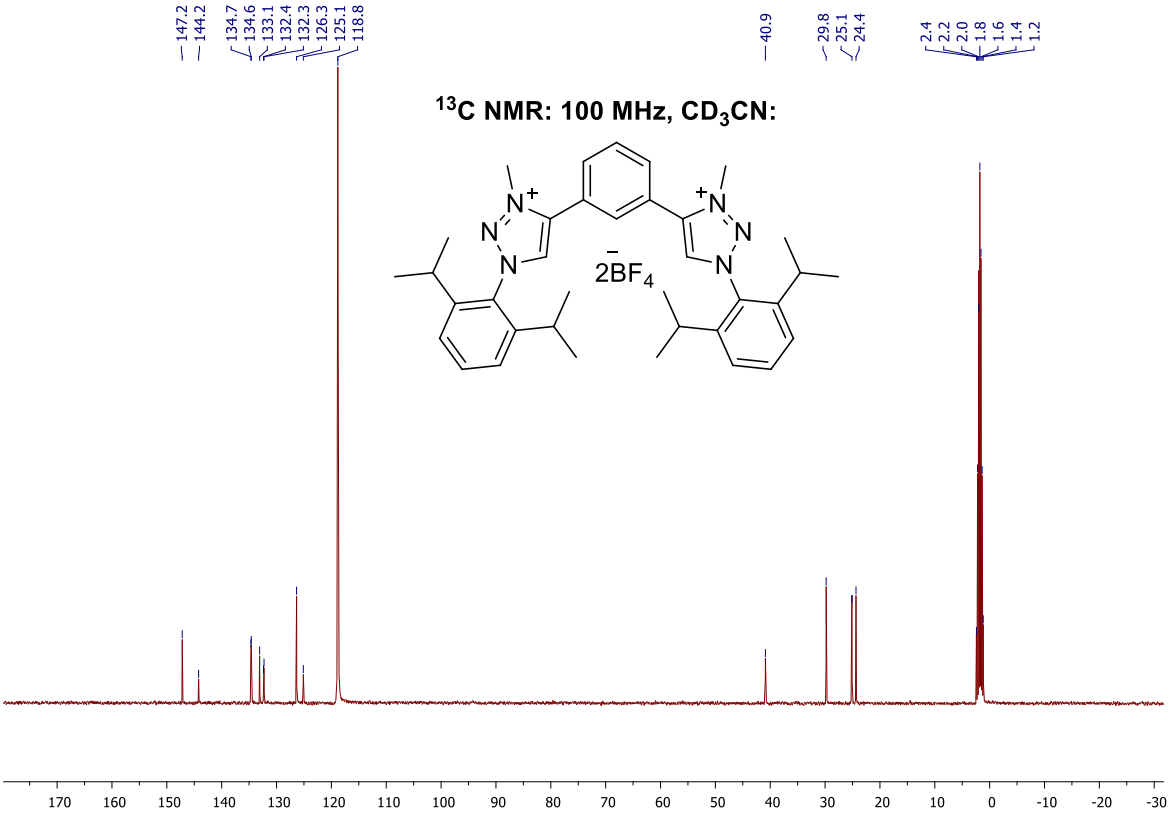

9.01
8.12
8.11
7.66
7.65
7.41
7.39
7.28
4.67
2.54
2.52
2.50
1.29
1.28
1.25
1.23
^{1}H NMR: 400 MHz, CDCl$_3$
$^-$BF$_4$
0.91
1.94
3.94
2.00
3.00
2.05
12.21

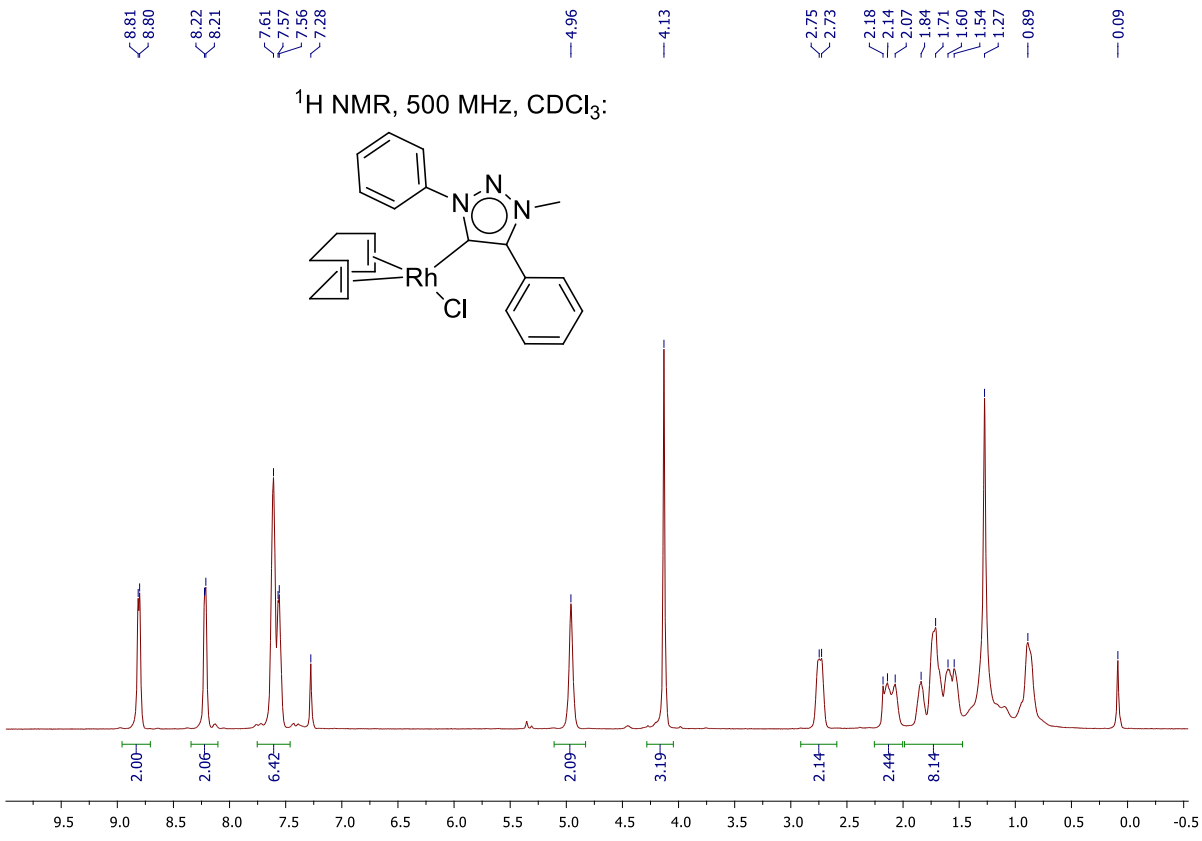

146.0
144.8
133.2
132.5
131.1
130.6
130.1
125.1
121.8
40.5
29.2
24.9
24.3
^{13}C{^{1}H} NMR: 100 MHz, CDCl$_3$
$^-$BF$_4$

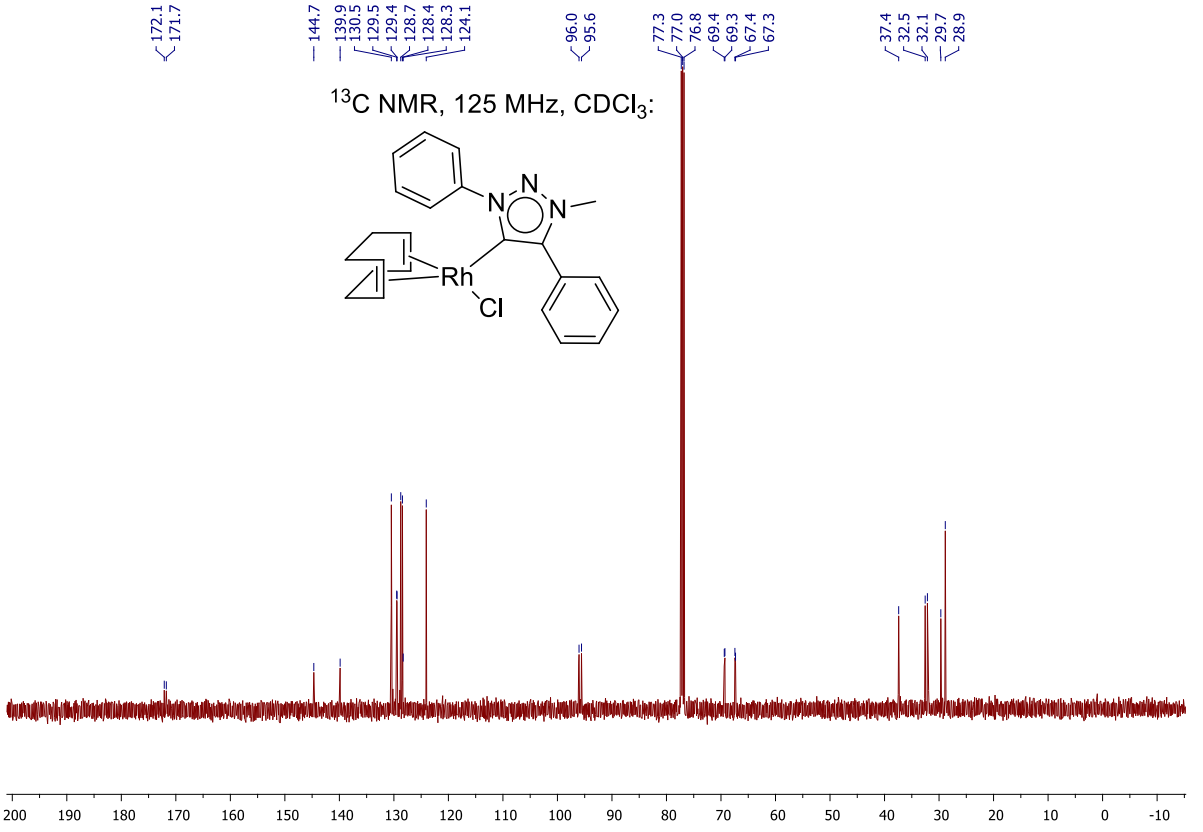

8.76
8.66
8.04
8.04
8.02
8.02
7.61
7.60
7.59
7.57
7.44
7.43
2.39
2.37
2.35
2.06
2.05
2.05
2.04
2.04
1.19
1.17
1.16
^{1}H NMR: 400 MHz, Acetone-d_6:
2.00
0.93
1.87
3.10
4.29
3.99
25.80
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


206.2
147.8
147.0
134.6
132.8
131.9
130.5
126.2
125.0
124.8
123.8
30.5
30.3
30.1
29.9
29.8
29.6
29.4
24.5
24.2
^{13}C NMR: 100 MHz, Acetone-d_6:
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

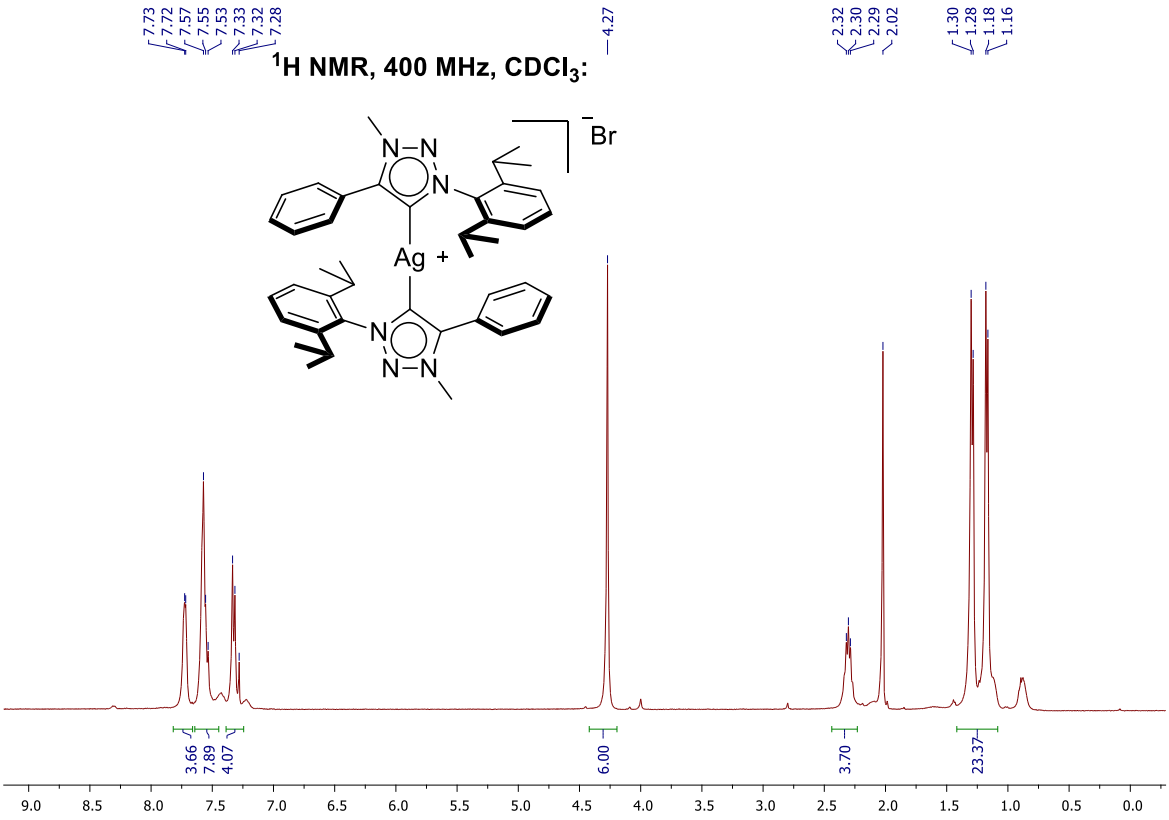

8.93
8.24
8.21
8.19
8.18
8.13
7.86
7.84
7.82
7.65
7.63
4.52
2.60
2.58
2.56
2.04
1.35
1.33
1.32
1.30
1H NMR: 400 MHz, CD3CN:
1.80
0.96
1.87
1.01
1.87
3.84
6.00
3.97
25.84
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0


147.2
144.2
134.7
134.6
133.1
132.4
132.3
126.3
125.1
118.8
40.9
29.8
25.1
24.4
2.4
2.2
2.0
1.8
1.6
1.4
1.2
13C NMR: 100 MHz, CD3CN:
2BF4
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30

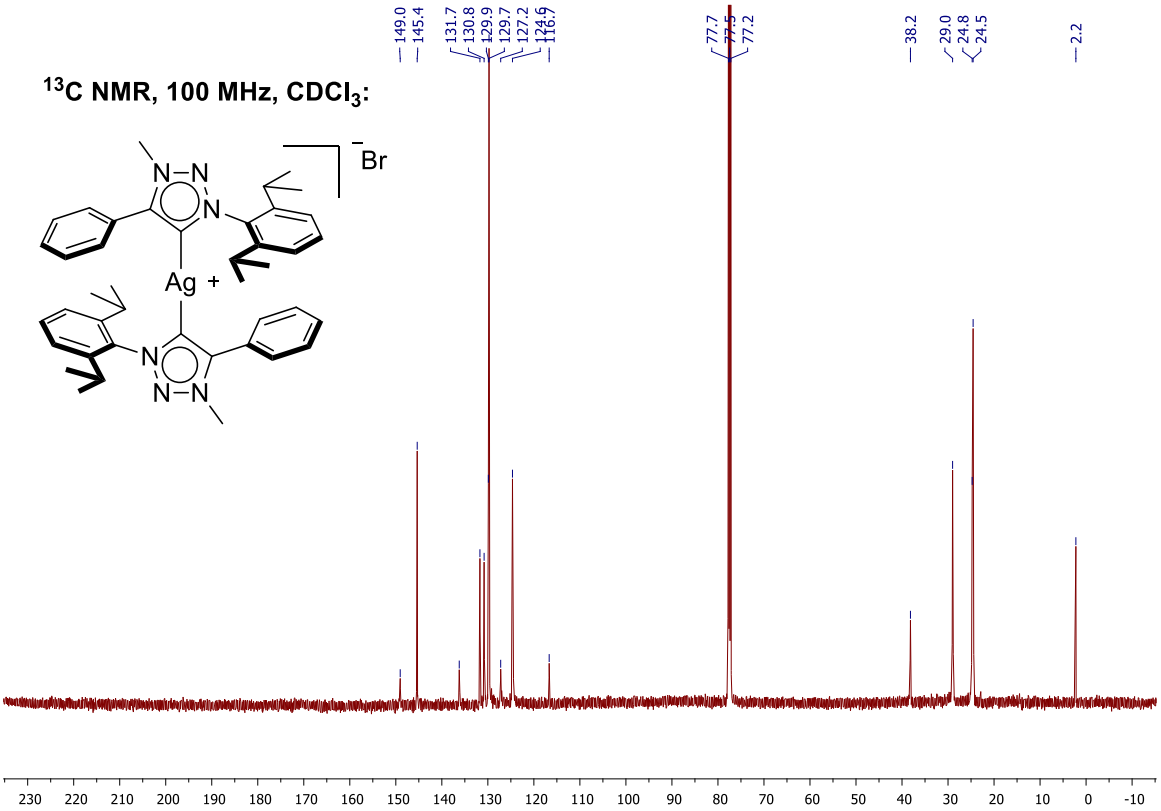

8.81
8.80
8.22
8.21
7.61
7.57
7.56
7.28
4.96
4.13
2.75
2.73
2.18
2.14
2.07
1.84
1.71
1.60
1.54
1.27
0.89
0.09
^{1}H NMR, 500 MHz, $CDCl_3$:
N
N
N
Rh
Cl
2.00
2.06
6.42
2.09
3.19
2.14
2.44
8.14
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

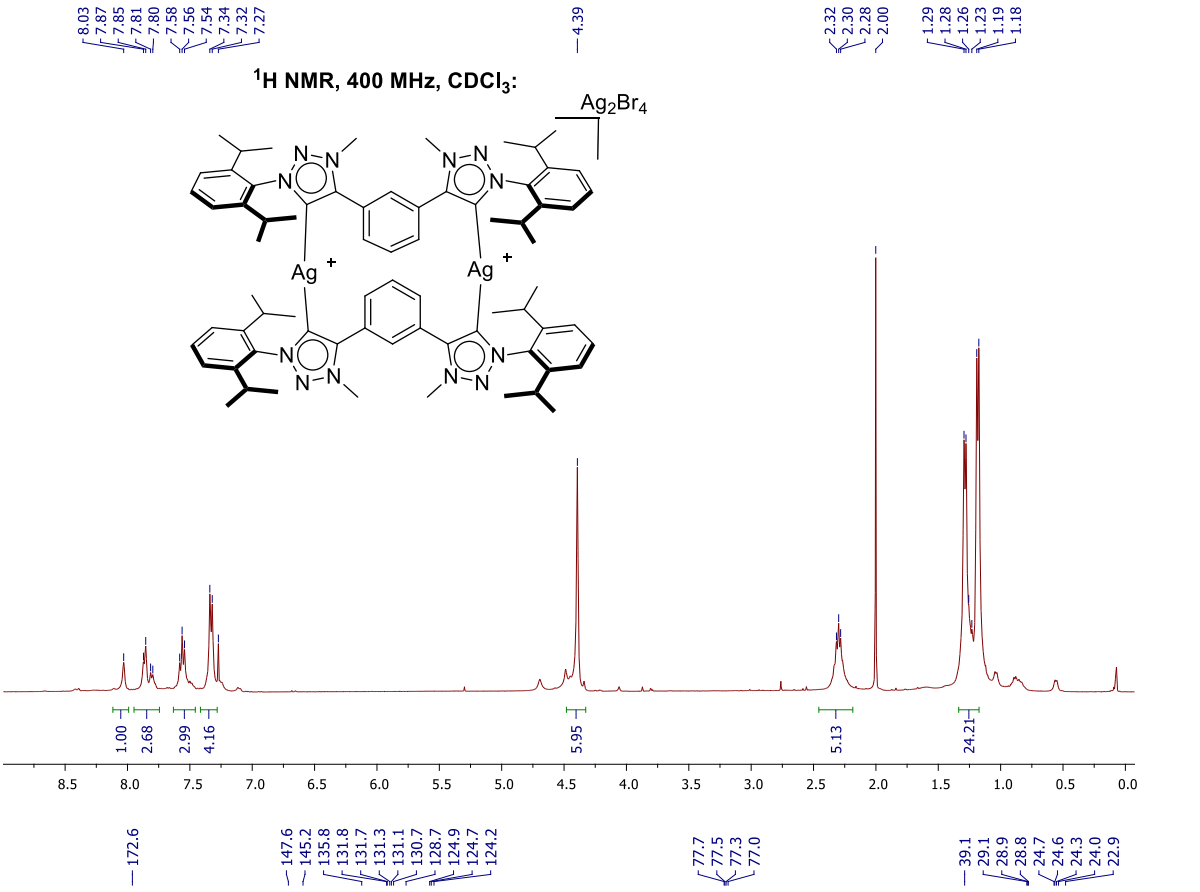

172.1
171.7
144.7
139.9
130.5
129.5
129.4
128.7
128.4
128.3
124.1
96.0
95.6
77.3
77.0
76.8
69.4
69.3
67.4
67.3
37.4
32.5
32.1
29.7
28.9
^{13}C NMR, 125 MHz, $CDCl_3$:
N
N
N
Rh
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

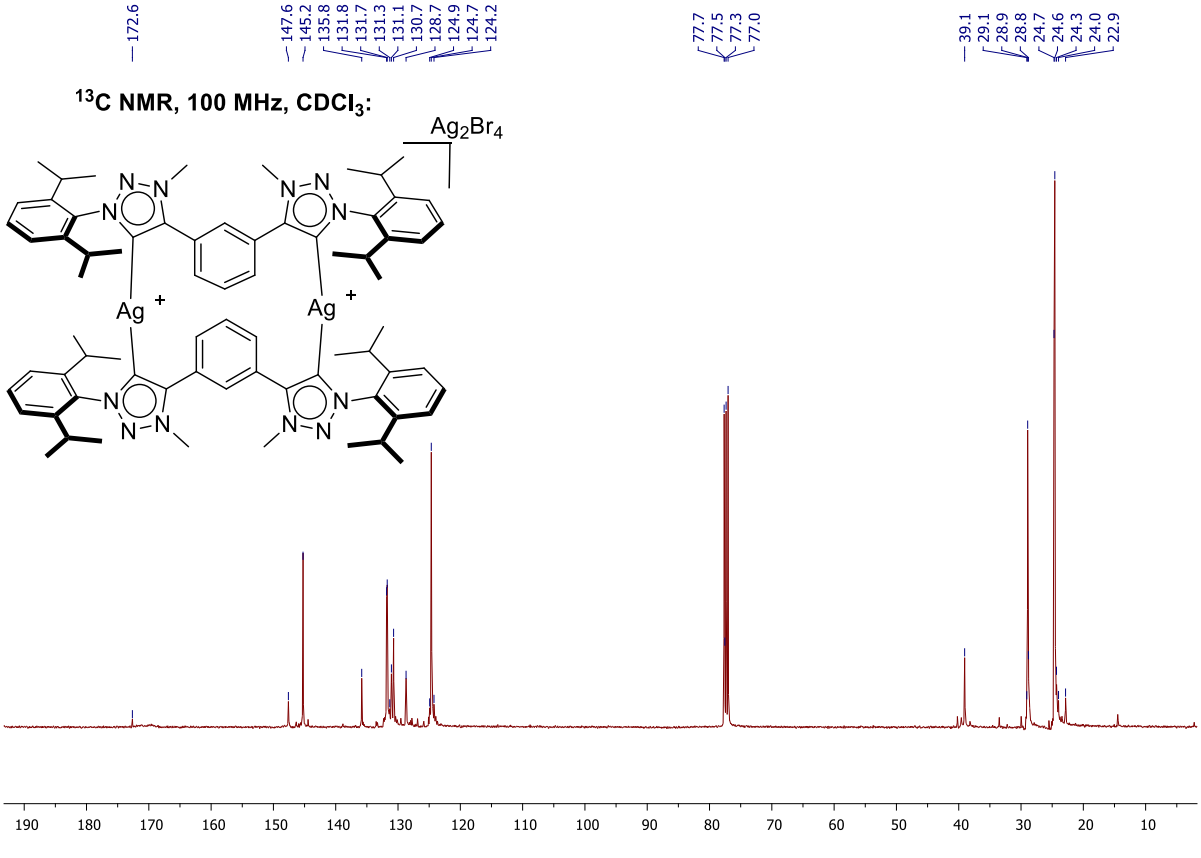
^{1}H NMR, 400 MHz, $CDCl_3$:



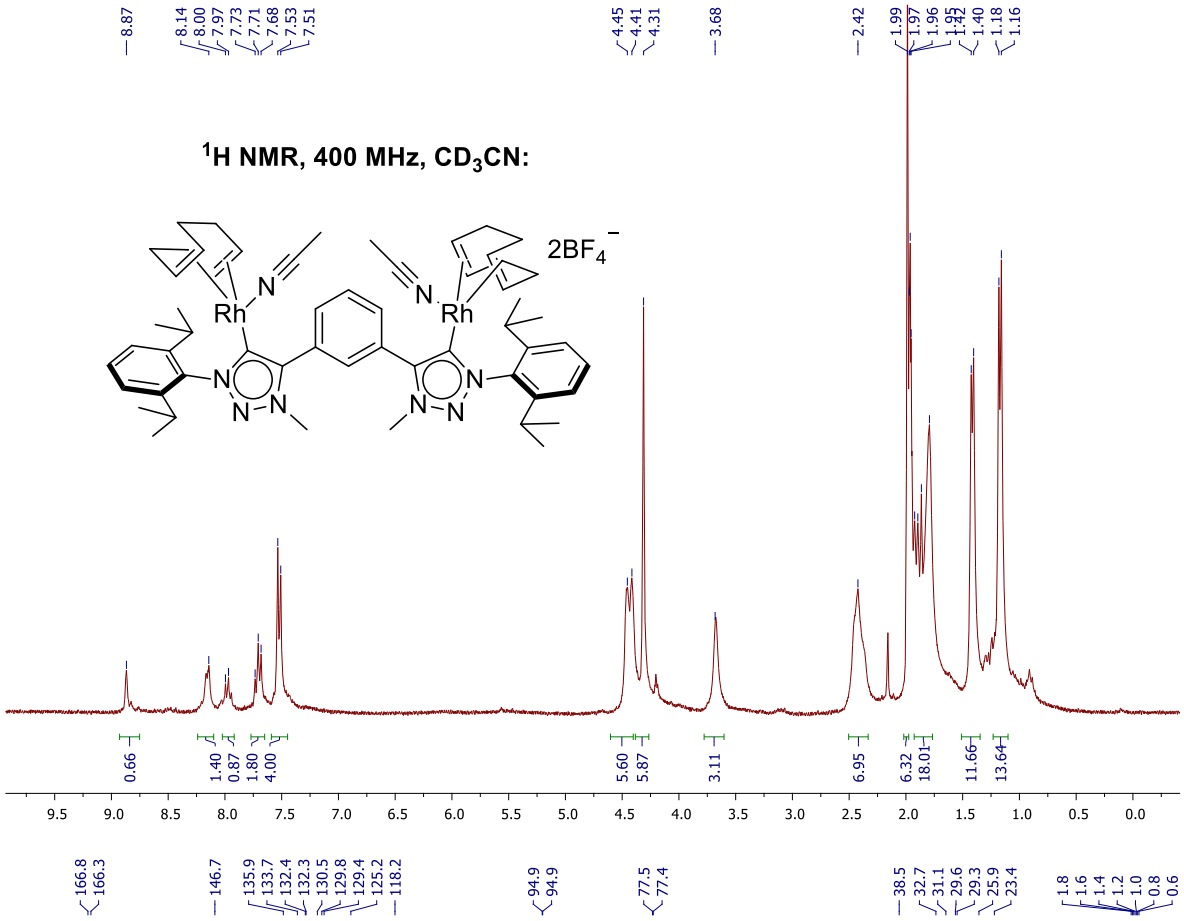
^{13}C NMR, 100 MHz, $CDCl_3$:



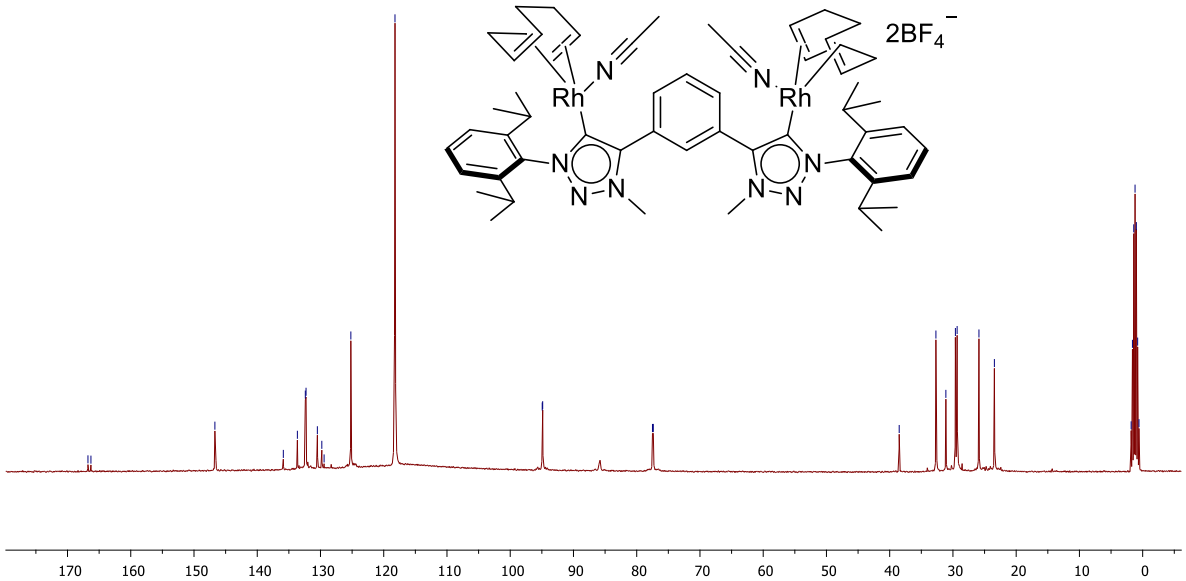

8.03
7.87
7.85
7.81
7.80
7.58
7.56
7.54
7.34
7.32
7.27
4.39
2.32
2.30
2.28
2.00
1.29
1.28
1.26
1.23
1.19
1.18
1H NMR, 400 MHz, CDCl3:
Ag2Br4
Ag +
Ag +
1.00
2.68
2.99
4.16
5.95
5.13
24.21
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


172.6
147.6
145.2
135.8
131.8
131.7
131.3
131.1
130.7
128.7
124.9
124.7
124.2
77.7
77.5
77.3
77.0
39.1
29.1
28.9
28.8
24.7
24.6
24.3
24.0
22.9
13C NMR, 100 MHz, CDCl3:
Ag2Br4
Ag +
Ag +
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

^{1}H NMR, 400 MHz, CD_3CN:

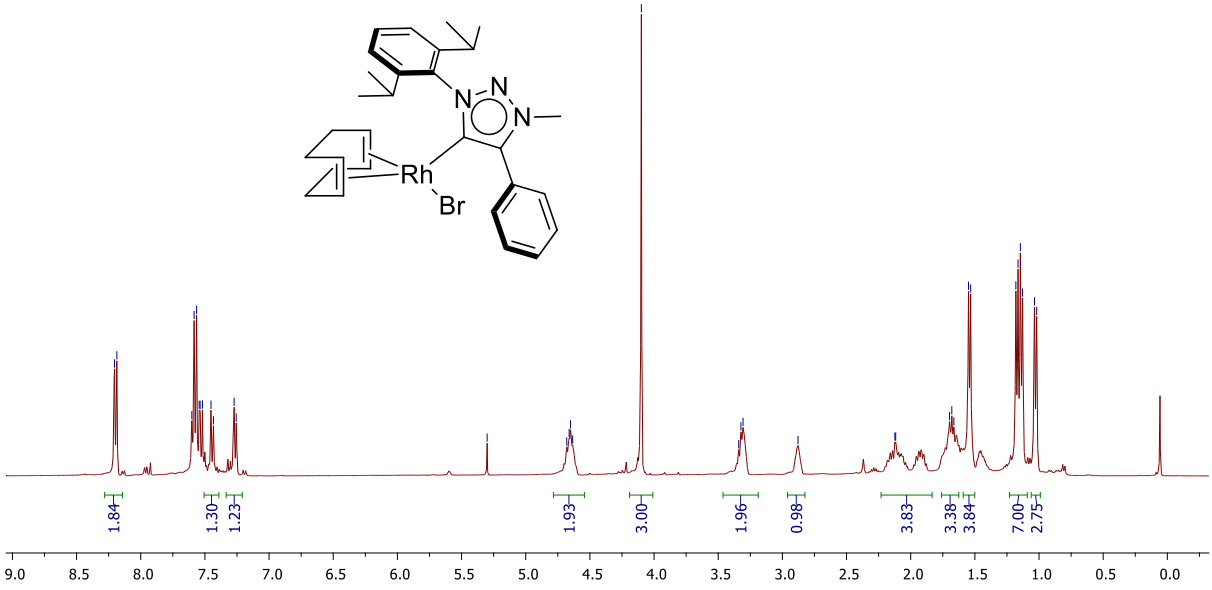


^{13}C NMR, 100 MHz, CD_3CN:



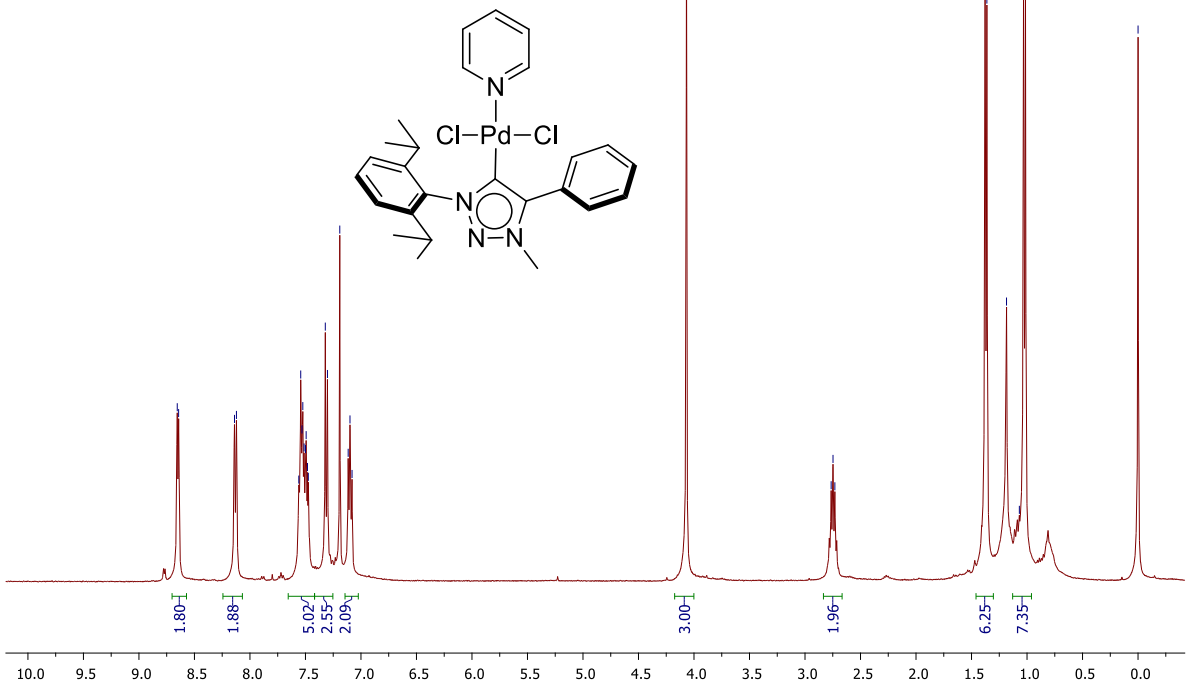
8.20 8.19 7.60 7.58 7.56 7.54 7.54 7.52 7.45 7.43 7.27 7.26 — 5.30 — 4.68 4.66 4.65 4.63 — 4.10 — 3.34 3.32 3.31 — 2.88 — 2.12 2.12 — 1.70 1.68 1.55 1.53 1.18 1.16 1.15 1.13 1.04 1.02

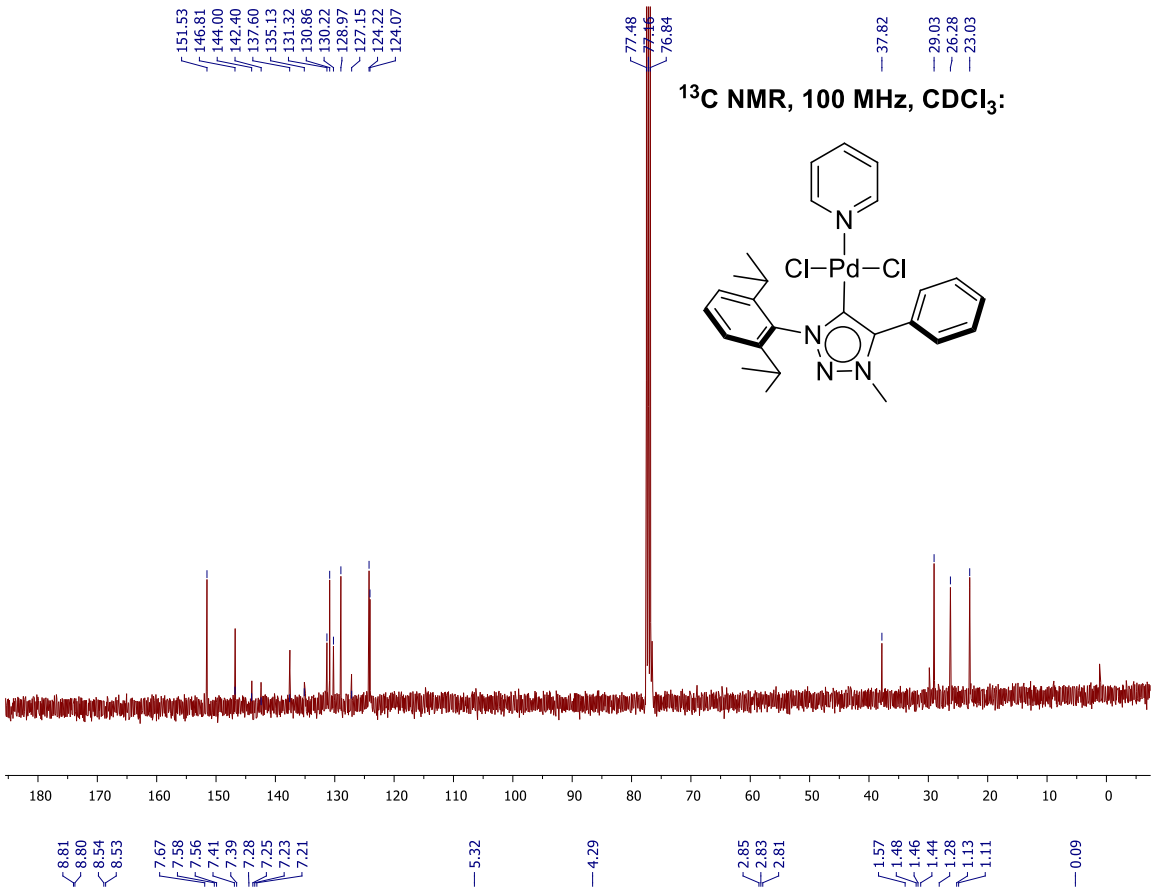
^{1}H NMR, 400 MHz, $CDCl_3$:

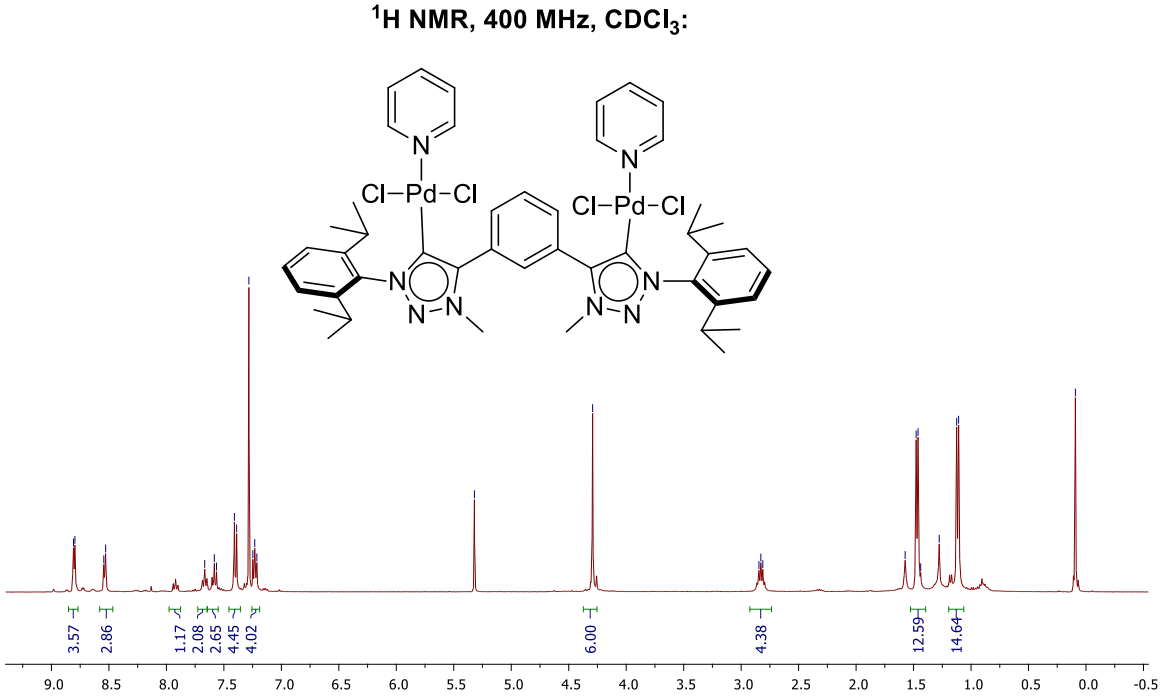


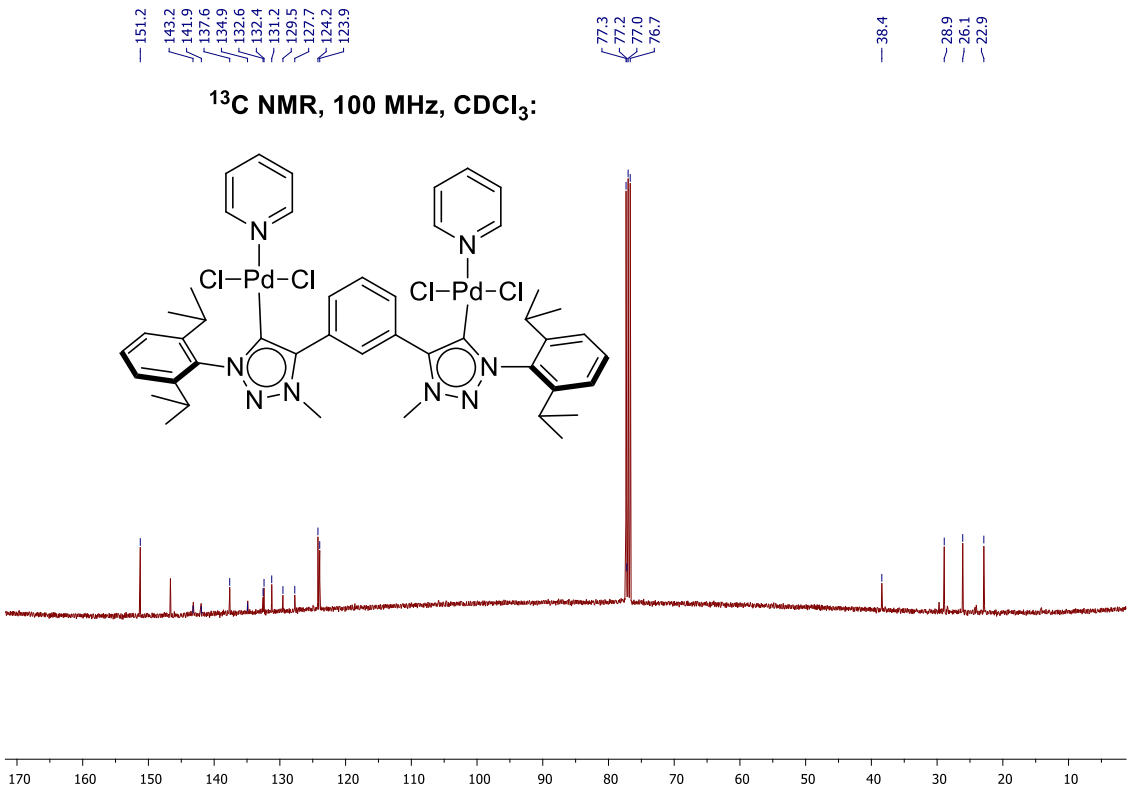
8.65 8.64 — 8.14 8.12 — 7.56 7.54 7.53 7.52 7.51 7.50 7.49 7.48 7.47 7.32 7.30 7.19 7.12 7.10 7.08 — 4.07 — 2.76 2.75 2.73 — 1.38 1.36 1.18 1.07 1.03 1.01 — -0.00

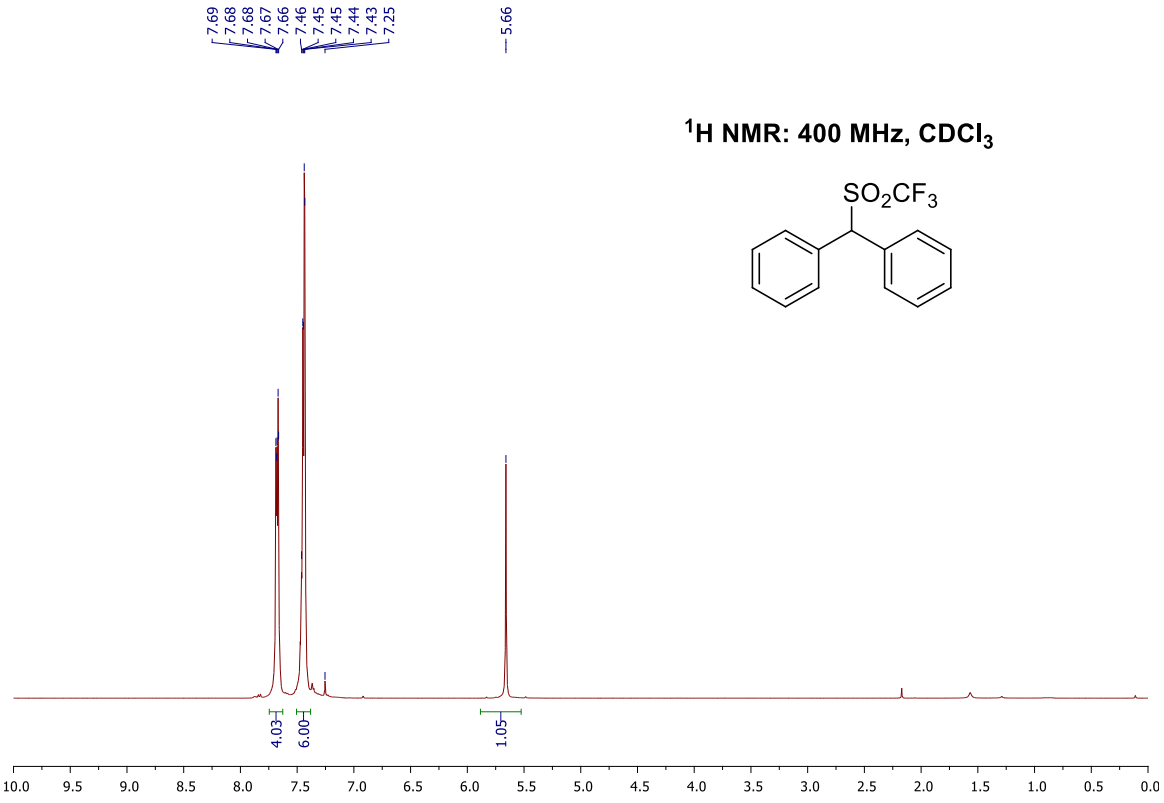
^{1}H NMR, 400 MHz, $CDCl_3$:

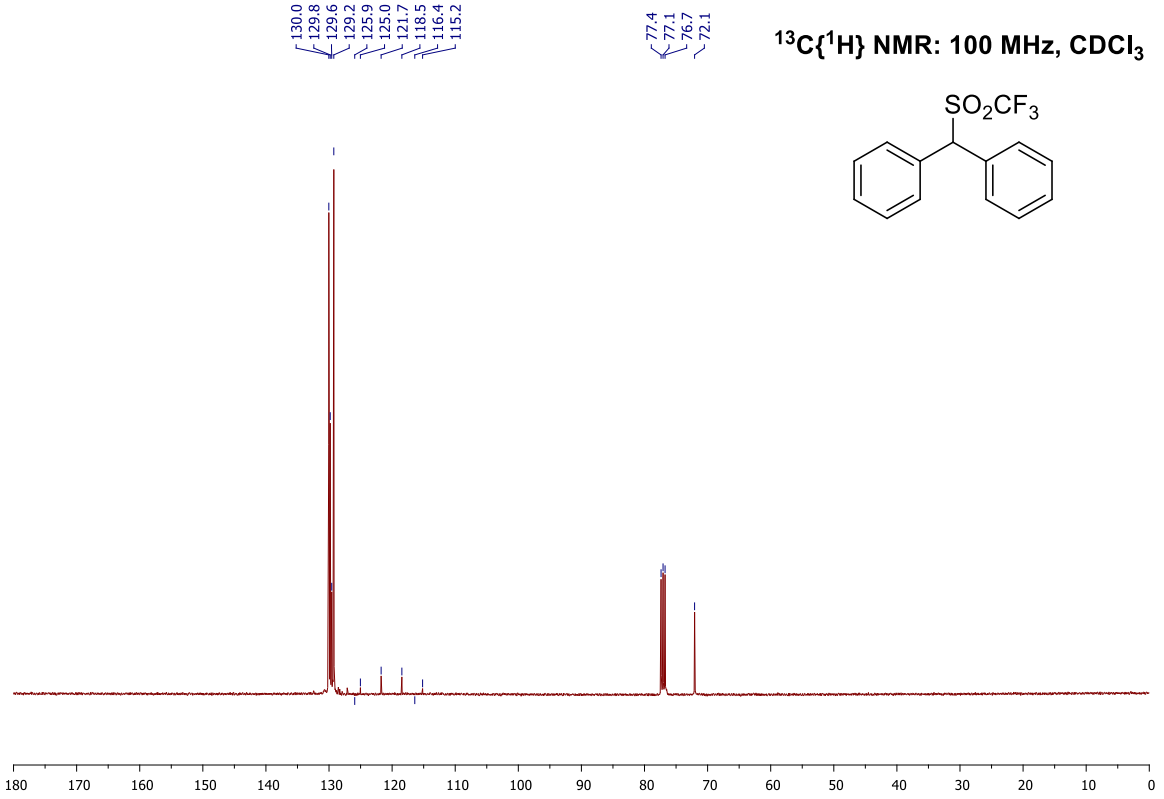


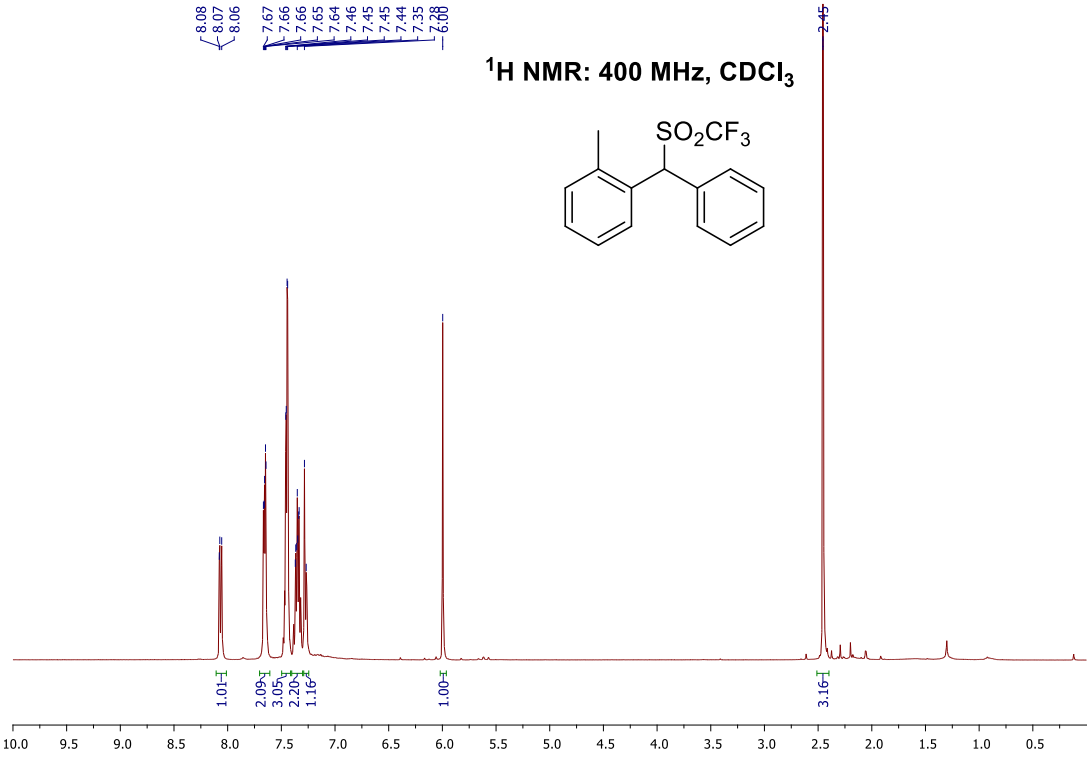

151.53
146.81
144.00
142.40
137.60
135.13
131.32
130.86
130.22
128.97
127.15
124.22
124.07
77.48
77.16
76.84
37.82
29.03
26.28
23.03
13C NMR, 100 MHz, CDCl3:
Cl–Pd–Cl
N
N–N
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
8.81
8.80
8.54
8.53
7.67
7.58
7.56
7.41
7.39
7.28
7.25
7.23
7.21
5.32
4.29
2.85
2.83
2.81
1.57
1.48
1.46
1.44
1.28
1.13
1.11
0.09

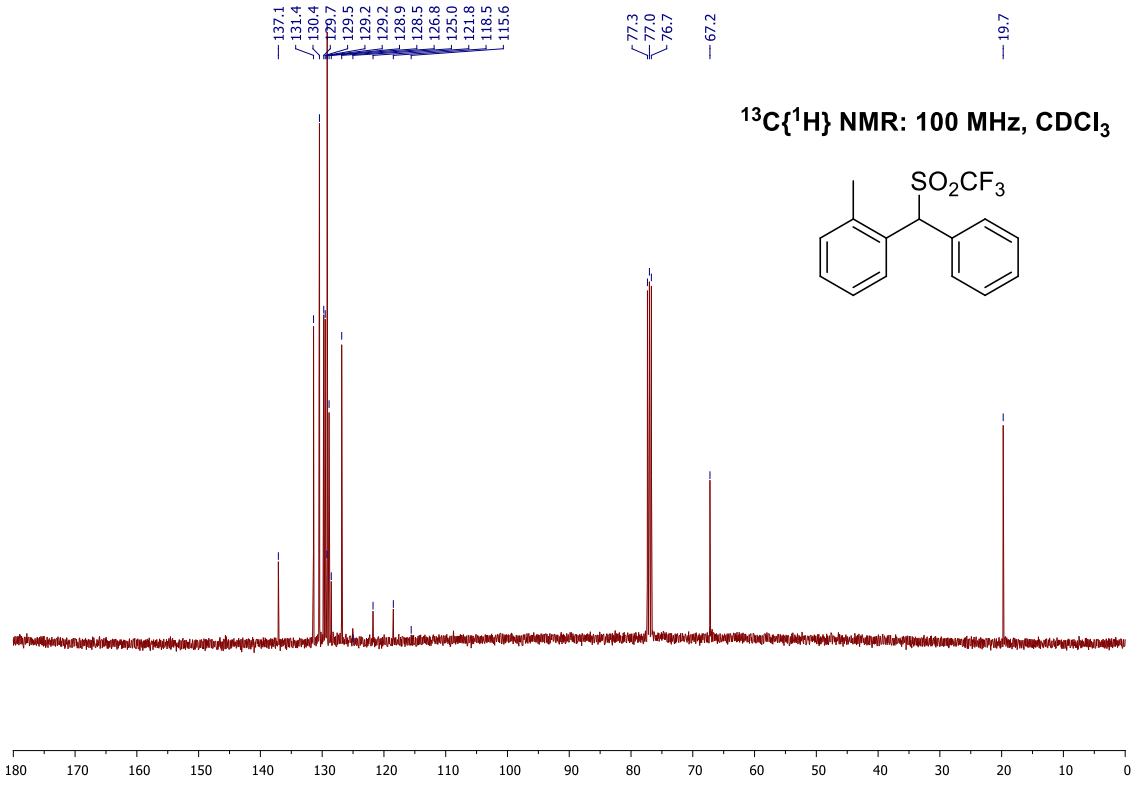

1H NMR, 400 MHz, CDCl3:
Cl–Pd–Cl
Cl–Pd–Cl
N
N–N
3.57
2.86
1.17
2.08
2.65
4.45
4.02
6.00
4.38
12.59
14.64
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

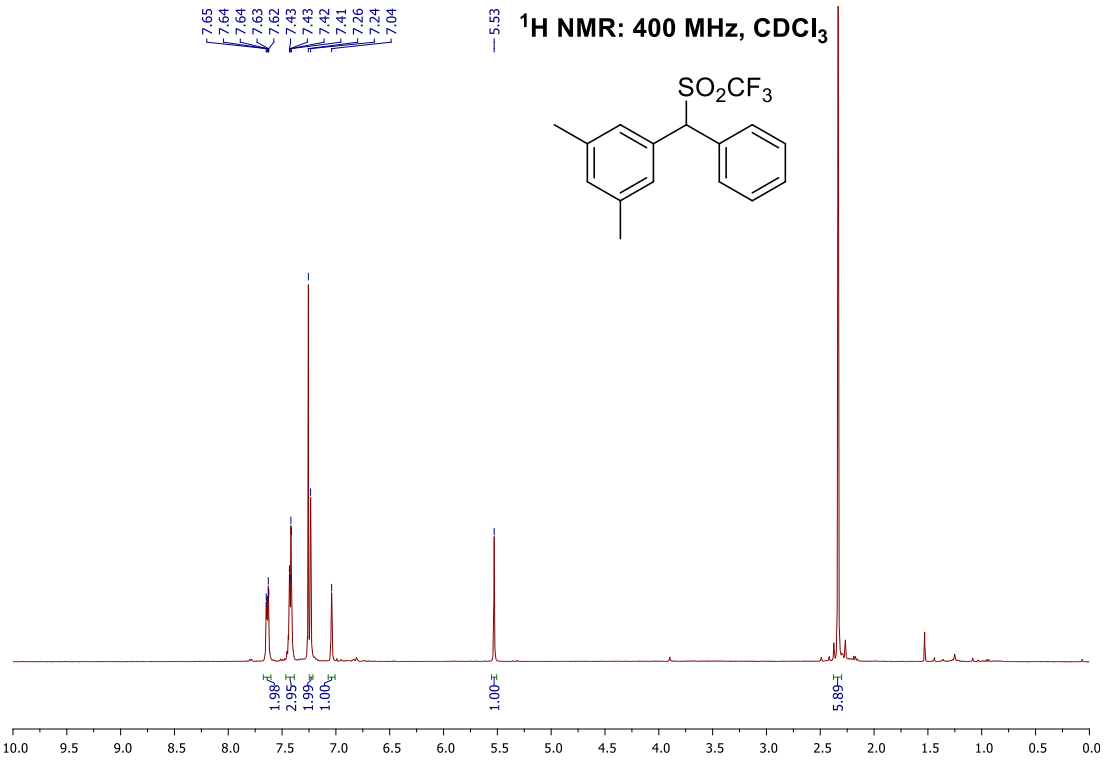

151.2
143.2
141.9
137.6
134.9
132.6
132.4
131.2
129.5
127.7
124.2
123.9
77.3
77.2
77.0
76.7
38.4
28.9
26.1
22.9
13C NMR, 100 MHz, CDCl3:
N
Cl–Pd–Cl
N
N–N
N
Cl–Pd–Cl
N
N–N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

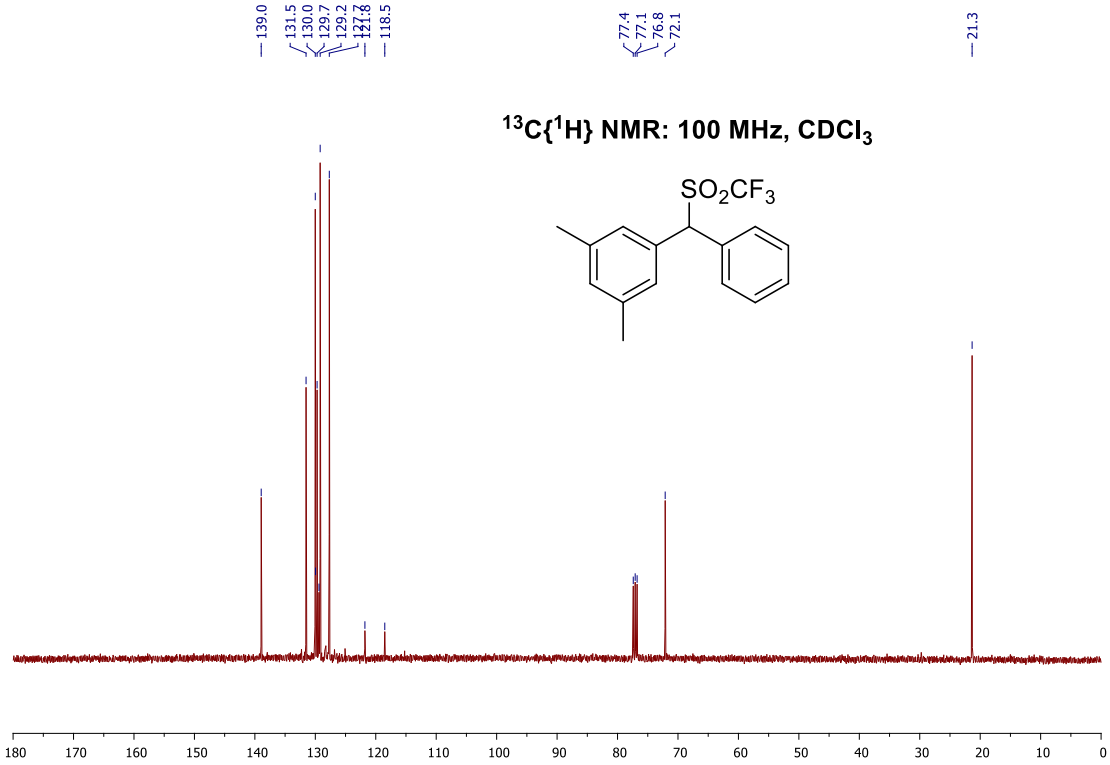

7.69
7.68
7.68
7.67
7.66
7.46
7.45
7.45
7.44
7.43
7.25
5.66
^{1}H NMR: 400 MHz, CDCl$_3$
SO$_2$CF$_3$
4.03
6.00
1.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

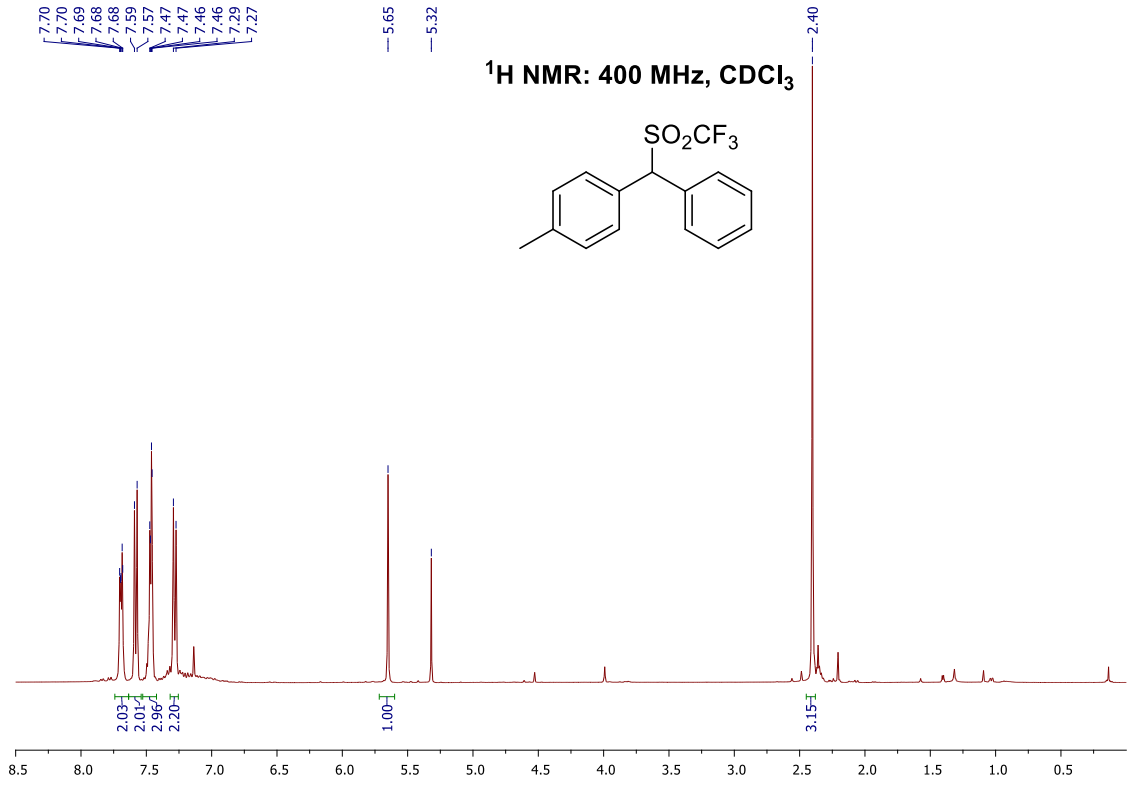

130.0
129.8
129.6
129.2
125.9
125.0
121.7
118.5
116.4
115.2
77.4
77.1
76.7
72.1
^{13}C{^{1}H} NMR: 100 MHz, CDCl$_3$
SO$_2$CF$_3$
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

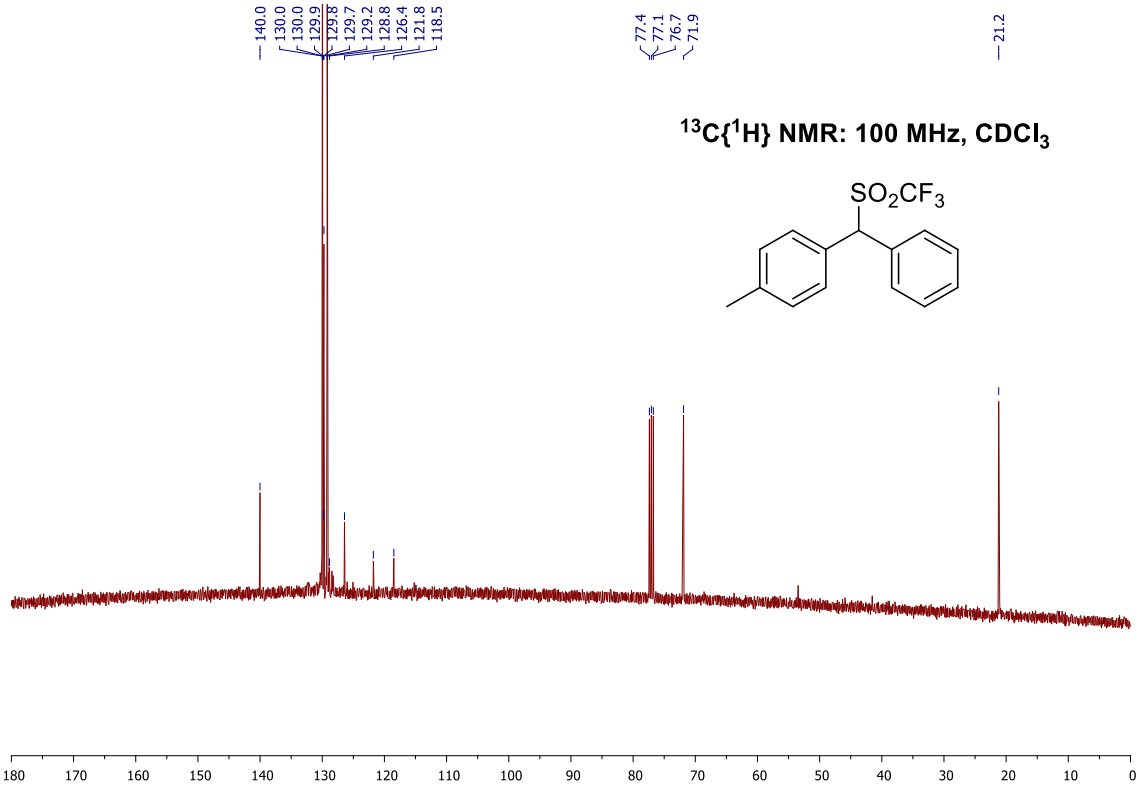

8.08
8.07
8.06
7.67
7.66
7.66
7.65
7.64
7.46
7.45
7.45
7.44
7.35
7.28
6.00
2.45
^{1}H NMR: 400 MHz, CDCl$_3$
SO$_2$CF$_3$
1.01
2.09
3.05
2.20
1.16
1.00
3.16
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

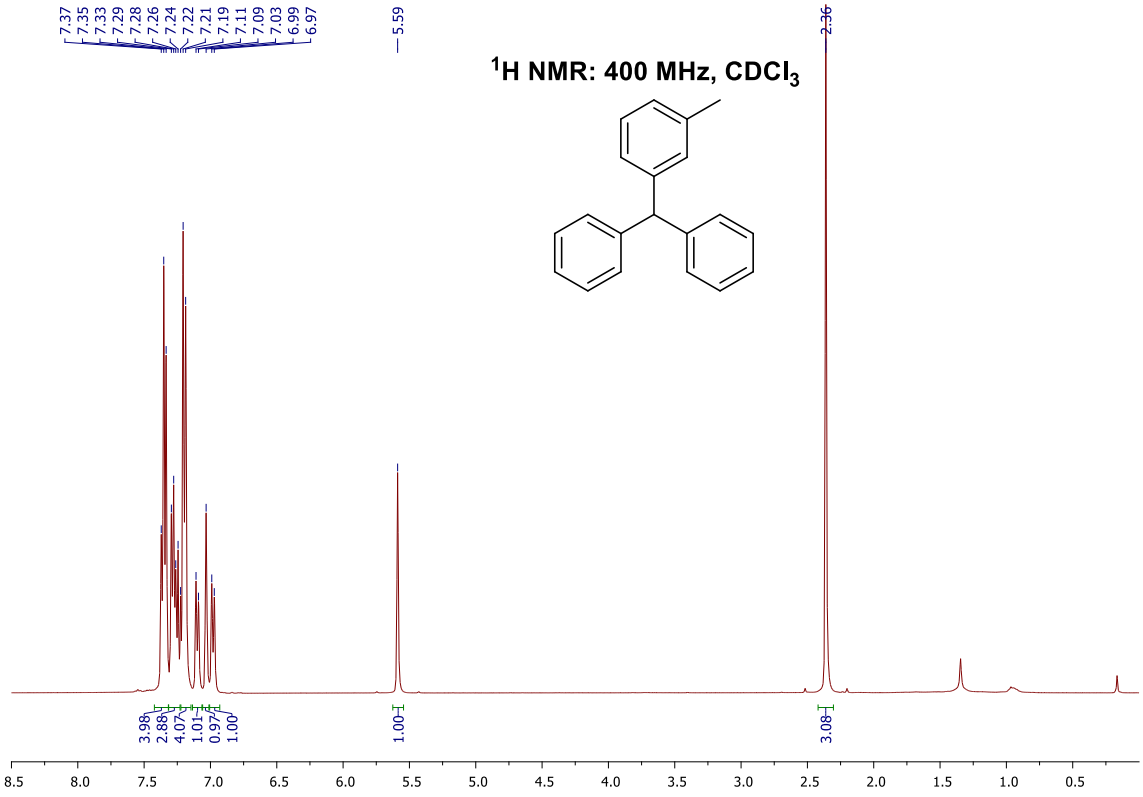

137.1
131.4
130.4
129.7
129.5
129.2
129.2
128.9
128.5
126.8
125.0
121.8
118.5
115.6
77.3
77.0
76.7
67.2
19.7
^{13}C{^{1}H} NMR: 100 MHz, CDCl$_3$
SO$_2$CF$_3$
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

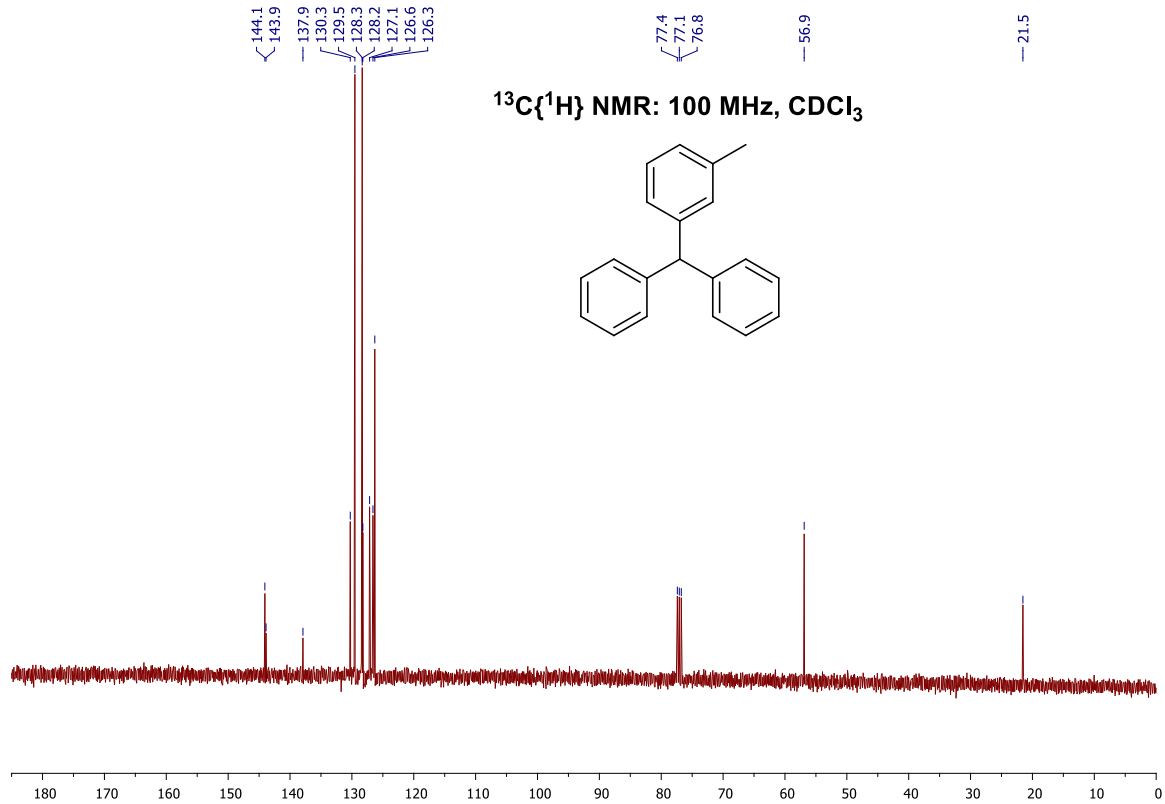

7.65
7.64
7.64
7.63
7.62
7.43
7.43
7.42
7.41
7.26
7.24
7.04
5.53
^{1}H NMR: 400 MHz, $CDCl_3$
SO_2CF_3
1.98
2.95
1.99
1.00
1.00
5.89
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

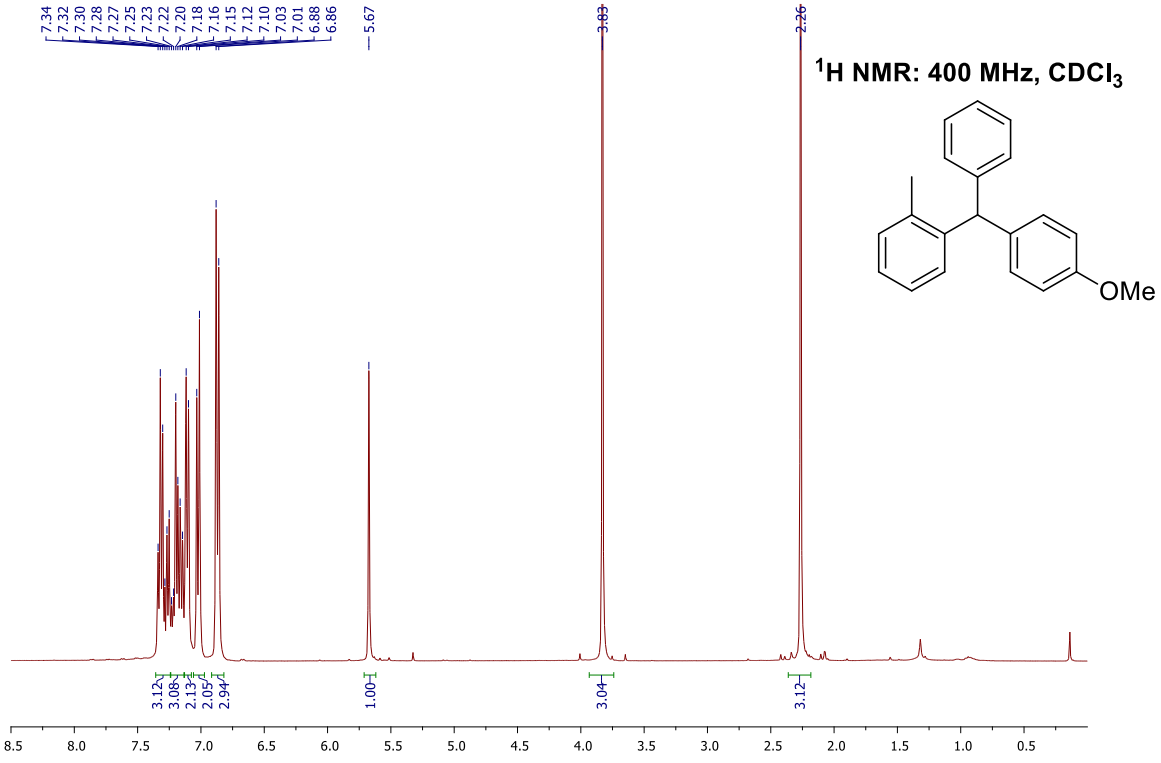

139.0
131.5
130.0
129.7
129.2
127.7
121.8
118.5
77.4
77.1
76.8
72.1
21.3
^{13}C{^{1}H} NMR: 100 MHz, $CDCl_3$
SO_2CF_3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


7.70
7.70
7.69
7.68
7.68
7.59
7.57
7.47
7.47
7.46
7.46
7.29
7.27
5.65
5.32
2.40
^{1}H NMR: 400 MHz, $CDCl_3$
SO_2CF_3
2.03
2.01
2.96
2.20
1.00
3.15
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

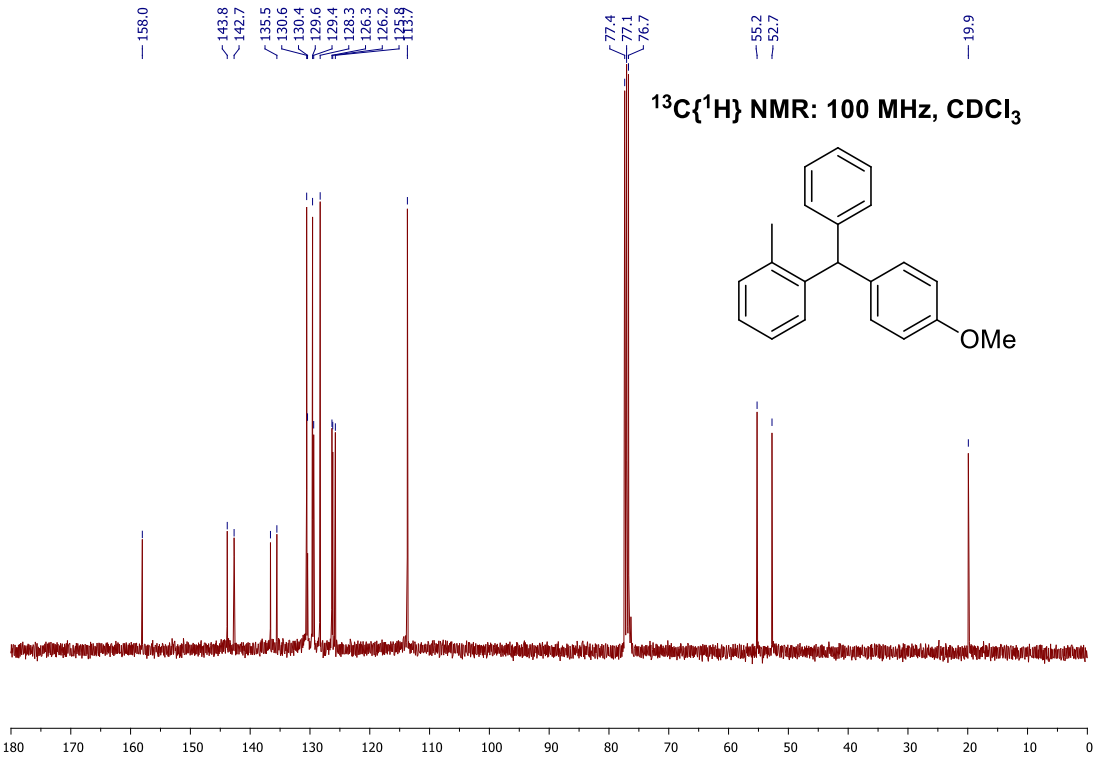

140.0
130.0
130.0
129.9
129.8
129.7
129.2
128.8
126.4
121.8
118.5
77.4
77.1
76.7
71.9
21.2
^{13}C{^{1}H} NMR: 100 MHz, $CDCl_3$
SO_2CF_3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


7.37
7.35
7.33
7.29
7.28
7.26
7.24
7.22
7.21
7.19
7.11
7.09
7.03
6.99
6.97
5.59
2.36
^{1}H NMR: 400 MHz, CDCl$_3$
3.98
2.88
4.07
1.01
0.97
1.00
1.00
3.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


144.1
143.9
137.9
130.3
129.5
128.3
128.2
127.1
126.6
126.3
77.4
77.1
76.8
56.9
21.5
^{13}C{^{1}H} NMR: 100 MHz, CDCl$_3$
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



^{1}H NMR: 400 MHz, $CDCl_3$



^{13}C{^{1}H} NMR: 100 MHz, $CDCl_3$

Appendix B: Crystallographic Data

Table A-1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2-28**.

	x	y	z	U(eq)
Rh(1)	1274(1)	2141(1)	860(1)	31(1)
Cl(1)	1942(1)	2172(2)	914(1)	48(1)
Cl(2)	598(1)	2045(2)	785(1)	48(1)
O(1)	681(3)	2259(7)	1061(4)	42(1)
O(2)	658(2)	1755(7)	514(4)	42(1)
O(3)	1859(2)	1916(6)	657(4)	42(1)
O(4)	1898(2)	2554(7)	1161(3)	42(1)
N(1)	1244(1)	-623(2)	1044(1)	42(1)
N(2)	1530(1)	297(2)	1820(1)	46(1)
N(3)	1248(1)	4028(2)	-91(1)	37(1)
N(4)	1026(1)	4808(2)	628(1)	41(1)
C(1)	1352(1)	479(3)	1273(1)	35(1)
C(2)	1528(2)	-1000(3)	2001(2)	60(1)
C(3)	1376(2)	-1654(3)	1436(2)	64(1)
C(4)	1050(1)	-882(3)	462(1)	35(1)
C(5)	627(1)	-1103(3)	345(1)	40(1)
C(6)	445(1)	-1410(3)	-212(2)	46(1)
C(7)	668(1)	-1523(3)	-642(1)	51(1)
C(8)	1088(1)	-1316(3)	-509(2)	52(1)
C(9)	1290(1)	-993(3)	41(2)	44(1)
C(10)	372(1)	-1047(4)	806(2)	59(1)
C(11)	456(2)	-1866(5)	-1242(2)	87(2)
C(12)	1748(1)	-795(4)	161(2)	67(1)
C(13)	1664(1)	1228(3)	2246(1)	45(1)
C(14)	2083(1)	1443(3)	2420(1)	49(1)
C(15)	2207(1)	2265(4)	2873(2)	58(1)
C(16)	1930(2)	2831(4)	3155(2)	61(1)
C(17)	1517(2)	2596(4)	2968(2)	63(1)

C(18)	1373(1)	1800(4)	2510(1)	53(1)
C(19)	2398(1)	827(4)	2138(2)	70(1)
C(20)	2071(2)	3656(5)	3667(2)	96(2)
C(21)	919(2)	1571(5)	2330(2)	84(2)
C(22)	1189(1)	3800(3)	437(1)	32(1)
C(23)	1093(1)	5253(3)	-305(2)	51(1)
C(24)	1000(2)	5853(3)	231(2)	67(1)
C(25)	1437(1)	3214(3)	-444(1)	36(1)
C(26)	1202(1)	2313(3)	-768(1)	40(1)
C(27)	1402(1)	1540(3)	-1096(1)	47(1)
C(28)	1816(1)	1655(4)	-1108(1)	53(1)
C(29)	2037(1)	2591(4)	-792(1)	52(1)
C(30)	1853(1)	3379(3)	-454(1)	42(1)
C(31)	751(1)	2143(4)	-763(2)	52(1)
C(32)	2038(2)	765(5)	-1437(2)	81(2)
C(33)	2109(1)	4333(4)	-85(2)	55(1)
C(34A)	975(2)	5003(8)	1209(2)	53(1)
C(35A)	1332(2)	5152(8)	1623(2)	53(1)
C(36A)	1303(2)	5322(6)	2195(2)	53(1)
C(37A)	917(2)	5342(6)	2354(2)	53(1)
C(38A)	559(2)	5193(6)	1939(2)	53(1)
C(39A)	588(2)	5023(6)	1367(2)	53(1)
C(40A)	1750(3)	5130(20)	1467(5)	59(2)
C(41A)	876(6)	5520(20)	2980(4)	120(4)
C(42A)	199(4)	4934(15)	915(6)	76(5)
C(34B)	982(4)	5057(14)	1207(3)	53(1)
C(35B)	1300(3)	5180(15)	1672(4)	53(1)
C(36B)	1215(3)	5477(11)	2202(4)	53(1)
C(37B)	811(3)	5651(10)	2266(3)	53(1)
C(38B)	493(3)	5528(10)	1800(4)	53(1)
C(39B)	579(3)	5231(10)	1270(3)	53(1)
C(40B)	1747(5)	5140(40)	1627(9)	59(2)
C(41B)	748(10)	5780(40)	2893(7)	120(4)
C(42B)	215(5)	5020(30)	778(10)	71(8)
C(43)	3(10)	7780(18)	2720(11)	213(4)

C(44)	365(4)	8527(11)	2425(6)	213(4)
C(45)	-40(9)	9850(19)	2762(10)	213(4)
O(5)	399(4)	9330(12)	2881(5)	170(5)

Table A-2: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2-29**.

	x	y	z	U(eq)
Rh(1)	5000	0	9058(1)	19(1)
Cl(1)	5000	0	11228(1)	36(1)
Cl(2)	5000	0	6875(7)	33(3)
O(1)	5525(4)	-65(2)	7316(5)	28(1)
N(1)	4571(2)	1461(1)	9414(3)	26(1)
N(2)	6049(2)	1290(1)	8539(3)	25(1)
C(1)	5219(2)	994(1)	9025(3)	21(1)
C(2)	4950(3)	2118(1)	9158(4)	57(1)
C(3)	6007(3)	1999(2)	8652(4)	40(1)
C(4)	3512(2)	1404(1)	9801(3)	25(1)
C(5)	2751(2)	1342(2)	8869(3)	28(1)
C(6)	1721(2)	1340(2)	9265(4)	35(1)
C(7)	1466(3)	1404(2)	10505(4)	35(1)
C(8)	2227(3)	1478(2)	11411(4)	35(1)
C(9)	3272(2)	1483(2)	11072(3)	29(1)
C(10)	2996(3)	1305(2)	7480(3)	34(1)
C(11)	2715(5)	1944(2)	6829(4)	83(2)
C(12)	2419(3)	751(2)	6838(4)	52(1)
C(13)	4077(3)	1596(2)	12092(3)	40(1)
C(14)	4111(4)	2321(2)	12442(5)	67(1)
C(15)	3884(3)	1184(2)	13262(4)	56(1)
C(16)	7036(2)	1023(2)	8201(3)	26(1)
C(17)	7729(2)	867(2)	9159(3)	28(1)
C(18)	8742(3)	706(2)	8791(4)	37(1)

C(19)	9027(3)	715(2)	7557(4)	39(1)
C(20)	8326(3)	867(2)	6640(4)	37(1)
C(21)	7306(3)	1018(2)	6927(4)	31(1)
C(22)	7450(3)	883(2)	10543(3)	33(1)
C(23)	7964(4)	1465(2)	11192(5)	52(1)
C(24)	7728(3)	249(2)	11192(3)	43(1)
C(25)	6555(3)	1174(2)	5859(4)	39(1)
C(26)	6529(3)	643(2)	4871(4)	56(1)
C(27)	6827(4)	1818(2)	5231(5)	66(1)
C(28)	10263(7)	1370(5)	4092(10)	61(1)
C(29)	10484(8)	688(4)	3591(10)	61(1)
C(30A)	9790(20)	159(7)	4010(30)	61(1)
C(30B)	9890(30)	133(7)	4140(30)	61(1)
C(31)	10066(9)	-503(4)	3474(8)	61(1)
C(32)	9521(7)	-1038(5)	4307(10)	61(1)
C(33)	9923(8)	-1698(5)	3900(8)	61(1)

Table A-3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2-37**.

	x	y	z	U(eq)
Rh(1)	3634(1)	4879(1)	775(1)	21(1)
Cl(1)	6136(1)	5308(1)	1068(1)	31(1)
N(1)	2711(2)	4558(2)	2740(2)	22(1)
N(2)	4469(2)	6512(2)	3249(2)	22(1)
C(1)	3587(2)	5281(2)	2320(2)	20(1)
C(2)	3980(3)	6710(3)	4287(2)	29(1)
C(3)	3134(3)	5263(2)	4000(2)	27(1)
C(4)	1832(3)	3113(2)	2189(2)	21(1)
C(5)	359(3)	2665(2)	2164(2)	23(1)
C(6)	-460(3)	1297(3)	1762(2)	29(1)
C(7)	153(3)	397(3)	1409(2)	35(1)

C(8)	1594(3)	852(3)	1420(2)	32(1)
C(9)	2472(3)	2212(2)	1800(2)	25(1)
C(10)	-380(3)	3606(3)	2547(2)	28(1)
C(11)	-1032(3)	3569(3)	3520(2)	34(1)
C(12)	-1541(3)	3239(3)	1543(2)	37(1)
C(13)	4047(3)	2640(3)	1781(2)	29(1)
C(14)	4902(3)	2555(4)	2683(3)	50(1)
C(15)	4203(3)	1822(3)	597(3)	48(1)
C(16)	5561(3)	7675(2)	3273(2)	22(1)
C(17)	5143(3)	8501(2)	3005(2)	26(1)
C(18)	6239(3)	9665(3)	3113(2)	34(1)
C(19)	7678(3)	9992(3)	3483(2)	38(1)
C(20)	8063(3)	9168(3)	3758(2)	32(1)
C(21)	7020(3)	7996(2)	3665(2)	26(1)
C(22)	3578(3)	8225(3)	2649(2)	30(1)
C(23)	3222(3)	8147(3)	1498(2)	40(1)
C(24)	3208(3)	9277(3)	3561(3)	45(1)
C(25)	7512(3)	7151(3)	4011(2)	33(1)
C(26)	8835(3)	7003(3)	3605(3)	45(1)
C(27)	7881(3)	7768(3)	5314(3)	44(1)
C(28)	1546(3)	4770(3)	429(2)	31(1)
C(29)	1463(3)	3481(3)	-21(2)	31(1)

Table A-4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2-38**.

	x	y	z	U(eq)
Rh(1)	47(1)	1584(1)	10134(1)	24(1)
Rh(2)	2341(1)	1893(1)	9745(1)	25(1)
Cl(1)	641(1)	2190(1)	9464(1)	29(1)
Cl(2)	1869(1)	1538(1)	11145(1)	30(1)
N(1)	32(2)	723(1)	10483(2)	38(1)
N(2)	-1122(2)	1007(1)	11102(2)	35(1)
N(3)	2046(2)	2149(1)	7585(2)	34(1)
N(4)	3463(2)	2425(1)	8621(2)	34(1)
C(1)	-366(2)	1083(1)	10625(2)	29(1)
C(2)	-1148(3)	586(1)	11403(4)	51(1)
C(3)	-523(3)	383(1)	10774(4)	50(1)
C(4)	-1594(3)	1288(1)	11630(3)	34(1)
C(5)	-972(3)	1480(1)	12531(3)	36(1)
C(6)	-1476(3)	1742(1)	13030(3)	45(1)
C(7)	-2554(3)	1809(1)	12677(3)	49(1)
C(8)	-3146(3)	1608(1)	11807(3)	50(1)
C(9)	-2693(3)	1342(1)	11265(3)	39(1)
C(10)	195(3)	1408(1)	12973(3)	47(1)
C(11)	-3076(4)	2100(2)	13229(4)	75(2)
C(12)	-3367(3)	1132(1)	10304(3)	56(1)
C(13)	881(3)	638(1)	10052(3)	40(1)
C(14)	1859(3)	537(1)	10755(4)	49(1)
C(15)	2667(4)	425(1)	10335(4)	62(1)
C(16)	2514(4)	414(1)	9273(5)	67(1)
C(17)	1535(4)	509(1)	8611(4)	59(1)
C(18)	687(3)	621(1)	8981(3)	46(1)
C(19)	2055(4)	543(1)	11903(4)	64(1)
C(20)	3418(5)	303(2)	8854(6)	105(2)
C(21)	-377(4)	707(1)	8229(3)	63(1)
C(22)	2637(3)	2177(1)	8595(2)	29(1)

C(23)	2474(3)	2374(1)	6866(3)	47(1)
C(24)	3400(3)	2593(1)	7585(3)	44(1)
C(25)	1128(3)	1909(1)	7120(2)	35(1)
C(26)	1249(3)	1511(1)	6871(3)	44(1)
C(27)	343(4)	1300(1)	6324(3)	56(1)
C(28)	-645(4)	1472(2)	6026(3)	61(1)
C(29)	-728(3)	1869(2)	6265(3)	54(1)
C(30)	142(3)	2095(1)	6801(3)	42(1)
C(31)	2320(4)	1314(1)	7175(3)	57(1)
C(32)	-1610(5)	1230(2)	5438(4)	91(2)
C(33)	8(3)	2530(1)	7000(3)	48(1)
C(34)	4141(3)	2630(1)	9508(3)	34(1)
C(35)	3742(3)	2951(1)	9935(3)	37(1)
C(36)	4433(3)	3154(1)	10762(3)	49(1)
C(37)	5498(3)	3055(2)	11144(3)	56(1)
C(38)	5869(3)	2744(1)	10678(3)	55(1)
C(39)	5218(3)	2530(1)	9854(3)	44(1)
C(40)	2602(3)	3082(1)	9485(3)	42(1)
C(41)	6238(4)	3285(2)	12044(4)	86(2)
C(42)	5640(3)	2197(1)	9350(4)	55(1)
C(43)	-1361(3)	1584(1)	8894(3)	42(1)
C(44)	-1465(3)	1843(1)	9671(3)	38(1)
C(45)	3587(3)	1497(1)	9830(3)	39(1)
C(46)	3909(3)	1778(1)	10631(3)	37(1)

Table A-5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2-42**.

	x	y	z	U(eq)
Rh(1)	8833(1)	8436(1)	2179(1)	31(1)
Rh(2)	6156(1)	9325(1)	2553(1)	34(1)
Cl(1)	7155(1)	8138(1)	2820(1)	58(1)
Cl(2)	7870(1)	9657(1)	1954(1)	40(1)
N(1)	10280(2)	7477(1)	2888(1)	34(1)
N(2)	9470(2)	6732(1)	2221(1)	36(1)
C(1)	9536(2)	7476(1)	2410(1)	32(1)
C(2)	10679(2)	6743(2)	2995(1)	39(1)
C(3)	10180(2)	6279(2)	2582(1)	40(1)
C(4)	10553(2)	8211(2)	3198(1)	42(1)
C(5)	9763(3)	8815(2)	2899(2)	58(1)
C(6)	10358(3)	8126(2)	3883(2)	66(1)
C(7)	11761(3)	8397(2)	3092(2)	66(1)
C(8)	8750(2)	6415(2)	1716(1)	47(1)
C(9)	8004(3)	5805(2)	1990(2)	79(1)
C(10)	9496(4)	6064(3)	1236(2)	96(2)
C(11)	8028(3)	7035(2)	1434(2)	74(1)
C(12)	10047(3)	8618(2)	1552(2)	56(1)
C(13)	10322(3)	9418(2)	1391(2)	75(1)
C(14A)	5413(4)	10273(2)	2318(2)	35(1)
N(3A)	4725(4)	10261(2)	1809(2)	40(1)
C(15A)	4279(4)	10982(2)	1739(2)	53(1)
C(16A)	4691(4)	11440(2)	2204(2)	53(1)
N(4A)	5392(3)	11002(3)	2562(2)	40(1)
C(17A)	4506(4)	9568(3)	1456(3)	54(1)
C(18A)	5330(4)	8976(3)	1736(2)	63(1)
C(19A)	4699(5)	9749(4)	776(3)	83(1)
C(20A)	3288(6)	9345(5)	1540(3)	83(1)
C(21A)	6044(4)	11285(3)	3099(2)	54(1)
C(22A)	6692(5)	12000(4)	2905(3)	83(1)

C(23A)	5241(6)	11485(4)	3595(3)	83(1)
C(24A)	6898(5)	10684(3)	3327(2)	73(1)
C(14B)	5405(13)	10278(7)	2299(8)	35(1)
N(3B)	5586(10)	10960(9)	2604(6)	40(1)
C(15B)	4926(13)	11510(6)	2336(7)	53(1)
C(16B)	4337(12)	11169(7)	1864(7)	53(1)
N(4B)	4633(13)	10408(6)	1842(6)	40(1)
C(17B)	6188(14)	11055(9)	3178(7)	54(1)
C(18B)	6620(12)	10192(8)	3243(7)	63(1)
C(19B)	6946(16)	11749(11)	3124(9)	83(1)
C(20B)	5371(18)	11230(13)	3709(9)	83(1)
C(21B)	4324(15)	9762(9)	1437(8)	54(1)
C(22B)	4217(16)	10010(13)	748(7)	83(1)
C(23B)	3208(19)	9474(17)	1663(11)	83(1)
C(24B)	5039(15)	9037(9)	1380(8)	73(1)
C(25)	4814(3)	9008(2)	3047(2)	69(1)
C(26)	5022(4)	8688(4)	3636(2)	112(2)

Table A-6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2-45**.

	x	y	z	U(eq)
Rh(1)	6879(1)	6556(1)	-16(1)	28(1)
Rh(2)	589(1)	6778(1)	5002(1)	24(1)
P(1)	7874(1)	6250(1)	739(1)	28(1)
P(2)	-427(1)	6483(1)	5748(1)	26(1)
N(1)	5379(2)	6740(2)	-972(3)	43(1)
N(2)	5829(3)	7524(2)	-460(3)	38(1)
N(3)	2099(2)	6886(2)	4055(2)	29(1)
N(4)	1690(2)	7696(2)	4512(3)	30(1)
Cl(1)	7872(1)	7067(1)	-674(1)	40(1)

Cl(2)	-358(1)	7308(1)	4309(1)	32(1)
C(1)	5973(3)	6959(2)	-570(3)	34(1)
C(2)	5049(4)	7711(3)	-747(4)	57(2)
C(3)	4834(4)	7199(3)	-1229(4)	59(2)
C(4)	6295(3)	7929(2)	-65(4)	35(1)
C(5)	6239(3)	7963(2)	680(4)	36(1)
C(6)	6679(4)	8378(3)	1054(4)	44(2)
C(7)	7144(3)	8777(2)	669(4)	46(2)
C(8)	7174(3)	8733(2)	-75(5)	47(2)
C(9)	6766(4)	8315(2)	-460(4)	44(2)
C(10)	5715(4)	7559(2)	1116(4)	49(2)
C(11)	7593(4)	9242(3)	1094(4)	67(2)
C(12)	6835(4)	8283(3)	-1262(4)	58(2)
C(13)	5392(3)	6203(3)	-1360(3)	38(1)
C(14)	4831(3)	5780(3)	-1205(4)	47(2)
C(15)	4849(4)	5266(3)	-1596(4)	50(2)
C(16)	5397(4)	5164(3)	-2119(4)	46(2)
C(17)	5939(3)	5594(2)	-2282(3)	43(2)
C(18)	5949(3)	6115(3)	-1901(3)	38(1)
C(19)	4215(4)	5871(3)	-630(5)	79(3)
C(20)	5425(4)	4593(3)	-2531(4)	64(2)
C(21)	6547(3)	6575(3)	-2084(4)	47(2)
C(22)	8289(3)	6809(2)	1335(3)	33(1)
C(23)	8248(3)	7387(2)	1126(4)	41(2)
C(24)	8574(4)	7814(3)	1562(4)	58(2)
C(25)	8928(4)	7671(3)	2206(4)	58(2)
C(26)	8959(3)	7102(3)	2428(4)	50(2)
C(27)	8649(3)	6674(3)	1990(3)	40(2)
C(28)	7621(3)	5678(2)	1389(3)	34(1)
C(29)	7182(3)	5819(3)	2006(3)	40(1)
C(30)	6930(4)	5396(3)	2476(4)	49(2)
C(31)	7108(4)	4822(3)	2342(4)	57(2)
C(32)	7533(4)	4672(3)	1741(4)	56(2)
C(33)	7793(3)	5098(2)	1271(4)	41(2)
C(34)	8728(3)	5961(2)	274(3)	30(1)

C(35)	9504(3)	6069(2)	494(3)	34(1)
C(36)	10129(3)	5827(2)	121(4)	41(2)
C(37)	9995(4)	5484(2)	-467(4)	44(2)
C(38)	9252(4)	5372(3)	-695(4)	50(2)
C(39)	8620(4)	5621(3)	-331(4)	47(2)
C(40)	5975(3)	6155(2)	601(4)	43(2)
C(41)	6299(3)	5759(2)	104(5)	51(2)
C(42)	1511(3)	7131(2)	4440(3)	28(1)
C(43)	2655(3)	7324(2)	3767(4)	44(2)
C(44)	2476(3)	7844(2)	4228(4)	47(2)
C(45)	2079(3)	6333(2)	3710(3)	30(1)
C(46)	2642(3)	5916(2)	3892(3)	36(1)
C(47)	2609(4)	5377(3)	3546(4)	40(2)
C(48)	2046(4)	5250(3)	3039(4)	44(2)
C(49)	1513(3)	5677(2)	2860(3)	39(1)
C(50)	1514(3)	6219(2)	3177(3)	33(1)
C(51)	3253(3)	6027(3)	4460(4)	56(2)
C(52)	1990(4)	4658(3)	2691(4)	62(2)
C(53)	913(3)	6663(3)	2966(3)	45(2)
C(54)	1220(3)	8131(2)	4863(4)	33(2)
C(55)	1216(3)	8180(2)	5606(4)	39(2)
C(56)	765(4)	8619(3)	5911(4)	51(2)
C(57)	340(4)	9011(3)	5503(4)	48(2)
C(58)	376(4)	8956(3)	4756(4)	49(2)
C(59)	804(3)	8511(2)	4422(4)	38(2)
C(60)	1697(4)	7789(3)	6087(4)	51(2)
C(61)	-133(4)	9494(3)	5843(5)	74(3)
C(62)	791(4)	8443(3)	3611(4)	56(2)
C(63)	-908(3)	7049(2)	6285(3)	31(1)
C(64)	-876(3)	7617(2)	6050(3)	42(2)
C(65)	-1226(4)	8059(3)	6454(4)	55(2)
C(66)	-1606(4)	7934(3)	7093(4)	50(2)
C(67)	-1643(3)	7375(3)	7334(3)	42(2)
C(68)	-1299(3)	6932(2)	6939(3)	36(1)
C(69)	-164(3)	5957(2)	6447(3)	30(1)

C(70)	197(3)	6133(3)	7087(3)	41(2)
C(71)	466(4)	5729(3)	7592(4)	52(2)
C(72)	393(4)	5152(3)	7459(4)	51(2)
C(73)	59(4)	4965(3)	6818(4)	45(2)
C(74)	-221(3)	5369(2)	6326(3)	34(1)
C(75)	-1222(3)	6111(2)	5270(3)	29(1)
C(76)	-1951(3)	5986(2)	5582(3)	38(1)
C(77)	-2524(3)	5691(2)	5209(4)	43(2)
C(78)	-2385(4)	5507(3)	4510(4)	47(2)
C(79)	-1669(3)	5629(2)	4186(4)	43(2)
C(80)	-1096(4)	5926(2)	4569(4)	38(2)
C(81)	1157(3)	5986(2)	5179(3)	41(2)
C(82)	1474(3)	6394(2)	5671(3)	38(2)

Table A-7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2-51**.

	x	y	z	U(eq)
Rh(1)	6300(1)	4251(1)	9028(1)	21(1)
Cl(1)	8475(1)	3992(1)	9260(1)	34(1)
N(1)	6893(2)	4208(1)	8147(1)	28(1)
N(2)	7318(2)	5792(1)	8441(1)	24(1)
N(4)	5881(2)	3801(1)	9596(1)	23(1)
N(3)	4392(2)	4254(1)	8914(1)	26(1)
C(1)	6768(2)	4773(2)	8501(1)	22(1)
C(2)	7523(2)	4850(2)	7890(1)	34(1)
C(3)	7780(2)	5835(2)	8070(1)	31(1)
C(4)	6354(2)	3128(2)	8024(1)	34(1)
C(5)	5242(2)	3102(2)	7740(1)	42(1)
C(6)	4740(3)	2054(2)	7619(1)	55(1)
C(7)	5324(3)	1091(2)	7772(1)	63(1)
C(8)	6432(3)	1135(2)	8042(1)	58(1)
C(9)	7001(3)	2159(2)	8170(1)	43(1)

C(10)	4625(3)	4143(2)	7540(1)	52(1)
C(11)	3164(3)	4128(3)	7490(1)	83(1)
C(12)	5024(4)	4301(3)	7119(1)	77(1)
C(13)	8295(3)	2223(2)	8426(1)	51(1)
C(14)	8591(4)	1241(3)	8718(1)	79(1)
C(15)	9326(3)	2330(3)	8148(1)	60(1)
C(16)	7260(2)	6788(2)	8685(1)	23(1)
C(17)	8344(2)	7145(2)	8944(1)	29(1)
C(18)	8256(2)	8146(2)	9151(1)	36(1)
C(19)	7149(2)	8766(2)	9102(1)	40(1)
C(20)	6101(2)	8410(2)	8836(1)	34(1)
C(21)	6136(2)	7418(2)	8621(1)	27(1)
C(22)	9593(2)	6513(2)	8991(1)	32(1)
C(23)	10514(2)	7066(3)	8737(1)	53(1)
C(24)	10211(2)	6419(2)	9434(1)	42(1)
C(25)	5011(2)	7078(2)	8311(1)	31(1)
C(26)	5032(3)	7730(3)	7915(1)	61(1)
C(27)	3736(2)	7232(2)	8462(1)	44(1)
C(28)	3619(2)	4406(2)	8564(1)	36(1)
C(29)	2295(2)	4338(2)	8526(1)	44(1)
C(30)	1708(2)	4101(2)	8857(1)	42(1)
C(31)	2470(2)	3920(2)	9232(1)	33(1)
C(32)	1969(2)	3669(2)	9600(1)	40(1)
C(33)	2740(2)	3492(2)	9953(1)	40(1)
C(34)	4094(2)	3519(2)	9972(1)	31(1)
C(35)	4949(2)	3306(2)	10325(1)	37(1)
C(36)	6227(2)	3331(2)	10305(1)	37(1)
C(37)	6664(2)	3582(2)	9937(1)	30(1)
C(38)	4606(2)	3767(2)	9614(1)	25(1)
C(39)	3799(2)	3991(2)	9246(1)	26(1)
C(40A)	4437(16)	1427(12)	8855(6)	97(9)
C(41A)	3355(18)	1001(11)	8644(4)	88(6)
C(42A)	2726(13)	164(11)	8806(4)	62(3)
C(43A)	3180(16)	-247(12)	9179(5)	62(5)
C(44A)	4263(17)	179(16)	9391(4)	87(6)

C(45A)	4892(12)	1016(16)	9229(6)	95(8)
C(40B)	4773(15)	1426(12)	9011(4)	71(5)
C(41B)	3763(18)	1278(13)	8717(3)	99(8)
C(42B)	2851(13)	519(16)	8769(6)	101(8)
C(43B)	2951(17)	-92(14)	9116(7)	85(7)
C(44B)	3960(20)	56(14)	9410(5)	72(4)
C(45B)	4873(14)	815(16)	9358(4)	67(4)
C(46)	884(3)	581(3)	9823(1)	66(1)
C(47)	-311(3)	1016(3)	9818(1)	62(1)
C(48)	-1189(3)	433(3)	9995(1)	62(1)

Table A-8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2-63**.

	x	y	z	U(eq)
Rh(1)	5000	0	9057(1)	18(1)
Cl(1)	5000	0	6907(1)	30(1)
Cl(2)	5000	0	11190(2)	30(1)
N(1)	4596(1)	1456(1)	9441(2)	25(1)
N(2)	6056(1)	1296(1)	8522(2)	25(1)
N(3)	5000	0	10832(6)	30(1)
N(4)	5000	0	11874(7)	46(1)
N(5)	5000	0	7253(12)	30(1)
N(6)	5000	0	6204(17)	46(1)
C(1)	5236(1)	988(1)	9016(2)	20(1)
C(2)	4955(2)	2116(1)	9129(3)	58(1)
C(3)	6017(2)	2004(1)	8684(3)	41(1)
C(4)	3540(1)	1395(1)	9828(2)	24(1)
C(5)	2778(2)	1326(1)	8907(2)	27(1)
C(6)	1758(2)	1324(1)	9296(2)	34(1)
C(7)	1502(2)	1396(1)	10546(2)	36(1)
C(8)	2268(2)	1473(1)	11437(2)	33(1)
C(9)	3299(1)	1475(1)	11104(2)	27(1)

C(10)	3021(2)	1282(1)	7515(2)	34(1)
C(11)	2687(3)	1909(1)	6837(3)	74(1)
C(12)	2491(2)	711(1)	6900(2)	48(1)
C(13)	4108(2)	1593(1)	12111(2)	40(1)
C(14)	4179(3)	2322(2)	12428(3)	72(1)
C(15)	3888(2)	1202(2)	13309(2)	58(1)
C(16)	7056(1)	1037(1)	8205(2)	24(1)
C(17)	7728(1)	870(1)	9170(2)	27(1)
C(18)	8736(2)	704(1)	8847(2)	34(1)
C(19)	9058(2)	720(1)	7613(2)	38(1)
C(20)	8373(2)	893(1)	6672(2)	34(1)
C(21)	7361(2)	1047(1)	6939(2)	28(1)
C(22)	7427(2)	887(1)	10551(2)	30(1)
C(23)	7969(2)	1451(1)	11229(3)	48(1)
C(24)	7653(2)	243(1)	11193(2)	42(1)
C(25)	6643(2)	1231(1)	5859(2)	36(1)
C(26)	6682(2)	742(1)	4782(2)	47(1)
C(27)	6918(2)	1908(1)	5348(3)	59(1)

Table A-9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2-64**.

	x	y	z	U(eq)
Rh(1)	5000	10000	967(1)	20(1)
Cl(1)	5000	10000	3068(3)	31(2)
Cl(2)	5000	10000	-1161(2)	34(1)
O(1)	5000	10000	-1830(20)	57(2)
C(1A)	5000	10000	-739(12)	47(5)
O(2)	5000	10000	3750(20)	57(2)
C(2A)	5000	10000	2632(11)	47(5)
N(1)	5402(2)	8546(1)	561(2)	28(1)
N(2)	3940(2)	8701(1)	1479(2)	28(1)

C(1)	4764(2)	9013(1)	993(2)	23(1)
C(2)	5046(3)	7883(1)	855(3)	60(1)
C(3)	3975(2)	7995(1)	1305(4)	47(1)
C(4)	6457(2)	8609(1)	177(2)	26(1)
C(5)	7219(2)	8676(1)	1097(3)	31(1)
C(6)	8242(2)	8677(1)	724(3)	38(1)
C(7)	8497(2)	8605(1)	-528(3)	39(1)
C(8)	7736(2)	8532(1)	-1425(3)	34(1)
C(9)	6700(2)	8527(1)	-1094(2)	29(1)
C(10)	6976(3)	8716(1)	2497(3)	38(1)
C(11)	7312(4)	8092(2)	3173(3)	76(1)
C(12)	7495(3)	9293(2)	3117(3)	52(1)
C(13)	5893(2)	8414(2)	-2101(3)	43(1)
C(14)	5843(4)	7684(2)	-2433(4)	76(1)
C(15)	6113(3)	8811(2)	-3295(3)	63(1)
C(16)	2946(2)	8961(1)	1801(3)	26(1)
C(17)	2265(2)	9128(1)	838(2)	30(1)
C(18)	1255(2)	9294(1)	1168(3)	38(1)
C(19)	941(2)	9278(2)	2400(3)	40(1)
C(20)	1630(2)	9110(1)	3335(3)	37(1)
C(21)	2639(2)	8952(1)	3067(3)	31(1)
C(22)	2566(2)	9110(1)	-539(3)	33(1)
C(23)	2025(3)	8545(2)	-1214(3)	53(1)
C(24)	2332(3)	9756(2)	-1187(3)	46(1)
C(25)	3359(2)	8768(1)	4136(3)	40(1)
C(26)	3307(3)	9252(2)	5234(3)	55(1)
C(27)	3094(3)	8092(2)	4650(4)	67(1)
C(30)	10163(8)	9847(3)	5891(6)	80(3)
C(29)	9523(8)	9314(4)	6393(11)	94(3)
C(28)	9627(6)	8648(5)	5791(7)	60(2)
C(31)	9960(7)	10473(3)	6587(5)	52(1)
C(32)	10512(7)	10968(5)	5715(9)	78(3)
C(33)	10101(8)	11634(4)	6083(8)	79(2)

Table A-10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3-9**.

	x	y	z	U(eq)
Rh(1)	1937(1)	1696(1)	7074(1)	26(1)
Cl(1)	2604(1)	1692(1)	8556(1)	41(1)
N(1)	4326(2)	1752(2)	6388(2)	27(1)
N(2)	3306(2)	3177(2)	5372(2)	28(1)
N(3)	508(2)	1040(2)	7840(2)	32(1)
N(4)	751(2)	-675(2)	6489(2)	36(1)
C(1)	3268(2)	2244(2)	6265(2)	25(1)
C(2)	4983(2)	2339(2)	5579(2)	31(1)
C(3)	4353(2)	3233(3)	4952(2)	32(1)
C(4)	4822(2)	898(2)	7314(2)	29(1)
C(5)	4804(2)	-235(3)	7571(2)	34(1)
C(6)	5368(3)	-1005(3)	8432(3)	46(1)
C(7)	5912(3)	-650(3)	8983(3)	51(1)
C(8)	5906(3)	473(3)	8711(3)	44(1)
C(9)	5368(2)	1276(3)	7870(2)	34(1)
C(10)	4199(2)	-642(3)	6992(3)	39(1)
C(11)	3384(3)	-1392(4)	7685(4)	67(1)
C(12)	4953(4)	-1247(5)	6441(4)	78(2)
C(13)	5402(3)	2513(3)	7589(2)	37(1)
C(14)	6520(3)	2837(3)	7142(3)	48(1)
C(15)	5093(3)	2824(3)	8486(3)	52(1)
C(16)	2433(2)	4095(2)	4945(2)	30(1)
C(17)	2045(2)	4763(2)	5470(2)	34(1)
C(18)	1239(3)	5669(3)	5016(3)	41(1)
C(19)	874(3)	5913(3)	4078(3)	46(1)
C(20)	1287(3)	5266(3)	3566(3)	43(1)
C(21)	2075(2)	4328(3)	3993(2)	36(1)
C(22)	2526(3)	4599(3)	6439(2)	37(1)
C(23)	1708(3)	4930(3)	7153(3)	54(1)

C(24)	3486(3)	5256(3)	6182(3)	53(1)
C(25)	2507(3)	3657(3)	3382(3)	43(1)
C(26)	3165(4)	4342(3)	2439(3)	61(1)
C(27)	1586(4)	3237(3)	3091(3)	66(1)
C(28)	-157(2)	1352(3)	8516(2)	33(1)
C(29)	-63(3)	2348(3)	8595(2)	39(1)
C(30)	-761(3)	2690(3)	9225(3)	46(1)
C(31)	-1553(3)	2036(3)	9832(3)	48(1)
C(32)	-1646(3)	1066(3)	9787(2)	42(1)
C(33)	-961(2)	700(3)	9112(2)	36(1)
C(34)	-1059(2)	-268(3)	8996(2)	40(1)
C(35)	-442(2)	-552(3)	8283(2)	39(1)
C(36)	319(2)	171(3)	7676(2)	33(1)
C(37)	937(2)	82(2)	6788(2)	32(1)
C(38)	1243(2)	-662(3)	5609(2)	37(1)
C(39)	1038(3)	-1454(3)	5261(3)	45(1)
C(40)	1480(3)	-1429(3)	4357(3)	48(1)
C(41)	2146(3)	-642(3)	3764(3)	42(1)
C(42)	2374(2)	130(3)	4076(3)	38(1)
C(43)	1926(2)	134(2)	5011(2)	33(1)
C(44)	2134(2)	905(2)	5379(2)	32(1)
C(45)	1668(2)	895(2)	6272(2)	29(1)
C(46)	-538(5)	-1676(5)	8244(5)	51(2)
C(47A)	-1290(7)	-2478(7)	9059(7)	62(2)
C(47B)	395(18)	-2650(20)	8400(20)	62(2)
C(48)	4529(15)	-4643(17)	9766(16)	285(8)
C(49)	3474(14)	-5024(15)	9640(13)	255(7)
C(50)	2739(16)	-5890(20)	9949(17)	225(9)
C(51)	1573(19)	-5360(20)	9965(19)	132(8)

Table A-11: Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$) and site occupancy factors for **3-18**.

Atom	x	y	z	U(eq)	s.o.f.
N(1)	8791(1)	229(1)	3095(1)	42(1)	
C(1)	10052(1)	159(1)	3550(1)	39(1)	
C(2)	10885(2)	-629(1)	3328(1)	48(1)	
C(3)	10422(2)	-1336(1)	2633(1)	58(1)	
C(4)	9140(2)	-1256(1)	2167(1)	60(1)	
C(5)	8345(2)	-468(1)	2419(1)	55(1)	
C(6)	10331(1)	1007(1)	4242(1)	38(1)	
C(7)	9220(1)	1642(1)	4247(1)	41(1)	
C(8)	9371(2)	2492(1)	4863(1)	49(1)	
C(9)	10557(2)	2698(1)	5450(1)	49(1)	
C(10)	11626(2)	2025(1)	5430(1)	48(1)	
C(11)	11525(1)	1173(1)	4836(1)	43(1)	
O(1A)	7460(17)	1844(11)	2726(13)	45(1)	0.718
O(2A)	6790(2)	731(1)	3867(1)	43(1)	0.718
C(12A)	6033(2)	1832(2)	2566(2)	50(1)	0.718
C(13A)	5669(8)	1308(5)	3557(4)	46(1)	0.718
C(14A)	5594(2)	1207(2)	1645(2)	67(1)	0.718
C(15A)	5553(3)	2924(2)	2392(2)	77(1)	0.718
C(16A)	4425(4)	644(5)	3409(4)	75(1)	0.718
C(17A)	5459(3)	2108(2)	4343(2)	75(1)	0.718
O(1B)	7330(50)	1950(30)	2770(30)	45(1)	0.282
O(2B)	6949(5)	1050(3)	4239(3)	36(1)	0.282
C(12B)	5986(5)	2216(4)	3072(4)	45(1)	0.282
C(13B)	5570(20)	1451(15)	3762(14)	46(1)	0.282
C(14B)	6128(6)	3259(3)	3573(4)	53(1)	0.282
C(15B)	5045(7)	2332(7)	2141(5)	72(2)	0.282
C(16B)	4924(10)	460(9)	3252(9)	64(3)	0.282
C(17B)	4815(7)	1722(5)	4604(5)	58(2)	0.282
C(18)	10710(2)	3630(1)	6099(1)	69(1)	
C(19)	11596(2)	4434(1)	5706(2)	81(1)	
B(1)	7953(2)	1222(1)	3525(1)	44(1)	

Table A-12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4-46**

	x	y	z	U(eq)
Ag(1)	10000	6551(1)	5000	32(1)
Ag(2)	5284(1)	5000	6498(2)	87(1)
N(1)	7273(4)	6235(3)	2637(6)	40(1)
N(2)	7315(4)	6742(3)	2168(6)	40(1)
N(3)	8162(3)	6890(2)	2871(5)	32(1)
Br(1)	5555(1)	5000	8771(2)	86(1)
Br(2)	6352(1)	5000	5449(2)	86(1)
C(1)	9030(7)	5000	6218(10)	44(2)
C(2)	8768(5)	5514(3)	5574(7)	40(2)
C(3)	8239(4)	5518(3)	4266(7)	36(1)
C(4)	7968(6)	5000	3613(9)	35(2)
C(5)	8063(4)	6068(3)	3594(6)	33(1)
C(6)	8662(4)	6503(3)	3756(7)	34(1)
C(7)	6414(5)	5937(4)	2102(10)	57(2)
C(8)	8468(4)	7427(3)	2574(7)	38(1)
C(9)	8433(5)	7920(3)	3197(7)	40(2)
C(10)	8716(6)	8430(3)	2881(9)	53(2)
C(11)	9024(7)	8429(4)	1987(11)	64(3)
C(12)	9071(6)	7928(4)	1415(10)	62(2)
C(13)	8802(5)	7404(4)	1710(8)	47(2)
C(14)	8108(5)	7920(3)	4206(8)	46(2)
C(15)	7372(7)	8355(5)	3882(11)	68(3)
C(16)	8869(7)	8035(6)	5512(10)	72(3)
C(17)	8915(6)	6843(4)	1150(9)	58(2)
C(18)	8491(8)	6858(6)	-266(10)	84(3)
C(19)	9909(8)	6717(7)	1729(12)	99(5)
Cl(2)	8224(9)	5298(7)	792(11)	340(9)
Cl(1)	8678(14)	5000	-994(17)	340(9)
C(21)	7980(20)	5000	-510(30)	146(17)

C(20)	8840(30)	5000	380(30)	146(17)

Table A-13. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4-49**.

	x	y	z	U(eq)
Rh(1)	5396(1)	5326(1)	1199(1)	19(1)
Br(1)	5785(1)	6701(1)	1796(1)	46(1)
N(1)	8354(5)	5176(3)	591(3)	16(1)
N(2)	9271(5)	5514(3)	99(3)	21(1)
N(3)	8586(6)	6071(3)	-286(3)	19(1)
C(1)	7092(6)	5508(4)	535(3)	18(1)
C(2)	7264(6)	6106(4)	-57(4)	18(1)
C(3)	8795(6)	4457(4)	1006(3)	19(1)
C(4)	8988(7)	3750(4)	563(4)	26(2)
C(5)	9488(11)	3055(5)	953(4)	43(2)
C(6)	9724(11)	3074(5)	1784(5)	53(2)
C(7)	9480(10)	3788(4)	2208(4)	40(2)
C(8)	9025(7)	4496(4)	1843(4)	23(1)
C(9)	8724(7)	3707(4)	-336(4)	24(2)
C(10)	10047(8)	3641(6)	-807(5)	43(2)
C(11)	7796(9)	3013(5)	-540(5)	45(2)
C(12)	8805(7)	5245(4)	2338(4)	26(1)
C(13)	10078(8)	5495(5)	2783(5)	40(2)
C(14)	7656(8)	5102(5)	2938(4)	35(2)
C(15)	9325(8)	6555(4)	-893(4)	31(2)
C(16)	6269(6)	6643(4)	-431(3)	19(1)
C(17)	4945(7)	6361(4)	-502(4)	24(2)
C(18)	3967(7)	6840(4)	-862(4)	28(2)
C(19)	4250(7)	7596(4)	-1146(4)	24(1)
C(20)	5568(8)	7888(4)	-1073(4)	31(2)
C(21)	6545(7)	7429(4)	-713(4)	25(1)

C(22)	3246(7)	5447(5)	1432(4)	35(2)
C(23)	3815(8)	5045(5)	2096(5)	37(2)
C(24)	3637(10)	4128(6)	2187(6)	55(3)
C(25)	4761(9)	3648(5)	1849(5)	42(2)
C(26)	5407(8)	4044(4)	1115(4)	29(1)
C(27)	4718(8)	4370(4)	456(4)	30(2)
C(28)	3210(9)	4364(5)	359(6)	44(2)
C(29)	2489(9)	5088(7)	789(6)	56(3)

Table A-14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4-50**.

	x	y	z	U(eq)
Rh(1)	367(1)	1220(1)	5494(1)	30(1)
N(1)	2496(2)	1234(1)	7992(3)	29(1)
N(2)	3088(2)	1434(1)	9075(3)	33(1)
N(3)	2509(2)	1676(1)	9062(3)	30(1)
C(1)	0	2468(2)	7500	38(1)
C(2)	778(3)	2269(1)	7755(4)	36(1)
C(3)	786(2)	1864(1)	7775(3)	28(1)
C(4)	0	1663(1)	7500	28(1)
C(5)	1591(2)	1634(1)	8025(3)	28(1)
C(6)	1562(3)	1341(1)	7288(3)	28(1)
C(7)	2915(3)	1950(1)	10115(4)	43(1)
C(8)	2937(3)	941(1)	7733(4)	34(1)
C(9)	3192(3)	586(1)	8388(4)	40(1)
C(10)	3662(3)	316(1)	8175(5)	52(1)
C(11)	3842(4)	393(2)	7337(5)	61(1)
C(12)	3575(4)	744(2)	6695(5)	55(1)
C(13)	3112(3)	1030(1)	6878(4)	41(1)
C(14)	2988(3)	498(1)	9312(4)	43(1)
C(15)	2514(4)	102(1)	9066(5)	59(1)

C(16)	3891(4)	526(2)	10669(5)	62(1)
C(17)	2827(3)	1414(1)	6185(4)	44(1)
C(18)	2160(4)	1354(2)	4755(5)	64(1)
C(19)	3711(4)	1650(2)	6614(6)	77(2)
C(20)	-751(3)	1085(1)	3475(4)	50(1)
C(21)	-1162(3)	1229(1)	3985(4)	50(1)
C(22)	-1630(3)	992(2)	4415(5)	60(1)
C(23)	-1041(3)	634(1)	5211(4)	48(1)
C(24)	27(3)	702(1)	5992(4)	34(1)
C(25)	567(3)	613(1)	5592(4)	35(1)
C(26)	184(3)	458(1)	4306(4)	46(1)
C(27)	-725(4)	658(1)	3225(4)	54(1)
N(4)	486(2)	1777(1)	5032(3)	42(1)
C(28)	582(3)	2072(1)	4757(4)	51(1)
C(29)	735(5)	2450(2)	4409(6)	88(2)
C(30)	4368(8)	1417(4)	4133(11)	75(3)
Cl(1)	4046(4)	918(2)	4221(6)	165(3)
Cl(2)	4476(4)	1414(2)	2914(5)	137(2)
B(1)	2017(4)	2378(2)	2199(6)	73(2)
F(1A)	2808(7)	2088(3)	2784(9)	88(1)
F(2A)	1519(9)	2271(4)	969(9)	88(1)
F(1B)	2763(10)	2128(4)	2403(13)	88(1)
F(2B)	1362(10)	2353(5)	904(11)	88(1)
F(1C)	2109(11)	2172(4)	1480(14)	88(1)
F(2C)	1131(8)	2617(4)	1099(11)	88(1)
F(3)	2465(3)	2724(1)	2612(4)	88(1)
F(4)	1612(3)	2262(1)	2727(4)	88(1)

Table **A-15**. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) For **4-58**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	2500	2500	5000	41(1)
N(1)	2628(2)	-77(4)	4995(3)	33(1)
N(2)	2366(2)	-1049(4)	5086(3)	38(1)
N(3)	1884(2)	-732(4)	5247(3)	33(1)
C(1)	2307(3)	859(5)	5081(4)	37(1)
C(2)	1820(3)	408(5)	5248(4)	37(1)
C(3)	1505(3)	-1616(6)	5401(5)	54(2)
C(4A)	1316(3)	1030(6)	5381(4)	64(1)
C(5A)	1419(3)	1945(5)	5895(4)	64(1)
C(6A)	955(3)	2553(5)	6000(4)	64(1)
C(7A)	386(3)	2245(5)	5591(4)	64(1)
C(8A)	282(3)	1329(5)	5076(4)	64(1)
C(9A)	747(3)	722(5)	4971(4)	64(1)
C(4B)	1298(11)	960(20)	5425(18)	55(6)
C(5B)	1004(11)	1823(19)	4906(18)	55(6)
C(6B)	508(11)	2327(19)	5042(17)	55(6)
C(7B)	307(11)	1970(19)	5696(17)	55(6)
C(8B)	601(11)	1110(19)	6215(17)	55(6)
C(9B)	1096(11)	610(20)	6079(17)	55(6)
C(10)	3148(3)	-184(5)	4709(4)	40(2)
C(11)	3052(3)	-410(5)	3874(4)	47(2)
C(12)	3552(4)	-645(6)	3615(5)	60(2)
C(13)	4099(4)	-657(7)	4181(6)	68(2)
C(14)	4175(3)	-407(6)	4992(5)	60(2)
C(15)	3695(3)	-167(5)	5291(4)	47(2)
C(16)	2449(4)	-446(6)	3264(4)	53(2)
C(17)	2241(4)	-1646(6)	3114(5)	59(2)
C(18A)	2420(30)	230(70)	2460(30)	74(6)
C(18B)	2440(30)	80(70)	2420(30)	74(6)
C(19)	3788(3)	21(7)	6194(5)	56(2)

C(20)	3897(5)	-1071(9)	6664(6)	87(3)
C(21)	4277(4)	852(10)	6568(7)	97(4)
C(22)	800(14)	710(30)	2975(16)	140(11)
Cl(1)	2993(1)	2544(1)	6421(1)	44(1)
Cl(3)	617(4)	1349(12)	1979(5)	202(5)
Cl(2)	805(3)	-582(9)	3032(6)	154(3)

Table **A-16**. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4-59**.

	x	y	z	U(eq)
Pd(1)	7350(1)	6962(1)	7076(1)	26(1)
Pd(2)	2026(1)	8036(1)	3545(1)	28(1)
Cl(1)	9190(1)	6404(1)	7278(1)	40(1)
Cl(2)	5490(1)	7404(1)	6714(1)	39(1)
Cl(3)	3134(2)	7055(1)	2918(1)	48(1)
Cl(4)	946(1)	8999(1)	4221(1)	42(1)
N(1)	9330(4)	8533(3)	6997(2)	31(1)
N(2)	9807(4)	8946(3)	6591(2)	37(1)
N(3)	9092(4)	8396(3)	5969(2)	33(1)
N(5)	6282(4)	6212(3)	7578(2)	29(1)
N(6)	-458(4)	6543(3)	2702(2)	32(1)
N(7)	-1338(4)	5760(3)	2661(2)	35(1)
N(8)	-905(4)	5667(3)	3242(2)	31(1)
N(9)	3707(4)	9179(3)	3857(2)	33(1)
C(1)	8334(5)	7731(3)	6646(3)	30(1)
C(2)	8177(5)	7660(3)	5972(3)	28(1)
C(3)	9456(6)	8639(4)	5389(3)	41(1)
C(4)	9946(5)	9002(3)	7730(3)	35(1)
C(5)	9280(6)	9572(4)	8150(3)	41(1)
C(6)	9936(7)	10070(4)	8830(3)	54(2)
C(7)	11214(7)	10015(5)	9079(3)	62(2)
C(8)	11838(7)	9460(4)	8652(3)	54(2)
C(9)	11217(6)	8932(4)	7957(3)	42(1)

C(10)	7923(6)	9690(4)	7897(3)	47(2)
C(11)	6960(7)	9441(6)	8314(4)	79(3)
C(12)	8042(8)	10690(5)	7902(4)	66(2)
C(13)	11954(6)	8345(4)	7489(3)	42(1)
C(14)	12673(6)	7785(4)	7825(3)	49(2)
C(15)	12954(7)	8967(4)	7271(4)	57(2)
C(16)	7243(5)	6945(3)	5337(2)	30(1)
C(17)	6570(6)	7195(4)	4826(3)	37(1)
C(18)	5719(6)	6515(5)	4237(3)	48(2)
C(19)	5517(6)	5578(4)	4151(3)	48(2)
C(20)	6170(6)	5324(4)	4650(3)	40(1)
C(21)	7027(5)	5994(3)	5248(3)	32(1)
C(22)	5391(5)	6569(4)	7896(3)	36(1)
C(23)	4613(6)	6100(4)	8220(3)	45(1)
C(24)	4787(6)	5254(4)	8223(3)	48(2)
C(25)	5729(6)	4891(4)	7904(3)	42(1)
C(26)	6448(5)	5388(4)	7595(3)	36(1)
C(27)	510(5)	6935(3)	3290(2)	28(1)
C(28)	209(5)	6362(3)	3653(2)	28(1)
C(29)	-1614(6)	4845(3)	3347(3)	39(1)
C(30)	-693(5)	6830(4)	2117(3)	37(1)
C(31)	-270(7)	6370(5)	1535(3)	54(2)
C(32)	-544(9)	6702(7)	999(4)	80(3)
C(33)	-1144(10)	7396(7)	1043(4)	79(2)
C(34)	-1548(8)	7797(6)	1613(4)	65(2)
C(35)	-1369(5)	7536(4)	2165(3)	41(1)
C(36)	289(7)	5547(6)	1459(4)	71(2)
C(37A)	-730(30)	4650(20)	1000(18)	75(3)
C(38A)	1510(30)	5800(30)	1130(20)	75(3)
C(37B)	-760(30)	4579(19)	1240(20)	75(3)
C(38B)	1410(40)	5590(30)	1060(20)	75(3)
C(38C)	1340(30)	5290(20)	1076(15)	75(3)
C(37C)	-910(40)	4650(20)	1130(30)	75(3)
C(39)	-1910(6)	7934(4)	2808(3)	43(1)
C(40)	-2059(9)	8890(5)	2896(6)	86(3)

C(41)	-3296(8)	7332(5)	2728(5)	73(2)
C(42)	877(5)	6434(3)	4335(3)	28(1)
C(43)	166(5)	6358(4)	4825(3)	35(1)
C(44)	822(6)	6484(4)	5479(3)	39(1)
C(45)	2184(6)	6671(4)	5654(3)	39(1)
C(46)	2907(6)	6736(4)	5173(3)	41(1)
C(47)	2265(5)	6618(3)	4513(3)	34(1)
C(48)	3608(6)	10016(4)	3828(3)	39(1)
C(49)	4718(7)	10775(4)	4056(3)	53(2)
C(50)	5939(7)	10684(4)	4326(3)	51(2)
C(51)	6033(6)	9827(4)	4355(3)	44(1)
C(52)	4905(5)	9097(4)	4110(3)	37(1)

Table **A-17**. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4-60**.

	x	y	z	U(eq)
Pd(1)	7132(1)	-245(1)	1741(1)	32(1)
Pd(2)	11480(1)	4764(1)	3071(1)	37(1)
Cl(4)	5876(2)	1217(4)	1661(2)	48(1)
Cl(1)	11660(3)	3282(4)	2121(2)	50(1)
Cl(2)	11037(3)	5988(5)	4009(2)	83(2)
Cl(3)	8451(2)	-1564(4)	1942(2)	53(1)
N(1)	7775(6)	2075(11)	824(5)	31(2)
N(3)	8691(7)	3452(11)	1473(5)	35(3)
N(2)	8326(7)	3251(10)	814(5)	34(2)
N(6)	12451(7)	2357(11)	3979(5)	33(2)
N(5)	12349(7)	1117(13)	4355(5)	40(3)
N(4)	11484(7)	956(11)	4274(5)	36(3)
N(8)	6444(8)	-2135(12)	2005(6)	45(3)
N(7)	11332(7)	6746(11)	2434(6)	44(3)
C(25)	7287(8)	1456(15)	167(6)	37(3)
C(15)	11153(8)	-311(18)	4608(6)	49(3)

C(24)	9293(7)	4718(18)	1668(6)	42(3)
C(34)	8581(8)	-443(16)	205(7)	41(3)
C(19)	8182(8)	2099(14)	3151(7)	37(3)
C(28)	6437(9)	337(17)	-1075(7)	60(5)
C(36)	8656(10)	-2102(14)	119(8)	55(4)
C(4)	13756(9)	3913(15)	4399(7)	43(3)
C(29)	6073(9)	1663(15)	-827(7)	43(4)
C(30)	6513(9)	2225(17)	-209(7)	45(4)
C(16)	10029(8)	2074(13)	3647(7)	33(3)
C(26)	7685(9)	229(13)	-104(7)	41(4)
C(37)	6604(10)	-3466(14)	1724(7)	52(4)
C(44)	11247(10)	9189(17)	1580(9)	59(4)
C(23)	7807(8)	1521(15)	1478(6)	35(3)
C(35)	9289(8)	295(15)	-119(8)	58(5)
C(38)	6217(9)	-4768(13)	1930(6)	46(4)
C(41)	5871(9)	-2060(13)	2440(7)	43(4)
C(8)	13675(11)	4230(20)	5651(8)	101(8)
C(3)	14606(9)	4296(15)	4350(8)	54(4)
C(2)	15068(10)	3651(18)	3906(9)	64(5)
C(27)	7184(7)	-330(20)	-765(6)	47(3)
C(1)	14677(10)	2468(18)	3458(8)	57(4)
C(7)	13285(10)	4730(30)	4909(8)	75(4)
C(12)	13633(10)	-715(17)	3350(10)	76(6)
C(40)	5430(9)	-3302(17)	2642(8)	53(4)
C(46)	10771(10)	7835(14)	2491(8)	56(4)
C(11)	13576(10)	870(20)	2238(8)	85(6)
C(32)	5196(10)	3660(18)	44(8)	70(5)
C(31)	6191(9)	3633(15)	120(7)	44(4)
C(33)	6499(8)	5010(17)	-260(7)	48(4)
C(20)	8756(8)	2367(13)	2683(7)	34(3)
C(14)	11008(8)	2054(13)	3864(6)	30(3)
C(21)	9674(8)	2290(13)	2923(6)	32(3)
C(13)	11644(9)	2929(13)	3674(7)	36(3)
C(6)	13777(8)	2088(15)	3467(7)	38(3)
C(5)	13340(9)	2814(15)	3940(7)	39(3)

C(10)	13360(11)	810(20)	2993(8)	63(5)
C(39)	5624(9)	-4635(15)	2349(7)	48(4)
C(42)	11882(10)	6897(16)	1931(8)	56(5)
C(45)	10724(11)	9067(15)	2069(9)	68(5)
C(43)	11832(12)	8166(17)	1499(8)	68(5)
C(22)	8402(8)	2393(14)	1923(7)	34(3)
C(9)	13354(14)	6410(20)	4858(11)	112(8)
C(18)	8570(8)	1890(14)	3878(7)	38(3)
C(17)	9424(8)	1852(13)	4110(6)	32(3)