Strong Electron Donor Ligands and their Catalytic Applications

by

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Department of Chemistry
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Abstract

The coordination chemistry of several strong electron donor ligands, including anionic imidazol-4-ylidenes, cyclic bent allenes, carbodiphosphoranes, and carbodicarbenes were explored with transition metals including Au, Ag, Ru, Rh, Ir, and Fe.

Chapter 2 explores the transition metal coordination chemistry of an anionic imidazol-4-ylidene. Ru complexes of this ligand were accessed by transmetalation of an anionic imidazol-4-ylidene Ag complex - the first instance of Ag mediated transmetalation of an anionic imidazolylidene. A coordinatively unsaturated Ru complex of this ligand was shown to decompose through a unique metal assisted proton transfer reaction. Rh complexes of this ligand have revealed its overall moderately strong donor ability.

Chapter 3 details the synthesis of a family of Ru-hydrido species bearing strongly donating ‘cyclic bent allenes’ and reveals their very high activity in olefin hydrogenation catalysis. Chemoselective and diastereoselective hydrogenations, as well as hydrogenations of sterically hindered olefins are achieved at
exceptionally low catalyst loadings. Chiral modifications of the cyclic bent allene ligands have been explored in Ir based systems.

Chapter 4 explores the Fe chemistry of cyclic bent allenes and carbodiphosphoranes. These strong electron donors are shown to stabilize Fe in a rare highly unsaturated three-coordinate geometry in several instances.

Chapter 5 details the synthesis of a new type of carbodicarbene, a ‘carbodicyclopropenylidene’, which is the first example of a carbodicarbene without heteroatomic stabilization. The main group and transition metal coordination chemistry of this ligand is investigated. The carbodicyclopropenylidene is shown also to be a strong electron donor.
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List of Abbreviations

°C  degrees Celsius
Å  angstrom, 10⁻¹⁰ m
σ  sigma orbital

[xiii]
liPr  1,3-di-iso-propylimidazol-2-ylidene
IMes  1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene
l(EtOMe)  1,3-bis(methoxyethyl)imidazol-2-ylidene
lp-tol  1,3-bis(4-methylphenyl)imidazol-2-ylidene
iPr  iso-propyl
K  Kelvin
KHMD  potassium hexamethyldisilazide
LiHMDS  lithium hexamethyldisilazide
LDA  lithium diisopropylamide
m  meta
m  multiplet
Me  methyl
Me$_2$CAAC  3,3,5,5-tetramethyl-1-(2,6-diisopropylphenyl)pyrrolidin-2-ylidene
Me$_2$IMe  1,3,4,5-tetramethylimidazol-2-ylidene
Mes  2,4,6-trimethylphenyl
min  minute
mL  milliliter
mm  millimeter
mmol  millimole
NHC  N-heterocyclic carbene
$^n$J$_{X,Y}$  n-bond scalar coupling constant between atoms X and Y
nBu  n-butyl
NMR  nuclear magnetic resonance
o  ortho
p  para
Ph  phenyl
ppm  parts per million
q  quartet
r.t.  room temperature
SiMes  1,3-bis(mesityl)imidazolin-2-ylidene
t  triplet
t  time
TBDMS  tertbutyldimethylsilyl
TEP  Tolman Electronic Parameter
Tf  trifluoromethanesulfonyl
TOF  turn-over frequency
tol  Toluene, tolyl (methylphenyl)
TON  turn-over number
THF  tetrahydrofuran
TMS  trimethylsilyl
VT  variable temperature
Xyl  xylyl; 2,6-dimethylphenyl
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Chapter 1. The Coordination Chemistry of Divalent Carbon

1.1 Why Study Science?

Scientific study is transformative. Our study of science is what has elevated humankind from the other species of the earth. Scientific progress has been our only weapon against disease and famine: the applications of science, through technology, have allowed the easement and betterment of the human experience. While our advancement has been driven by scientific progress, our evolution is hampered by the vestiges of our tribal roots; to work only for the betterment of ourselves and those closest to us, without consideration of how our actions affect other human beings, our environment, and future generations. Our actions, empowered through technology, have the ability to affect global changes. With such power comes great responsibility that science is used for noble purposes, with foresight and consideration to other human beings born and unborn. The earth is a closed system: our actions as scientists must transcend economics, nationalism, and even religious belief if we are to sustain on our planet. It is with solemn respect that I sign the following pledge:

"I promise to work for a better world, where science and technology are used in socially responsible ways. I will not use my education for any purpose intended to harm human beings or the environment. Throughout my career, I will consider the ethical implications of my work before I take action. While the demands placed on me may be great, I sign this declaration because I recognize that individual responsibility is the first step on the path to peace."
1.2 Divalent Carbon Ligands and their Applications

1.2.1 Introduction

Carbon has long been known to form compounds by the formation of four bonds to other element centres, achieving a stable electronic octet. In contrast, divalent carbon species possessing only two bonding partners, known as carbenes, require two nonbonding electrons on the central carbon atom in order to remain electronically neutral, and are usually highly reactive and fleeting intermediates. Substitution patterns \( R_1R_2C \) featuring non-\( \pi \)-donating substituents \( R_1 \) and \( R_2 \) are triplet carbenes (Figure 1.2.1), where the two degenerate orbitals on carbon are each occupied by one electron.\(^1\) Such species can be stabilized kinetically via steric protection, the longest living members persisting for up to a week in solution.\(^2\) The stabilization of such species in the coordination sphere of a transition metal was first reported by Schrock in 1974.\(^3\) Such species, known as Schrock carbenes, are nucleophilic when metal bound, and are typically actor ligands in reactions at the metal centre. For example, transition metal olefin metathesis catalysts bear Schrock carbene 'alkylidene' fragments which react reversibly with olefin to produce a metallacyclobutane.\(^4\)

\[ R_1, R_2 = \text{alkyl, aryl} \]

\[ R_1 = \text{NR', OR', SR', halogens} \]

**Figure 1.2.1.** Singlet and triplet carbenes
Carbenes may also be stabilized thermodynamically by the introduction of a π-donor atom at R₁ such as nitrogen, oxygen, sulfur or a halogen. Such species are singlet carbenes and bear orthogonal filled and unfilled electronic orbitals and feature sp² hybridization at the carbene carbon (Figure 1.2.1). In the coordination sphere of a transition metal, such species are electrophilic, and are known as Fischer carbenes.⁵,⁶ Maximizing the heteroatomic stabilization by the introduction of flanking donor groups at both R₁ and R₂ reduces the electrophilicity of the metal bound carbene, leading to stable and even inert metal carbene complexes. Such species are often spectator ligands, and can be used to tune the electronic properties and the steric environment about the metal centre, a salient example being the imidazol-2-ylidenes of Arduengo and coworkers.⁷ Since the isolation of the first free singlet carbene in 1988 by Bertrand and coworkers,⁸ and the first crystalline carbenes in 1991 by Arduengo and coworkers,⁷ divalent carbon ligands have become a mainstay in chemical synthesis, greatly advancing the fields of organometallic catalysis, organocatalysis, and the stabilization and study of reactive main group fragments.⁹ The following sections will delve into the structures and the diverse electronic properties and applications of many members of the divalent carbon family.

1.2.2 Electron Donor and Acceptor Scales

Before we can begin analysis of divalent carbon ligands, we need to first discuss the methods by which the donor/acceptor properties of such species are evaluated. Quantification of the electron donor properties of monodentate ligands has been popularized by Tolman and coworkers, who examined the A₁ carbonyl stretching frequency in a series of complexes Ni(L)(CO)₃, now known as the Tolman electronic parameter (TEP).¹⁰ The electron richness at the metal centre is inductively affected by the electron releasing ability of the ligand L, and the stretching frequency of metal carbonyls is influenced by the extent of back donation from a filled metal d orbital to the unfilled π* antibonding C-O orbital, which largely resides on carbon. This population of the antibonding orbital reduces the C-O bond order, and results in a red-shifting of the C-O stretching frequency. Therefore, the electron donor ability of a ligand L can be quantified by
examination of the CO stretching frequencies of its metal carbonyl complexes, with more electron donating ligands yielding complexes with lower stretching frequencies. Importantly, such scales are a summative quantification of both the donor and acceptor properties of a ligand. Therefore, two ligands may possess nearly identical TEPs, while one ligand may be both a stronger $\sigma$-donor and a stronger $\pi$-acceptor than the other.

The use of Tolman’s original system, Ni(L)(CO)$_3$, has largely been ameliorated through the complexes cis-Rh(L)(CO)$_2$ and cis-Ir(L)(CO)$_2$, mainly due to the significant toxicity concerns in handling the precursor Ni(CO)$_4$. However, equations for the correlation of these modern scales to Tolman electronic parameter have been experimentally derived; therefore, measurements performed on any scale can be used to comparatively evaluate the donor properties of a ligand.

Another donor scale, reported by Gandon and coworkers in 2013, examines the degree of pyramidalization of the adducts Ga(L)Cl$_3$ in their solid state structures. In accord with Bent’s rule, which states that “atomic s character concentrates in orbitals directed toward electropositive substituents”, orbitals of greater s character are preferentially populated by more electron releasing (electropositive) donors. Therefore, an ideally weak (electronegative) donor would populate solely a vacant p orbital, while sp$^2$ orbitals are used in the formation of the three Ga-Cl bonds, which yield summative Cl-Ga-Cl angles around Ga of 360$^\circ$. Conversely, an ideally strong donor would populate exclusively an s orbital, and three p orbitals are used in the formation of Ga-Cl bonds, which yield summative Cl-Ga-Cl angles around Ga of 270$^\circ$. In reality, this pyramidalization has been experimentally observed to vary from 340.1$^\circ$ to 310.9$^\circ$. The obvious shortcoming of this scale is the requirement of a solid state structure of the GaCl$_3$ adduct of a ligand L, and as such, the steric influence of the ligand as well as crystallographic packing effects may affect this parameter. Nevertheless, a good linear correlation ($R^2 = 0.98$) of this parameter to the TEP has been reported across a wide distribution of ligands including ethers, amines, phosphines, carbenes, and carbones.
Donor scales examining the oxidation potential of complexes such as \( \text{IrCl(COD)(L)} \) and \([\text{Ru(bipy)}_2\text{L}_2]^{2+}\) have also been established.\(^{15-17}\) However, they have been less generally applied than scales based on IR spectroscopic measurement of metal carbonyls, and are of no relevance to this thesis.

Scales for the evaluation of the \(\pi\)-accepting ability of carbene ligands have been proposed by both Bertrand\(^{18}\) and Ganter.\(^{19,20}\) Bertrand’s scale, reported in 2013, examines the \(^{31}\text{P}\) NMR chemical shifts of a variety of carbene-(phenyl)phosphinidene complexes (Figure 1.2.2). Such species may be alternately be represented by an ylidic or doubly bonded canonical resonance forms, depending on the \(\pi\)-acceptor ability of the carbene ligand. As such, \(^{31}\text{P}\) resonances corresponding to the former case are significantly upfield of those of the latter, and resonances for a series of carbene-(phenyl)phosphinidene complexes been observed to range from -62.1 to 126.3 ppm.

\[
\begin{align*}
\text{IMes: poor } \pi \text{ acceptor} \\
\delta^{31}\text{P} &= -23.0 \text{ ppm} \\
\text{CyCAAC: good } \pi \text{ acceptor} \\
\delta^{31}\text{P} &= 68.9 \text{ ppm}
\end{align*}
\]

**Figure 1.2.2.** Carbene-phosphinidene complexes

Ganter’s scale, reported later in 2013, uses an analogous methodology in examining the \(^{77}\text{Se}\) NMR chemical shifts of various carbene selenium adducts.\(^{19}\) \(^{77}\text{Se}\) chemical shifts were observed to range from -4 to 856 ppm, and a reasonably good correlation to Bertrand’s phosphinidene scale \((R^2 = 0.92)\) over eleven carbene derivatives has been established.\(^{20}\)

Experimental scales for ligand \(\pi\)-donor ability have not been established. This figure is typically investigated computationally in the form of the 2\(^{\text{nd}}\) proton affinity (PA) of the ligand.\(^{21}\)
1.2.3 Imidazol-2-ylidenes and Related Species

Diamino carbenes are defined as a carbene centre flanked by two NRR' moieties. Of such species, imidazol[|n]-2-ylidenes are the most well studied. The first example of a free diaminocarbene, in the form of an N-heterocyclic carbene (NHC) was isolated by Arduengo in 1991, 1,3-bis(adamantyl)imidazol-2-ylidene “IAd” (see Figure 1.2.3 for some common imidazol-2-ylidene shorthand nomenclature), which was prepared by the deprotonation of the corresponding imidazolium salt with NaH in the presence of a catalytic amount of DMSO (Scheme 1.2.1). This carbene is exceptionally stable, and can be heated to its melting point of 240 °C without decomposition. The stability of this species is derived from the inductively electron withdrawing, but π-donating, nitrogen atoms which flank the central carbon, stabilizing both the filled and unfilled electronic orbitals at the carbene centre. Other contributions to the stability of this system stem from the steric protection of the carbene centre afforded by the bulky N-adamantyl substituents, as well as minor contributions from the aromaticity of the imidazole based ring system. After this initial report, numerous examples of other N-substituted imidazole-2-ylidene and imidazolin-2-ylidene derived species rapidly appeared in the literature. Sterically unencumbered NHCs such as IiPr and even IMe have also been isolated and characterized, although such species are much more reactive and fleeting than more sterically protected analogues. Almost ironically, the NHC that Wanslick and coworkers had attempted to prepare in the 1970s, IPh, is one of the only NHCs which cannot be isolated by a conventional deprotonation methodology. The very similar NHC Ip-tol has since been accessed, but the isolation of IPh has remained elusive.

Scheme 1.2.1. Synthesis of the NHC 1,3-bis(adamantyl)imidazol-2-ylidene “IAd”
Imidazol-2-ylidene and imidazolin-2-ylidene based NHCs are characterized as strong \(\sigma\)-donors, but relatively weak \(\pi\)-acceptors, the saturated analogues being slightly more \(\sigma\)-donating and \(\pi\)-accepting than the unsaturated analogues, and overall have quite similar donor strengths according to their Tolman electronic parameters (IMes = 2050.5 cm\(^{-1}\); SIMes = 2051.2 cm\(^{-1}\)).\(^{12}\) The additional \(\pi\)-accepting ability of the saturated analogue is revealed by the relatively downfield shift of their adducts on both the phosphinidine and selenium scales (\(\delta^{31}\)P (NHC)P(Ph): IMes = -23.0 ppm; SIMes = -10.4 ppm),\(^{18}\) (\(\delta^{77}\)Se (NHC)Se: IMes = 35 ppm; SIMes = 113 ppm).\(^{19}\) The electronic properties of such systems may be further tuned by the addition of donor or acceptor moieties on the backbone 4,5 positions: for example Cl\(_2\)IMes (TEP = 2052.6 cm\(^{-1}\)), and Me\(_2\)IMes (TEP = 2046.7 cm\(^{-1}\)).\(^{12}\) Variation of the N bound substituents effect both the steric and electronic properties of the system. In general, N,N’-dialkyl substituted imidazol[in]-2-ylidenes are slightly stronger donors than N,N’-diaryl substituted analogues.
1.2.4 Applications of N-Heterocyclic Carbenes

Transition metal complexes of imidazol-2-ylidene and imidazolin-2-ylidenes can be accessed via a number of methods. Direct combination of a free NHC with an appropriate transition metal precursor is common, as is combination of an imidazolium salt and a metal precursor under basic conditions.\textsuperscript{26} Additionally, metal imidazol[in]-2-ylidene complexes may be conveniently be accessed via transmetalation from their analogous NHC-Ag halide complexes.\textsuperscript{27}
reactions involving oxidative addition of NHC C-H and C-X bonds are also known.\textsuperscript{28}

Such ligands have been extensively applied as spectator ligands in transition metal catalyzed reactions. Two of the most well studied instances are detailed here. The Ru-alkylidene complex Ru(PCy\textsubscript{3})\textsubscript{2}(CHPh)Cl\textsubscript{2} was reported in 1995 by Grubbs and coworkers, was found to be an efficient catalyst for a variety of olefin metathesis reactions (Scheme 1.2.2).\textsuperscript{29} In 1999, the NHC derivative Ru(SIMes)(PCy\textsubscript{3})(CHPh)Cl\textsubscript{2} was reported by Grubbs and coworkers, and found to be significantly more active than the original bis-phosphine species.\textsuperscript{30} Mechanistic studies have indicated that although the NHC containing species is slower initiating than the bis-phosphine species,\textsuperscript{31} its increased activity is derived from the stabilization of the unsaturated metal centre by the strongly donating NHC ligand. Dozens of modifications of this original system have been reported in the ensuing years, affecting the selectivity and activity of the catalysis.\textsuperscript{32} For his efforts, Robert Grubbs shared the 2005 Nobel prize in chemistry with Richard Schrock and Yves Chauvin for the development of the olefin metathesis reaction.\textsuperscript{33}
Scheme 1.2.2. The mechanism of Ru catalyzed olefin metathesis catalyzed by Grubbs’ 2\textsuperscript{nd} generation NHC containing catalyst, Ru(SIMes)(PCy\textsubscript{3})(CHPh)Cl\textsubscript{2}

Another application of imidazolin-2-ylidenes in catalysis is the development of so called ‘PEPPSI’ (pyridine enhanced precatalyst preparation, stabilization, and initiation) systems, Pd(NHC)(3-chloropyridine)Cl\textsubscript{2}, for various cross coupling reactions bearing very bulky NHCs reported by Organ and coworkers in 2006.\textsuperscript{34,35} PEPPSI catalysts catalyze a wide variety of C-C bond formation reactions such as Suzuki,\textsuperscript{34} Negishi\textsuperscript{35} and Kumada\textsuperscript{36} couplings, as well as Buchwald-Hartwig\textsuperscript{37} amination reactions. PEPPSI precatalysts are exceptionally stable, and form
catalytically active NHC-Pd(0) species in situ (Scheme 1.2.3).\textsuperscript{38} The catalysts are generally more active than other Pd(0) sources, as the sterically bulky NHC ligands are believed to facilitate reductive elimination of the product from the metal centre, as well as providing steric and electronic stability to the low valent Pd(0) active catalyst.

![PEPPSI Precatalyst](image)

Scheme 1.2.3. General mechanism for PEPPSI catalyzed cross coupling reactions.

NHCs have also been used in the stabilization and study of a number of low valent main-group complexes.\textsuperscript{39} For example, Braunschweig and coworkers have in 2012 reported the isolation of a boron-boron triply bonded species stabilized by IDipp in the complex (IDipp)\textsuperscript{–}B≡B←(IDipp) (Figure 1.2.4, A).\textsuperscript{40} This species is stabilized by strong σ-donation of the NHC into the vacant sp orbital on boron,
steric shielding of the electron rich B-B π bonds by the bulky flanking groups on the NHC, as well as some resonance delocalization of the B-B π bonds to the mildly π-acidic carbene centre. Similar methodology has also been used on the synthesis of other low valent main group multiply-bonded species such as Si=Si, Ge=Ge, and P-P (Figure 1.2.4, B, C). Carbenes have also been used in the stabilization of formally carbon(0) compounds (Figure 1.2.4, D); Known as ‘carbones’, these complexes will be discussed at length in section 1.2.9.

Figure 1.2.4. NHC stabilized low valent main group species

The NHC stabilization of unsaturated main group centres has also been applied to catalytic transformations. For example, NHC stabilized borenium cations are known to catalyze transformations including the “Frustrated Lewis Pair” (FLP) type hydrogenation of imines (Scheme 1.2.4), as well as the trans selective hydroboration of alkynes. The stabilization of the net positive charge on boron via the strongly donating NHC affords rare examples of stable crystalline borenium cations. Catalyst optimization for catalysts of the type [(NHC)-9-BBN][B(C₆F₅)₄] in the hydrogenation of olefins identified the electron poor and sterically slim NHC Cl₂Me as the most active species.
The emergence and rise of N-heterocyclic carbenes in the last 25 years, in particular carbenes based on an imidazol[2-ylidene framework, has opened the door to many new and useful catalytic reactions, as well as the stabilization and study of reactive main group intermediates. The strong σ-donating, mildly π-accepting, and sterically tunable properties of these ligands have provided a versatile platform for a rich diversity of chemistry. Several excellent reviews on this subject have been published.9,22,26,49,50

1.2.5 Acyclic Diaminocarbenes

Acyclic diaminocarbenes (ADCs) have also been synthesized, and are in general very strong electron donors, for example ((iPr)2N)2C (TEP = 2037 cm⁻¹) (Figure 1.2.5).18 It has been found that these species also have π-acceptor properties significantly greater than imidazol-2-ylidenes, and have been placed on Bertrand’s phosphinidene scale (δ 31P (((iPr)2N)2C)P(Ph): 69.5 ppm).18 Such species are more basic and sensitive than NHCs,51 and cannot always be isolated in free form. The N-C-N angles of ADCs are markedly wider than those of NHCs, (iPr)2N)2C having an N-C-N angle of 121.0(5)° (a typical imidazol-2-ylidene has an N-C-N angle of approximately 105°).51 Slow rotation of the flanking di-isopropylamino groups is also observed for this carbene at room
temperature, supporting the presence of an out of plane three centre four
electron (3c-4e) π bond delocalized over the NCN moiety. While applications of
such species as spectator ligands in Pd based cross coupling catalysis have
been investigated with some success,\textsuperscript{52} this branch of carbenes remains much
less explored than NHCs.

\begin{center}
\includegraphics[width=0.3\textwidth]{figure1.png}
\end{center}

\textbf{Figure 1.2.5. An Acyclic Diaminocarbene}

1.2.6 Alkylaminocarbenes

Cyclic alkylaminocarbenes (CAACs) were first synthesized by Bertrand and
coworkers in 2005.\textsuperscript{53} In contrast to imidazolin-2-ylidenes, these species bear one
NRR' group and one saturated carbon centre proximal to the central carbene
carbon. The absence of the second amino substitution makes the central carbene
more σ-donating, due to the relatively electronegative nature of the flanking
carbon atom, but also more π-accepting, due to the substitution of one of the
stabilizing π-donor amino groups with a saturated centre.\textsuperscript{54} The TEP of CAACs
indicate their strong donor ability (MenthCAAC: TEP = 2041.0 cm\textsuperscript{-1}; CyCAAC:
TEP = 2047.4 cm\textsuperscript{-1}) (Figure 1.2.6).\textsuperscript{12} The strong π-accepting nature of these
species is revealed by their chemical shifts on Bertrand’s phosphinidene scale
((CyCAAC)P(Ph): δ\textsuperscript{31}P = 68.9 ppm; (MenthCAAC)P(Ph): δ\textsuperscript{31}P = 56.2).\textsuperscript{18} Acyclic
alkylamino carbenes have also been accessed,\textsuperscript{55} and are even more σ-donating
and π-accepting than CAACs, for example (Cy\textsubscript{2}N)(tBu)C (TEP = 2043.8 cm\textsuperscript{-1};
((Cy\textsubscript{2}N)(tBu)C)P(Ph) δ\textsuperscript{31}P = 126.3 ppm).\textsuperscript{12,18} The modular construction of CAACs
allows the incorporation of rigid or flexible frameworks on the saturated carbon
flanking position, allowing the isolation of CAACs with a range of steric
requirements. Bulky rigid CAACs have been used in the isolation of rare 3-
coordinate Rh species.\textsuperscript{56} Transition metal complexes of CAACs been accessed
via combination of the free carbene with a metal source, as well as oxidative
addition of C-X and C-H bonds.\textsuperscript{28,57}
Alkylaminocarbenes excel at resonance stabilization of electron rich centres due to the presence of their electrophilic vacant p orbital. For example, CAACs have been used in the stabilization of species including (CAAC)-B-N(TMS)$_2$ and (CAAC)$_2$BH, both of which are formally B(I) species. While CAACs have become known in the past decade as important and accessible members of the carbene family with emerging catalytic applications, CAACs do not play a significant role in this thesis and will not be discussed at length.

### 1.2.7 Imidazol-4-ylidenes (abnormal carbenes)

The first example of a metal bound ‘abnormal carbene,’ an imidazol-4-ylidene (aNHC), was reported by Crabtree and coworkers in 2002 by the reaction of a chelating pyridyl imidazolium salt with an Ir–pentahydride species (Figure 1.2.7). Instead of the anticipated C2 metalated system, the C4 metalated regioisomer was obtained, despite the fact that the pKa of the C4 position of an imidazolium salt is approximately 33, significantly greater than the pKa of approximately 24 for the C2 position. In this case, C4 metalation may be considered the kinetic product of the reaction, although no interconversion of C2/C4 metalated products could be induced upon heating. The selectivity of this reaction is dependent on multiple factors. Unsurprisingly, sterically bulky N-substituents favour the formation of the C4 product. In addition, imidazolium salts featuring weakly coordinating anions incapable of hydrogen bonding, such as BF$_4^-$, favour the abnormal product, while small anions such as chloride tend to favour the normal species. This can be rationalized as a result of hydrogen bonding of the C2 position with a chloride anion which acidifies this position and facilitates C-H bond heterolysis and formation of the ‘normal’ adduct. In contrast,
formation of the C4 product is thought to stem from an oxidative addition pathway.

While sterically bulky N substituents may be used to encourage C4 metalation, this is more conveniently achieved by simply blocking the C2 position with an alkyl or aryl substituent. Bertrand and coworkers have used this methodology to synthesize the first example of an isolable crystalline imidazol-4-ylidene (Figure 1.2.8). However, this species is much less stable than a conventional imidazol-2-ylidene, and decomposes if heated to 50 °C in solution. In general, ‘abnormal’ imidazol-4-ylidenes are much more donating than their ‘normal’ imidazol-2-ylidene analogues: the TEP of Bertrand’s aNHC is 2038.4 cm\(^{-1}\). Interestingly, the 2\(^{nd}\) proton affinity (PA) of this species (1\(^{st}\) PA: 287.0 kcal/mol; 2\(^{nd}\) PA: 144.6 kcal/mol) is significantly higher than those of imidazol-2-ylidenes (2\(^{nd}\) PA: 38.9 – 106.5 kcal/mol). Additionally, the HOMO-1 of the abnormal carbene encompasses the C4-C5 π bond. This data collectively suggests that such species should perhaps be regarded as π donors, rather than π acceptors. Indeed, there is no reasonable resonance structure of an imidazol-4-ylidene that places a vacant p orbital on the carbenoid carbon atom, and all valid resonance structures are zwitterionic. This has led some authors to question (correctly, in this author’s opinion) whether imidazolin-4-ylidenes should be considered carbenes at all (see section 1.2.11.3 for further discussion). ‘Mesoionic’ carbenes is a term that has been invoked for such species.

![Chemical structure](image)

**Figure 1.2.7.** Synthesis of the first imidazol-4-ylidene
Transition metal imidazolin-4-yldenides have been accessed by direct combination of a free carbene with a transition metal, as well as by oxidative addition and transmetalation protocols. Imidazol-4-ylidenes are known to transfer significant electron density to transition metal centres, and have seen some applications in catalysis, including Rh based transfer hydrogenation, Ru catalyzed β-alkylation of alcohols, as well as in Pd catalyzed cross coupling reactions. In many cases, abnormal carbenes outperform their analogous normal carbene complexes, as the electron rich metal centres may more easily undergo processes such as oxidative addition, and the activation of π-acidic substrates. However, as a point of caution, it has been observed that C4 bound imidazolylidenes are more prone to reductive elimination than C2 bound imidazolylidenes from the metal centre. For example, bis-aNHC-Pd(II) species were observed to be more active catalysts for the hydrogenation of olefins than their bis-NHC analogues. It was discovered that this effect was due to reductive elimination of the abnormal NHC salt, and the formation of colloidal Pd(0), which was serving as the actual catalyst in this reaction. Further supporting this, Cavell and coworkers have demonstrated that a mixed Pd(NHC)(aNHC)HBr species preferentially undergoes reductive elimination to form (NHC)Pd(0) species and [aNHC]HBr (Scheme 1.2.5).

**Figure 1.2.8.** Synthesis and decomposition of an isolable imidazol-4-ylidene (aNHC)
1.2.8 Triazolyldenenes

Triazolyldenenes are five-membered aromatic heterocycles featuring three nitrogen atoms and one carbenoid carbon centre.\textsuperscript{28,65,73} There are two major variants; 1,2,4-triazol-5-ylidenes and 1,2,3-triazol-5-ylidenes. 1,2,4-triazol-5-ylidenes are poorer electron donors than imidazol-2-ylidenes\textsuperscript{12} and are less explored of the two classes. 1,2,3-triazol-5-ylidenes were first reported in 2008 by Albrecht and coworkers.\textsuperscript{72} In general, 1,2,3-triazol-5-ylidenes are slightly more electron donating than imidazol-2-ylidenes, but are less donating than imidazol-4-ylidenes, for example MeTrIDipp (TEP = 2046.1 cm\textsuperscript{-1}) (Figure 1.2.9).\textsuperscript{12} A wide variety of triazolium precursors to 1,2,3-triazol-5-ylidenes are readily available via Cu catalyzed ‘click’ reaction of an alkyne with an azide to form a triazole, followed by alkylation of the 3-position to form the precursor salt. In most cases, the free triazolylidenes are not directly accessed, but are readily reacted with Ag\textsubscript{2}O to form triazolylidene-Ag complexes, which can readily be used as a carbene transfer reagent to other metal centres.\textsuperscript{74} However, direct reaction of isolated 1,2,3-triazolylidenes has also been reported by Bertrand and coworkers.\textsuperscript{75}
imidazol-2-ylidenes.⁷⁴ 1,2,3-Triazol-5-ylidenes form robust bonds to transition metal centres which are less prone to acidolysis and reductive elimination than imidazol-4-ylidenes.⁷⁴ Catalysts for the hydrogenation of olefins,⁷⁶ C-C cross coupling reactions,⁷⁷-⁷⁹ olefin metathesis,⁸⁰,⁸¹ alkyne hydroarylation,⁸² and various organic oxidation reactions⁸³ have been reported. In some cases, such as Ru catalyzed oxidation of benzyl alcohols,⁸³ 1,2,3-triazol-5-ylidenes outperform analogous imidazol-2-ylidene derivatives. However, the opposite is true in the case of C-C cross coupling and olefin metathesis reactions. Due to their relative ease of synthesis and desirable donor properties, 1,2,3-triazol-5-ylidenes will continue to influence the direction of NHC catalysis. However, 1,2,3-triazol-5-ylidenes play no role in this thesis and will not be discussed further.

1.2.9 Ditopic N-Heterocyclic Carbenes

Ditopic NHCs are defined as an N-heterocycle possessing carbenoid centres at two positions, and hence may be used to coordinate multiple main group/transition element species.⁹⁴ Such species have been most commonly based on an imidazole framework, and have been accessed by three methods: C-H activation of an imidazol-2-ylidene NHC metal complex at the C4 position (Scheme 1.2.6),⁸⁵-⁸⁸ reduction of a imidazol-2-ylidene metal complex (Scheme 1.2.7),⁸⁹-⁹³ and deprotonation of a free imidazol-2-ylidene or imidazol-2-ylidene metal complex (Scheme 1.2.8).⁹⁴,⁹⁵ The first example of an anionic dicarbene synthon was isolated by Robinson in 2010, who reported the lithiation of free IDipp at the C4 position to form an anionic dicarbene coordination polymer, which crystallizes from THF as a one dimensional chain with bridging lithium cations between the C2 and C4 carbene centres.⁹⁵ Coordination of a Lewis acidic moiety such as BÉt₃ or AlCl₃ occurs selectively at the more basic C4 position to afford anionic imidazolin-2-ylidenes.⁹⁶ Interestingly, if a Lewis acid is relatively weak or bulky, lithiation (or reduction) of ‘normal’ imidazol-2-ylidene-Lewis acid adducts results in ‘normal to abnormal’ rearrangement, with the stronger Lewis acid ending up at the C4 position of the ring.⁹⁷ In contrast, Stalke and coworkers have reported that the lithiation of the strong adduct IDipp-BH₃ yields the isolable C4
lithiated product,

suggesting that some lability of the C2 coordinated species is necessary for this rearrangement to occur.

Scheme 1.2.6. Ditopic carbene formation via C-H activation

Scheme 1.2.7. Ditopic carbene formation via reduction

Scheme 1.2.8. Ditopic carbene formation via deprotonation of an abnormal NHC-borane adduct

Tamm and coworkers have reported the use of a ‘normal’ anionic NHC derived from the lithiation of an abnormal NHC-B(C₆F₅)₃ adduct as a spectator
ligand in Crabtree type olefin hydrogenation catalysts (Scheme 1.2.8). The resulting complexes \( \text{Ir}(\text{NHC-B(C}_6\text{F}_5)_3)\text{(COD)} \) are neutral and pseudo 3-coordinate, completing the coordination sphere at Ir with an interaction of the \textit{ipso} carbon of the N-aryl wingtip group of the NHC. The resulting hydrogenation catalysts are exceptionally active, and can be often used in neat substrate without the addition of a co-solvent. It was discovered that these ditopic carbenes are somewhat more donating than their parent neutral imidazol-2-ylidenes; the abnormal adduct \( \text{IDipp-B(C}_6\text{F}_5)_3 \) has a TEP of 2041.9 cm\(^{-1}\).

1.2.10 Cyclopropenylidenes

The coordination chemistry of 1,2-diaminocyclopropenylidenes (DACs) has been known since the 1970s, however, the first example of an isolable cyclopropenylidene was not reported until 2006, where Bertrand and coworkers reported the isolation of 1,2-

bis-(diisopropylamino)cyclopropenylidene from the reaction of the corresponding cyclopropenium salt with KHMS (Scheme 1.2.9). This species is a rare example of a stable carbocyclic carbene. DACs are characterized as strong electron donors but poor \( \pi \)-acceptors, for example 1,2-

bis-(diisopropylamino)cyclopropenylidene (TEP = 2044.1 cm\(^{-1}\); \( \text{(DAC)}\text{P(Ph) } \delta ^{31}\text{P} = -34.9 \text{ ppm}) \). The stability of such species is remarkable given their lack of steric protection of the carbene centre. Computational studies indicate that the stability of such systems is as a result of charge delocalization from the donor amino substituents, which raises the energy of the carbene LUMO. The sterically slim profile of the carbene has led to their incorporation in the main group trication [(carbene)\(_3\text{P}\)]\(^{3+}\) by Alcarazo and coworkers (Scheme 1.2.10), which has shown to be a highly \( \pi \)-accepting ligand with applications in Pt based catalyzed cycloisomerization of ortho-alkynated biaryls. The net electron withdrawing nature of this tricationic phosphine ligand imparts substantial Lewis acidity to the metal centre, which in turn, allows it to more strongly bind and activate the alkynyl fragment, which has been shown to be the rate limiting step of this reaction.
Another prominent subclass of the cyclopropenylidene family are the singlet 1,2-diarlycyclopropenylidenes. These species are unstable in free form, but have been known as ligands in transition metal chemistry for several decades. Their complexes can readily be formed by oxidative addition of 3,3-dichloro-1,2-diaryl-cyclopropene to a low valent metal centre, such as Pd(0), Rh(I) or Cr(-II) (Scheme 1.2.11). While the TEP of these ligands have never been determined, evaluation of their donor properties is possible via the earlier Mn scale of Müller and coworkers, which examines the carbonyl stretching frequency of phosphine complexes of the form Mn(Cp)(L)(CO)$_2$. The 1,2-diphenylcyclopropenylidene complex yields an asymmetric carbonyl stretch of 1948 cm$^{-1}$ (hexane), similar to that observed for P(OMe)$_3$ (1949 cm$^{-1}$ (CS$_2$), TEP = 2079.5 cm$^{-1}$), suggesting the overall poor donor ability of this carbene. Although correlation of this scale with the Tolman electronic parameter has not been established, and the quoted IR stretching frequencies above were obtained in different solvents, there does appear to be a casual correlation that more electron donating carbene ligands yield lower vCO stretching frequencies on this Mn based scale. For example PCy$_3$ (1925 cm$^{-1}$ (CS$_2$), TEP = 2056.4 cm$^{-1}$) and IDipp (1904 cm$^{-1}$ (nujol), TEP = 2050.2 cm$^{-1}$). However, this conclusion must be tempered by the π-acceptor ability of 1,2-diphenylcyclopropenylidene,
which can be evaluated on Ganter’s scale (see section 1.2.2) $\delta^{77}\text{Se} = 330$,\textsuperscript{131} which indicates a fairly high degree of $\pi$-acidity.\textsuperscript{19,20} Therefore, it is most reasonable to conclude that 1,2-diphenylcyclopropenylidene is a moderate $\sigma$-donor and a good $\pi$-acceptor. This suggestion is further supported by calculations of Bertrand and coworkers which have shown that the singlet-triplet gap in 1,2-diphenylcyclopropenylidene (38.8 kcal/mol) is substantially smaller than that of 1,2-diaminocyclopropenylidenes (58 – 59 kcal/mol).\textsuperscript{132} 1,2-diarylcyloprenylidenes have been applied as spectator ligands in Pd catalyzed C-C and C-N cross coupling reactions with much success by Wass and Herrmann, achieving exceptionally low catalytic loadings.\textsuperscript{124-127}

![Scheme 1.2.11.](image)

Scheme 1.2.11. Synthesis of a 1,2-diphenylcyclopropenylidene Cr complex by oxidative addition of 3,3-dichloro-1,2-diphenylcyclopropene.

1.2.11 Carbones

1.2.11.1 Carbodiphosphoranes

Carbones, a term coined by Frenking and co-workers,\textsuperscript{21} are a family of divalent carbon ligands which bear fundamental differences to carbenes. The unifying electronic structure of members of the singlet carbene family consists of orthogonal filled and vacant orbitals of $\sigma$ and $\pi$ symmetry, respectively, which may be stabilized by donor and/or acceptor interactions with the flanking groups. Carbones differ in that they possess two filled atomic orbitals on the central carbon atom.\textsuperscript{39,44,133-136} This configuration is enforced by coordination of two donor moieties to the central carbon atom (Scheme 1.2.12). Carbones have been alternatively represented as highly polarized allenes, as mesoionic carbenes, and as dative donor-acceptor complexes.\textsuperscript{133}
The first example of such a species was synthesized by Ramirez and coworkers in 1961, and features flanking PPh$_3$ groups (Ph$_3$PCPPh$_3$), and is known as hexaphenylcarbodiphosphorane (Scheme 1.2.13).$^{137}$ Although originally thought to be linear, a 1972 molecular structure of this species determined it is in fact bent in the solid state, with P-C-P angles of 130.1(6)$^\circ$ and 143.8(6)$^\circ$ for two crystallographically independent molecules.$^{138}$ A higher quality 1978 molecular structure of a second polymorph of hexaphenylcarbodiphosphorane features one molecule in an asymmetric unit and a P-C-P angle of 131.7(3)$^\circ$.$^{139}$ This difference indicates a flexible structure with a low bending energy. This aspect was addressed almost 40 years later by Frenking and coworkers, who in 2009 determined computationally that the equilibrium geometry for hexaphenylcarbodiphosphorane was 136.9$^\circ$, although the energy needed to stretch the P-C-P fragment to 180$^\circ$ is only 3.1 kcal/mol, indicating that the crystallographic differences observed likely arise from minor packing effects.$^{140}$ DFT calculations have indicated that the HOMO and HOMO-1 incorporate the lone pairs of $\sigma$ and $\pi$ symmetry on the central carbon atom.$^{141}$ The 1$^{\text{st}}$ and 2$^{\text{nd}}$ proton affinities of the central carbon atom are 280.0 and 185.6 kcal/mol, respectively, indicating the substantial double basicity at the central carbon atom.$^{21}$ Therefore, the most accurate resonance structure of this species is the structure shown (Scheme 1.2.13), with two lone pairs of electrons on the
central carbon atom. The TEP of this ligand has been determined to 2032 cm\(^{-1}\), indicating its extreme electron donor properties.\(^{142}\) Despite its high degree of electron richness, free hexaphenylcarbodiphosphorane is highly stable and has a melting point of 208-210 °C.\(^{137}\)

![Scheme 1.2.13. Synthesis of hexaphenylcarbodiphosphorane](image)

**Scheme 1.2.13.** Synthesis of hexaphenylcarbodiphosphorane

![Scheme 1.2.14. Diauration of hexaphenylcarbodiphosphorane](image)

**Scheme 1.2.14.** Diauration of hexaphenylcarbodiphosphorane

The coordination chemistry of hexaphenylcarbodiphosphorane has been explored for some time, and complexes of numerous transition metal and main group species have been reported.\(^{143}-158\) Most interestingly, coordination complexes featuring double ligation of the central carbon atom have been reported,\(^{148,159}\) for example, combination of two equivalents of AuCl(THT) with one equivalent of hexaphenylcarbodiphosphorane results in the complex \((\text{Ph}_3\text{P})_2\text{C}(\text{AuCl})_2\) (Scheme 1.2.14). There is a weak aurophilic interaction in the solid state with a bond length of 3.1432(2) Å. Coordination complexes featuring mono-protonated carbodiphosphoranes are also known.\(^{136,148,152,156}\) The additional π-basicity of carbodiphosphoranes is further supported by the isolation of the low-coordinate complexes \([(\text{Ph}_3\text{P})_2\text{C} \text{BH}_2]^+,\(^{160}\) and \([(\text{Ph}_3\text{P})_2\text{C})\text{Ni}(\text{CO})_2,\(^{147}\) revealing the efficacy of these ligands in stabilizing highly unsaturated coordination centres via donation of two pairs of electrons. Vidovic and coworkers have also used the 4-electron donor capability of carbodiphosphoranes in the stabilization of two coordinate phosphonium dications.\(^{161,162}\)
Baceiredo and coworkers reported in 2006 the isolation of an amino-substituted cyclic carbodiphosphorane. Similar to the per-aryl analogue, this species is quite stable and has a melting point of 141 °C. Remarkably, this ligand has a TEP of 2019.9 cm⁻¹, the lowest so far measured of any ligand, revealing the extreme donor capabilities of this system. Despite their remarkable donor properties, carbodiphosphoranes have not been expensively applied in catalysis, the sole example being the Cu and Au catalyzed hydroamination and hydroxyalkylation of alkenes with Baceiredo’s cyclic carbodiphosphorane (Figure 1.2.10). It has also been computationally predicted by Frenking and coworkers that carbodiphosphoranes may serve as more efficient ligands in Grubbs type olefin metathesis catalysts.

![Figure 1.2.10](image_url). An amino-substituted cyclic carbodiphosphorane supported catalyst for hydroamination and hydroxyalkylation of alkenes

1.2.11.2 Carbodicarbenes

Carbodicarbenes – the carbene analogues of carbodiphosphoranes - are described as a carbon centre flanked by two singlet carbenes. The first example, an acyclic bis(1,3-dimethylbenzimidazol-2-ylidene) substituted derivative was synthesized by Bertrand and coworkers in 2008 (Figure 1.2.11). Similar to what was observed for acyclic carbodiphosphoranes, the central C-C-C angle is 134.8(2)°, and the TEP of this system is 2030.1 cm⁻¹, indicating its very strong electron donor capability. The HOMO and HOMO-1 of this system incorporate the lone pairs of σ and π symmetry on the central carbon atom. Frenking and coworkers have calculated the first and second proton affinities of 294.3 and 168.4 kcal/mol for a similar (but yet un-synthesized) bis(1,3-
dimethylimidazol-2-ylidene) substituted derivative.\textsuperscript{21} The bending potential has also been investigated and found to be quite low, requiring only 3.2 kcal/mol to stretch this species to 180\degree from its equilibrium geometry.\textsuperscript{140} Such species have also been termed as "bent allenes", as an allenic resonance form of these species may be drawn (however, this resonance form should be considered extreme) (Figure 1.2.11).

![Figure 1.2.11. The first synthesized carbodicarbene and its allenic resonance form](image)

Theoretically, the construction of carbodicarbenes is quite modular,\textsuperscript{170} in that the selection of singlet carbenes of varying $\sigma$-donor and $\pi$-acceptor strengths may be used to tune the electronic properties of the carbodicarbene. The coordination chemistry of a ‘masked’ carbodicarbene, known as a tetraaminoallene, stabilized with the strongly $\pi$-accepting carbene (Me\textsubscript{2}N)\textsubscript{2}C was reported by Fürstner and Alcarazo in 2008.\textsuperscript{171} At first glance, this species may appear to be a simple allene, having a computed equilibrium geometry of 179.9\degree (Scheme 1.2.15). However, the bending potential of this species is quite low, requiring only 5.3 kcal/mol to bend to an angle of 136.9\degree.\textsuperscript{140} Concordantly, in the presence of a transition metal complex, such as [(Ph\textsubscript{3}P)Au]+, this species reacts to form $\eta^1$ complexes via the central carbon centre, as is observed for other carbodicarbenes (Scheme 1.2.15). In contrast, the typical ground state coordination mode of allenes to transition metal centres is $\eta^2$: Frenking and coworkers have suggested that the $\eta^1$ complexation of transition metals can be used as a fundamental distinguishing feature of carbones and classical allenes.\textsuperscript{172} The tetraaminoallene has first and second proton affinities of 282.5 and 151.6 kcal/mol, indicating significant $\sigma$ and $\pi$-basicity of the carbon centre; the doubly protonated species had also been isolated.\textsuperscript{21} The TEP of this species is 2022 cm\textsuperscript{-1}, indicating a highly nucleophilic carbon centre.\textsuperscript{142} A second example of this type of 'masked' carbodicarbene, which can be regarded as a bis-cyclic
alkylaminocarbene stabilized carbodicarbene, has been reported in 2014 by Bertrand and coworkers with a central C-C-C angle of 164.4(1)°.\textsuperscript{173}

![Scheme 1.2.15. Coordination chemistry of tetraaminoallenes](image)

The low bending energy of such ‘carbodicarbene like’ allenes is further evidenced in that such systems may be easily constrained to a heterocycle. Three species of this type are known, all reported by Bertrand and coworkers in 2008.\textsuperscript{174,175} Such species are commonly known in the literature as “cyclic bent allenes” although their allenic resonance form should be considered extreme. Two such systems are derived from 1,2-diphenylpyrazol-4-ylidenes where additional donor alkylamino or aryloxy substituents are present at the 3,5-positions (Figure 1.2.12, complexes A,B).\textsuperscript{174} The 3,5-bis(aryloxy) derivative A is the more stable derivative and can be prepared on a large scale in free form. While highly basic and reactive, the species is stable in the solid state, and decomposes only at 95 °C. The 1\textsuperscript{st} and 2\textsuperscript{nd} proton affinities of this species are 284.8 and 133.3 kcal/mol, respectively.\textsuperscript{21} Bertrand and coworkers have demonstrated the double basicity of these systems by the isolation of the doubly protonated species of B upon treatment of the precursor salt with HBF\textsubscript{4}.\textsuperscript{176} Interestingly, HOMA and NICS calculations carried out on the free cyclic bent allene A reveal significantly reduced aromaticity compared to 1,2,3,5-H derivative (values shown in parentheses): NICS(0) = -7.35 (-17.50); NICS(1) = -5.76 (-13.13); HOMA = 0.58 (0.86).\textsuperscript{176} It has been determined that this loss of aromaticity occurs due to exocyclic delocalization of the ring π electrons to the heteroatom substituted 3,5 positions, rather than to the endocyclic N-Ph positions. This is evident in the molecular structure of the free cyclic bent allene A

[28]
(Figure 1.2.12), where the endocyclic nitrogen atoms diverge from planarity, the sum of the angles about nitrogen being 347.1(3)° and 351.0(3)°. Molecular orbital calculations identify the HOMO and HOMO-1 as the lone pairs on the central carbon atom, however, the HOMO-1 π-type lone pair is delocalized through the adjacent carbon atoms, with the largest coefficient remaining on the central carbon atom.\(^{141}\) C-C bond lengths of the central C-C-C fragment are 1.370(4) and 1.386(3) Å, supporting a bond order of less than two for these positions.\(^{174}\) The cyclic bent allene has a TEP of 2034.9 cm\(^{-1}\), indicating the high electron releasing character of this ligand.\(^{12}\) Another example of a cyclic bent allene constrained to a four membered ring has also been reported by Bertrand and coworkers, with a calculated central C-C-C angle of 85.0° and a TEP of 2033.1 cm\(^{-1}\) (Figure 1.2.12, complex C).\(^{12,175}\) This species is unstable at room temperature, although stable transition metal complexes have been accessed.

**Figure 1.2.12. Cyclic bent allenes**

Despite the attractive ligand properties of carbodicarbenes, only three examples of their use in catalysis have been reported. Ong and coworkers reported in 2014 the synthesis of Pd complexes supported by tridentate bis-pyridyl flanked acyclic carbodicarbene framework.\(^{177}\) This species was shown to be an active catalyst in Suzuki and Heck cross-coupling, although no comparison to known catalysts was made. In 2014, Liddle and coworkers reported Rh carbodicarbene complexes of a similar ligand bearing flanking phosphines, and demonstrated its activity in the hydroamination of 1,3-dienes.\(^{178}\) While the transformations proceed with a high degree of site selectivity, the catalysis reported is not a significant improvement over established hydroamination
methods. However, in 2015, this method was extended to include the hydroarylation of dienes with a cationic variant of the same Rh catalyst.\(^{179}\) Interestingly, the addition of Li\(^+\) salts to the reaction mixture gave the best product yields. This was postulated to be the result of coordination of Li\(^+\) to the π-type lone pair on the central carbon atom of the carbodicarbene. It was demonstrated that the addition of LiBF\(_4\) to the precatalyst (featuring coordinated styrene), resulted in loss of styrene, presumably due to decreased electron richness of the metal centre and decreased π-backbonding to styrene upon Li\(^+\) coordination to the carbon centre. The significant π-donor abilities of carbodicarbenes have also been used in the stabilization of a dicationic borane by Ong and coworkers in 2014 (Scheme 1.2.16).\(^{180}\) Amazingly, the electronic stabilization of the unsaturated boron centre by two flanking carbodicarbenes is significant enough to render this dicationic boron species essentially non-Lewis acidic, as this species is incapable of coordinating THF.

![Scheme 1.2.16](image)

**Scheme 1.2.16.** Synthesis of a dicationic borane

1.2.11.3 Carbones – Definitions and Unifying Characteristics

Several carbones bearing mixed donor groups have also been reported,\(^{44}\) sometimes bearing a more weakly donating flanking group, such as a carbonyl or isonitrile. Carbones bearing at least one donor phosphine are typically nucleophilic at the central carbon atom, and participate in η\(^1\) complexation of transition metals, and in some cases can form geminally diaurated complexes.\(^{44}\)
It is important to note, however, that not every choice of donor flanking group leads to a species with carbone-like properties. For example, carbon suboxide, OCCCOCO, can be described using a dative resonance structure analogous to carbodiphosphoranes and carbodicarbenes, featuring a C(0) centre ligated by two carbonyl ligands.\(^{140,141,172}\) Despite the low bending energy calculated for carbon suboxide, this molecule has been observed to form \(\eta^2\) complexes with transition metals, as one would anticipate for simple allenes.\(^{181-183}\) Additionally, carbon suboxide has a very low 2\(^{nd}\) proton affinity (28.7 kcal/mol)\(^{21}\) when compared with other members of the carbone family (typically 130 – 200 kcal/mol), and hence is probably better described as a simple heterocumulene.

While the term ‘carbone’ was coined by Frenking and coworkers in 2008 to describe divalent carbon species with both \(\sigma\) and \(\pi\)-basicity,\(^{21}\) the boundaries of this family are presently unclear, and the term has never been formally defined in the chemical literature. Therefore, the following description is proposed:

A carbone is defined by three properties: (1) A carbone is comprised of a carbon atom bearing two lone pairs of electrons, and directly coordinated by two neutral singlet two-electron donor moieties. The lone pairs on the carbon centre may be stabilized by vacant acceptor orbitals on the flanking donor groups. (2) In the coordination sphere of a transition metal, \(\eta^1\) coordination to the metal centre through the central carbon atom must be observed. (3) Carbones have a high 1\(^{st}\) and 2\(^{nd}\) proton affinity. Therefore, addition of two equivalents of \(H^+\) to a carbone must result in double protonation of the central carbon atom. Geminally dimetalated species may also be isolated.

While this description provides clear, experimentally determinable criteria which differentiate carbones from carbenes and allenes, it is important to realize that there is a continuum, rather than a sharp division, between these respective species, and characterizing a species as belonging exclusively to one family or another is not always appropriate. For example, Alcarazo and Phukan have commented on the existence of a carbone type resonance structure in imidazolylidenes.\(^{44,184}\) In most cases, due to significant donation of the carbone \(\pi\) lone pair electrons to the CN \(\pi^*\) orbital, this structure bears extremely little
contribution to the overall ground state. However, in the special case of a 2,2’-bipyridal derived carbene (Figure 1.2.13), this back donation becomes much less favourable due to the aromatic character of the exocyclic pyridyl groups, and the resulting divalent carbon species has a remarkably high 2\textsuperscript{nd} proton affinity (133.8 kcal/mol), much like that of a carbone.\textsuperscript{184} The doubly protonated derivative of this species has also been isolated by Weiss and coworkers.\textsuperscript{185}

![Figure 1.2.13. Carbone and carbene type resonance forms of a 2,2'-bipyridyl stabilized divalent carbon ligand](image)

Analogously, imidazol-4-ylidenes and other similar carbene derivatives have been termed ‘mesoionic carbenes’ in the chemical literature, due to the necessity of formally zwitterionic resonance structures when describing their ground state, and despite the absence of any reasonable resonance structures resembling a classical singlet carbene.\textsuperscript{28,65} However, it is possible to alternatively represent such molecules using a carbone type resonance form (Figure 1.2.14). While the contribution of this resonance structure to the ground state of imidazol-4-ylidenes has never been discussed in the literature to our knowledge, this suggestion is in line with the high 2\textsuperscript{nd} proton affinity that has been calculated for such species (144.6 kcal/mol).\textsuperscript{63}

![Figure 1.2.14. Carbone and carbene type resonance forms of imidazol-4-ylidenes](image)

Fundamentally, it is of significant importance to be always guided by the frontier molecular orbitals in predicting the chemical behavior and determining the
most accurate resonance forms of a divalent carbon ligand. Carbones have been alternatively described as allenes, mesoionic carbenes, or by invoking a captodative resonance structures. The true nature of the molecule depends largely on the donor/acceptor nature of the flanking groups, and often several resonance forms must be invoked to adequately describe the ground state structure of such species.

1.2.12 Ylids

The chemistry of ylids has been studied since the days of Wittig, and his famous use of phosphorus ylids in olefination reactions. Ylids are neutral dipolar molecules which bear a negative charge and a lone pair of electrons on carbon, which is proximal to a formally positively charged donor moiety. While such systems may be represented by olefinic resonance structures, their representation as zwitterionic dipolar molecules is probably more representative of their chemistry – a clear analogy to the allenic and zwitterionic resonance forms of carbones. Carbene ylids have been known for some time, and were explored as ligands for transition metals by Alacarazo and Fürstner in 2008 (Scheme 1.2.17). In general, such systems are very strong electron donors, the TEP of 1,3-dimethyl-2-methyleneimidazole is 2021.5 cm$^{-1}$. A recent report of the synthesis of non-symmetric carbodicarbenes involved the reaction of a carbene ylid with electrophillic thiomethoxy imidazolium salts. Ylides will not be play a significant role in this thesis.

Scheme 1.2.17. Synthesis of an Au Complex of an NHC ylid
1.2.13 Dative Bonding in Main Group Compounds – an Evolving Discussion

As we move down the periodic table, more diffuse orbitals less readily participate in π-bonding due to reduced orbital overlap,\(^{187}\) and as such, heavier elements tend to prefer structures with non-bonding electrons rather than forming multiple bonds. For example, in the crystallographically characterized main group complexes (CAAC)SiSi(CAAC) and (CAAC)CC(CAAC), the C-Si-Si fragment is significantly bent (101.22(13)°),\(^{188}\) indicating the presence of a lone pair of electrons in the Si atom (Figure 1.2.15). The analogous C-C-C fragment is essentially linear (178.86(14)°),\(^{189}\) indicating electron sharing between the vacant CAAC p orbital and the central C\(_2\) fragment. However, this bonding/nonbonding distinction between first row and heavier main group compounds is not absolute. Both NHC stabilized carbones and silylones have been accessed and display significantly bent structures,\(^{169,190}\) indicating the presence of non-bonding electrons on both element centres, despite the presence of acceptor p orbitals of the flanking carbenes. The geometric deformations that exist in species invalidate any conventional electron sharing resonance form, but which structure should be considered most appropriate in such cases; zwitterionic or dative? (Figure 1.2.16)

![Figure 1.2.15. Electron Structures of CAAC complexes of Si\(_2\) and C\(_2\)](image)

![Figure 1.2.16. Dative and zwitterionic resonance forms of a carbodicarbene](image)
While dative bonds are ubiquitous in transition metal chemistry, their application to main group and organic compounds remains somewhat controversial.\textsuperscript{191-193} Dative bonds are characterized as being weaker than normal covalent bonds, and favour heterolytic dissociation. The argument between a dative and dipolar structure is also based on the legitimacy of formal charges produced. Certainly we do not consider a coordination compound such as Pd(PPh\textsubscript{3})\textsubscript{4} to be a zwitterionic Pd(-IV) species, but rather is better described by dative structure featuring four phosphines coordinated to a Pd(0) centre. In main group compounds, however, this distinction becomes muddied. In cases such as H\textsubscript{3}N-BH\textsubscript{3} a dative structure is indicated, as a zwitterionic structure enforces incorrect charges on the B and N element centres.\textsuperscript{192} Conversely, It has been proposed that the carbene hexaphenylcarbodiphosphorane is best described by a dipolar structure.\textsuperscript{193} This is supported by computations which indicate a significant partial charge of -1.43e on the central carbon atom.\textsuperscript{140} However, Bertrand’s acyclic carbodicarbene (Figure 1.2.16) has similarly high σ and π-basicity, yet the calculated partial charge on the central carbon is only -0.50e, indicating a dipolar structure may be less accurate in this case.\textsuperscript{140}

While it is difficult to generalize about the bonding in such systems, it would seem that dative bonds are more appropriate in describing donor-acceptor bonds from more electronegative element centres to less electronegative ones. This condition alleviates the unrealistic formal charges resulting from enforcing conventional covalent bonding in such species. For example, a formal line structure of carbon monoxide (O≡C) would indicate a dipolar structure, with formal positive and negative charges on the oxygen and carbon atoms, respectively. This is obviously inaccurate due to the lack of any significant dipole moment in this molecule. A similar situation can be illustrated in H\textsubscript{3}N-BH\textsubscript{3}; the formal charges imparted by a dipolar covalent structure are the opposite of the true charge distribution.\textsuperscript{192} The use of dative bonds in such compounds ameliorates these issues.

In cases of a less electronegative ‘donor’ element bound to a more electronegative element, such as in carbodiphosphoranes and in phosphine
oxides, the zwitterionic representation is probably more correct, as this leads to realistic formal charges on the element centres. In cases involving donor-acceptor interactions between molecules of similar or the same electronegativity, such as in carbodicarbenes, both structures should be considered. The distribution of charges in the molecules is likely represented by a combination of both resonance structures. It is above all important to recognize that line structural drawing is simply a tool that chemists have invented to describe chemical bonding. While this system is adequate to describe most organic compounds accurately, its conventions are based on empirical observations, not fundamental chemical laws. Therefore, in rare cases where a molecule’s chemical properties are not described well by any classical structure, we should not hesitate to step outside the boundaries of convention.

In this thesis, every effort has been made to represent molecules accurately, where the frontier molecular orbitals are best described by the resonance structures shown. For the purpose of clarity, ligand structures are represented as ‘organometallic style’ arrowless dative structures; no attempt is made to distinguish between covalent and strong dative bonds within organic fragments. Formal charges within zwitterionic molecules are not typically assigned to specific atoms or fragments, except for the purposes of clarification, as the charges that arise from these conventions of bonding notation often bear little insight to reality.

1.3 Hydrogenation Catalysis

As chapter 3 will explore the synthesis of some novel olefin hydrogenation catalysts, it is appropriate to give a brief overview of the field. Hydrogenation catalysis was first observed by Sabatier in the early 1900s, who observed the addition of hydrogen to unsaturated oils over a finely divided Ni catalyst. A similar process bearing Sabatier’s name is used today for the hydrogenation of CO₂ to methane. For his efforts he was awarded the 1912 Nobel prize in chemistry. While heterogeneous hydrogenation has continued to play an important role in the development of the field, the more readily modifiable homogeneous catalysts developed in the 1960s and 70s allowed the
development of chemoselective, diastereoselective, and enantioselective hydrogenation methods, and have remained the subject of intense research.

1.3.1 Rh and Ir based Catalysts

The first highly active homogenous hydrogenation catalyst, Rh(PPh₃)₃Cl, was reported in 1965, and was studied for hydrogenation catalysts by Wilkinson and co-workers.¹⁹⁵,¹⁹⁶ This species, now commonly known as Wilkinson’s catalyst, hydrogenates olefins chemoselectively in the presence of other unsaturated functionalities, including carbonyl, nitrile and nitro groups.¹⁹⁷ Less hindered olefins are hydrogenated more efficiently than highly substituted or bulky olefins. The mechanism of this hydrogenation was elucidated by Halpern and coworkers (Scheme 1.3.1).¹⁹⁸ Phosphine dissociation frees a coordination site at the metal centre, which is followed by coordination and oxidative addition of H₂ to form a 16-electron Rh(III) dihydride species. Olefin coordination at the vacant site is followed by insertion of the olefin into a metal hydride. Reductive elimination of the alkane regenerates the catalytically active species.
Cationic Rh species of the form [Rh(diene)(phosphine)]+ were investigated for the hydrogenation of ketones, olefins, and alkynes by Schrock and Osborn.\textsuperscript{199-202} In general, these species are active hydrogenation catalysts that initially form unsaturated cationic [RhH\textsubscript{2}(phosphine)]\textsuperscript{+} species under hydrogen atmosphere, with loss of the hydrogenated diene. Many mechanistic pathways are known to exist with this system, which depend on the basicity of the phosphine ligand as well as the nature of the substrate.\textsuperscript{202} Enantioselective versions of these catalysts have been established, typically by incorporation of a chiral chelating diphosphine in complexes [Rh(P\textsubscript{2})(diene)]\textsuperscript{+}.\textsuperscript{203} Famously, Knowles and coworkers developed an asymmetric synthesis for L-DOPA, used to treat Parkinson’s disease, using [Rh(COD)(DiPAMP)][BF\textsubscript{4}] (Scheme 1.3.2).\textsuperscript{204} William Knowles shared the 2001 Nobel prize with Ryoji Noyori and Barry Sharpless for his development of asymmetric hydrogenation.\textsuperscript{205}
Scheme 1.3.2. Asymmetric hydrogenation in the synthesis of L-DOPA by a chiral Rh catalyst

While Ir analogues of Wilkinson’s catalyst do not hydrogenate olefins due to more robust Ir-PPh₃ bonds and a lack of catalyst pre-equilibrium with Ir(PPh₃)₂Cl,²⁰⁶ cationic Ir complexes were first studied by Crabtree and coworkers for the hydrogenation of olefins in 1977, and were found to be exceptionally active catalysts, surpassing activities obtained with Rh based systems.²⁰⁷,²⁰⁸ Remarkably, species including [Ir(COD)(py)(PCy₃)][PF₆] (now known as Crabtree’s catalyst), can efficiently hydrogenate tri-substituted and even tetra-substituted olefins; very challenging substrates that few modern catalysts are capable of reducing. Importantly, non-coordinating cations are necessary for efficient catalysis. The mechanism for this hydrogenation is thought to proceed through initial hydrogenation of the diene to form [IrL₂(solv)ₓ]⁺, which reacts with two equivalents of H₂ and an olefin to form [IrL₂H₂(H₂)(olefin)]⁺.²⁰⁹,²¹⁰ Olefin insertion into an Ir-H bond is followed by oxidative addition of the coordinated dihydrogen to form the Ir(V) species [IrL₂H₃(alkyl)]⁺, which reductively eliminates the alkane to turn over the catalytic cycle. These catalysts are also capable of functional group directed diastereoselective hydrogenations, whereby a functional group binds to the metal centre which delivers H₂ exclusively to one face of an olefin, making them attractive catalysts in organic synthesis (Scheme 1.3.3).²¹¹,²¹² However, Ir based catalysts are typically more sensitive to functional groups than Rh(PPh₃)Cl, and can be deactivated by strongly basic functionalities such as nitrile.²⁰⁶ Chiral chelating bidentate ligands have also been applied successfully in enantioselective versions of the catalyst.²¹⁰,²¹³,²¹⁴ A common asymmetric
framework is based on chiral phosphinoxazolines, known as Ir-PHOX systems (Figure 1.3.1).

Scheme 1.3.3. Directed hydrogenation of terpinen-4-ol by a cationic Ir catalyst

Figure 1.3.1. A cationic Ir-PHOX enantioselective olefin hydrogenation catalyst

1.3.2 Ru Catalysts.

Ru based olefin hydrogenation catalysts have typically received less attention than Rh and Ir based systems. RuHCl(PPh3)3 was known as early as 1965 to be a highly active catalyst for unactivated monosubstituted olefins, however, its activity drops off sharply as the bulk around the substrate is increased; the catalyst hydrogenates disubstituted olefins only very slowly. More recently reported catalysts include species such as RuHCl(CO)(PCy3)2 and RuHCl(CO)(NHC)(PR3). These species are active in the hydrogenation of unfunctionalized mono and disubstituted olefins, however at much slower rates than Rh or Ir based systems. Generally, Ru catalyzed hydrogenations of hindered olefins are often restricted to substrates where a directing group is present. Typically, the mechanism for Ru catalyzed hydrogenations of unfunctionalized olefins involves olefin coordination and insertion into a Ru-H bond to form a Ru-alkyl species. This is followed by rate limiting H2 coordination and σ-bond

[40]
metathesis of H$_2$ to generate alkane and reform the catalyst (Scheme 1.3.4). However, it is still a matter of debate in some systems whether the hydrogenolysis of the Ru-alkyl species proceeds through a $\sigma$-bond metathesis step or an addition-elimination route.

Ru has been much more widely studied as a C=X bond hydrogenation catalyst (X = O, NR). Ru-hydrido catalysts containing chiral chelating ligands featuring acidic N-H groups in the coordination sphere of the metal centre were developed by Noyori and coworkers and were found to be efficient catalysts for the asymmetric hydrogenation of ketones, as this functionality allowed an outer sphere mechanism whereby proton and hydride are simultaneously delivered to a ketone substrate (Scheme 1.3.5). For his efforts in the development of asymmetric ketone hydrogenation, Ryoji Noyori shared the 2001 Nobel prize with William Knowles and Barry Sharpless.

![Scheme 1.3.4. Mechanism of Ru catalyzed hydrogenation of unfunctionalized olefins](image-url)
Scheme 1.3.5. Schematic diagram for the outer sphere hydrogenation of ketones by an amido-Ru species

1.3.3 First Row Hydrogenation Catalysts

In recent years, several breakthroughs have been made in the field of hydrogenations catalysed by inexpensive first row metal complexes. Historically, highly active homogeneous hydrogenation catalysts have been universally based on precious metals including Rh, Ir, Ru or Pd. The development of base metal hydrogenation catalysts represents a significant advance toward green, sustainable catalyst technologies.

The most significant advances in the field of base metal catalyzed olefin hydrogenations have been made by the group of Paul Chirik. In 2004 they reported a Fe bis(dinitrogen) complex bearing a bis(imino)pyridine chelate as an active catalyst for the hydrogenation of unfunctionalized olefins.\(^{232}\) Subsequent studies indicated that this species, originally thought to be Fe(0), was actually Fe(II) and the two electrons instead reside on the dianionic diradical chelating ligand (Figure 1.3.2, left).\(^ {233}\) Further refinements to this original system have produced catalysts of remarkable activity based on both Fe and Co,\(^{234,235}\) and functional group directed diastereoselective hydrogenations,\(^ {236}\) as well as asymmetric hydrogenations\(^ {237-239}\) have been reported. Some functional group tolerance has been achieved,\(^ {240}\) although this is more limited than with classical Rh and Ir based systems. A notable drawback of these systems is their extreme sensitivity to air and moisture.
The asymmetric hydrogenation and transfer hydrogenation of ketones with base metal catalysts had been extensively studied by the groups of Morris, Gao and Mezzetti. Such catalysts are typically Fe complexes supported by multidentate chiral chelating ligands.\textsuperscript{241-246} Notably, Morris and coworkers synthesized a Fe system bearing a tetradentate amine(imine)diphosphine scaffold which was found to be highly active and selective in asymmetric ketone hydrogenations, achieving TOF as high as 242 s\textsuperscript{-1}, and ee as high as 99 \% (Figure 1.3.2, right).\textsuperscript{246} These hydrogenations are thought to proceed through an outer sphere hydrogen transfer, where hydride and proton are simultaneously delivered to an unsaturated substrate by a proximal Fe hydride and an N-H moiety, analogous to the mechanism for Noyori type Ru catalyzed ketone hydrogenations (Scheme 1.3.5).

1.4 The LANXESS Project

The chemistry in chapters 2 and 3 was carried out under industrial partnership with the multinational chemical firm LANXESS in search for new catalysts for hydrogenation of the olefinic residues in nitrile butadiene rubber (NBR) to produce hydrogenated nitrile butadiene rubber (HNBR) (Scheme 1.4.1).\textsuperscript{247} HNBR is known for its strength and long term resistance to degradation, as well as its durability in contact with oils, ozone, and other corrosive chemicals. HNBR is commonly found in high temperature applications in automotive industry and construction industries. Wilkinson’s catalyst, RhCl(PPh\textsubscript{3})\textsubscript{3}, is currently used for this hydrogenation on an industrial scale, however, due to the rising cost and
scarcity of Rh, we are interested in the development of a catalyst with comparable activity and selectivity which based on a less expensive metal. Ru was selected as a metal of choice due to its moderate cost (approximately 10% that of Rh), and the fact that some Ru based NBR hydrogenation catalysts are known in the literature, although their activity is poor compared to Rh based systems. The goal of this project is to develop a suitable ligand platform to promote highly active and selective hydrogenation catalyst which is based on Ru.

Scheme 1.4.1. The hydrogenation of Nitrile-Butadiene Rubber (NBR) to hydrogenated nitrile butadiene rubber (HNBR)

1.5 References

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Chapter 2. Coordination Chemistry of Anionic C4 bound Imidazolyldienes

2.1 Introduction

2.1.1 Motivation

The motivation of this research project was the synthesis of highly active and selective Ru based catalysts for the olefin selective hydrogenation of nitrile butadiene rubber (NBR) (Scheme 2.1.1), in conjunction with our industrial partners LANXESS. Wilkinson’s catalyst, RhCl(PPh₃)₃, is currently used for this process. As Rh is one of the most expensive metals on the periodic table, it is highly desirable to synthesize a catalyst of comparable activity based on a cheaper metal. Ru based catalysts for the hydrogenation of unfunctionalized olefins are generally much less active compared to systems based on Rh and Ir, however olefin selectivity in some catalytic systems has been observed.¹⁶ It has been established some in Ru catalysts that the replacement of phosphine ligands for an N-heterocyclic carbene (NHC) results in an increase in the catalytic activity.⁶,⁷ This effect is thought to be due to the stabilization of low coordinate Ru species formed during catalysis. Therefore, in an attempt to produce more highly active Ru based catalysts, we have attempted to synthesize coordinatively unsaturated Ru-hydride species incorporating spectator ligands that are significantly more electron donating than NHCs.

Scheme 2.1.1. The hydrogenation of nitrile-butadiene rubber (NBR)

2.1.2 Abnormal, Anionic and Ditopic Imidazolyldienes

N-heterocyclic carbenes (NHCs) have been responsible for significant advances in transition metal, organic and main group chemistry.⁸-¹⁸ Their tunable
steric demands together with their strong donor ability have proven useful in numerous catalytic transformations, notably in olefin metathesis and in cross coupling reactions. The utility of NHCs as organometallic ligands is often due to their ability to stabilize highly coordinatively unsaturated transition metal species. In this vein, an interesting extension to this ligand class involves the notion of generating anionic NHCs, which have been shown to be more strongly electron donating than their neutral counterparts. Additionally, NHCs bound at the “abnormal” C4 position represent an interesting subclass of carbenes, as they too have been shown to be more electron donating than their normally bound relatives.

The first example of an imidazol-4-ylidene or “abnormally bound” NHC was reported by the Crabtree group in 2002. Since that time, the synthesis and properties of abnormal NHCs have been the subject of much research. Although, generally more unstable than C2 bound ‘normal’ NHCs, Bertrand and coworkers have reported the isolation of a free imidazol-4-ylidene in 2010, where the C2 position was blocked by an aryl group (Scheme 2.1.2). In general, C4 bound NHCs are more electron donating than their normally bound relatives, which make them attractive spectator ligands in homogeneous catalysis. Indeed, there have been literature reports of catalysts with abnormal carbenes demonstrating superior activity when compared with normal NHCs. However, it has also been observed that C4 bound imidazolyldienes are more fragile than their C2 bound isomers, and can more readily be protonated or reductively eliminate from a metal centre.
Lithiated imidazolylidene based anionic dicarbenes were isolated by Robinson in 2010 by lithiation of IDipp at the C4 position. Selective coordination of a neutral electrophile to the C4 position allows isolation of the anionic NHC as its Li salt. To date, anionic carbenes and their metal complexes have been accessed by deprotonation of free or metal bound neutral N-heterocycles, C-H activation, and by reduction of an NHC in the presence of a metal source. These reactions often require that the metals involved are either stable to reducing conditions, or are tolerant of the strong basicity of the anionic NHC alkali salt. While Robinson has reported that `normal` anionic NHCs can be accessed by selective coordination of a Lewis acid to the more reactive C4 positions of a lithiated anionic dicarbene, Stalke and coworkers demonstrated in 2011 that precoordination of the NHC to the strong Lewis acid BH₃, followed by deprotonation leads to the C4 lithiated product. Interestingly, the use of a less Lewis acidic borane, such as BEt₃, results in C2 to C4 migration of the borane upon subsequent heating (Scheme 2.1.3). Despite Stalke’s viable route to C4 lithiated anionic NHCs, no coordination chemistry of such ligands had since appeared in the literature. This chapter describes the synthesis and characterization of the first imidazolylidenes that are both anionic and C4 bound to the metal centre.

Scheme 2.1.2. Preparation and decomposition of an abnormal NHC
2.2 Results and Discussion

2.2.1 Synthesis of a C4 Lithiated Imidazol-2-ylidene-Borane

We envisioned binding a metal at the C4 position of an anionic imidazolylidene. This configuration was anticipated to afford a ligand of exceptional donor strength, due to the potential additive effects of the strong donor properties of anionic carbenes and abnormal imidazolylidenes.

Addition of the NHC IDipp to BF₃(ET₂O) yielded the normal adduct IDippBF₃ 2-1, which was isolated in a 95% yield and is stable towards air and moisture (Scheme 2.2.1). This neutral adduct can be subsequently deprotonated by the addition of nBuLi solution at -45 °C, whereupon the lithiated species 2-2 was isolated by precipitation with pentane in a 97% yield as a colourless solid. In THF-d₈ solution, the remaining imidazol-5-yl proton resonates at 6.27 ppm in the ¹H NMR spectrum. The two flanking Dipp groups display magnetic inequivalence in their NMR spectra, affording two septets integrating to two protons each, and four doublets integrating to six protons each in the ¹H NMR spectrum. A ⁷Li NMR spectrum displays a singlet at -1.25 ppm. The ¹⁹F NMR spectrum reveals a 1:1:1:1 quartet at -141.3 ppm with a coupling constant of 36 Hz, arising from one bond coupling with the adjacent ¹¹B atom, which has a nuclear spin of 3/2. A corresponding normal quartet is observed in the ¹¹B NMR spectrum at -2.3 ppm. A ¹³C{¹H} resonance for the Li bound imidazolyl carbon atom could not be identified, likely due to coupling with the quadrupolar ⁷Li centre. A variable
amount of THF solvent remains bound to the Li centre, which ranges typically from 3 to 0.7 equivalents, and is dependent on how long 2-2 is dried under vacuum. This value can be readily quantified by simple integration of the $^1$H NMR spectrum to ensure correct stoichiometry in subsequent transformations.

Interestingly, a C$_6$D$_6$ solution of 2-2 displays multiple broad species in its $^1$H NMR spectrum. It is likely that aggregation of 2-2 occurs in non-coordinating solvents to yield clusters of differing nuclearity, giving rise to the broad signals observed. 2-2 decomposes slowly at ambient temperature but can be stored at -45 °C under N$_2$ atmosphere for a period of months without loss of purity.

Scheme 2.2.1. Synthesis of 2-1 and 2-2

Our initial foray into the coordination chemistry of 2-2 involved reactions with Ru sources including RuHCl(PPh$_3$)$_3$, RuCl$_2$(PPh$_3$)$_3$, RuHCl(CO)(PPh$_3$)$_3$, and [Ru(p-cymene)Cl$_2$]. In all cases, broad product distributions were observed. The formation of black insoluble material from several reactions suggested that reduction to Ru(0) may be a competing reaction to ligand substitution. Therefore, synthesis of a Ru complex via transmetalation from a Group 11 complex was attempted, as this is a well-established methodology for the incorporation of challenging ligands to the coordination sphere of a metal.$^{61}$

2.2.2 Group 11 Complexes of An Anionic Imidazolin-4-ylidene

Au is known to form stable complexes with reactive carbon centres due to its high carbophilicity,$^{62}$ so the isolation of an Au complex was first attempted.
Stirring a solution of 2-2 with 0.9 equivalents of AuCl(PPh₃) in THF results in the generation of the abnormally bound anionic NHC complex Au(IDippBF₃)(PPh₃) 2-3 which can be isolated in a 79% yield (Scheme 2.2.2).

**Scheme 2.2.2.** Synthesis of 2-3.

![Scheme 2.2.2. Synthesis of 2-3.](image)

**Figure 2.2.1.** Molecular structure of 2-3. Most of the molecule is positionally disordered and was modelled over two positions. Atoms were refined anisotropically where possible. Thermal ellipsoids are displayed at 50% probability. (right): A wireframe structure of 2-3 showing both components of the positional disorder. Colours: C, grey; Au, gold; P, purple; F, yellow-green; N, blue; B, pale yellow.

A highly disordered molecular structure of 2-3 was obtained from THF/pentane solution (Figure 2.2.1), confirming the C4 binding mode of the ligand. In the solid
state, 2-3 is disordered over two spatially close positions, both of which share the positions of the P atom and one of the phenyl rings in the PPh₃ ligand. Unfortunately, the extreme level of disorder precludes any meaningful discussion of the bond metrics. In C₆D₆ solution, 2-3 displays a singlet in the ³¹P {¹H} NMR spectrum at 42.3 ppm and a 1:1:1:1 quartet in the ¹⁹F NMR spectrum at -137.9 ppm with a coupling constant of 33 Hz. In the ¹H NMR spectrum, the remaining abnormal imidazolyl proton is observed at 6.83 ppm as a doublet with a ⁴Jₚ,ₜ coupling constant of 1.1 Hz.

Ag is commonly employed as an NHC transfer reagent, and therefore we next investigated whether a Ag complex of the anionic abnormal NHC 2-2 could be obtained. It was found that stirring a suspension of 2-2 with AgCl in THF cleanly generated a homoleptic anionic Ag complex of the formula Li[(IDipp-BF₃)₂Ag] 2-4 (Scheme 2.2.3). Crystals of the THF solvate, [(THF)₃Li][(IDipp-BF₃)₂Ag], were grown from THF/pentane and were analyzed by single crystal X-ray diffraction (Figure 2.2.2). In the solid state, the geometry at Ag is linear with coordination by two NHCs via the C4 positions. The average Ag–C distance is 2.090(3) Å. There is a F-Li dative interaction in the solid state with a bond length of 1.882(6) Å. In THF-d₈ solution, the Ag bound C atom was observed to resonate at 161.5 ppm in the ¹³C{¹H} NMR spectrum, and coupling of the carbon centre to ¹⁰⁹Ag and ¹⁰⁷Ag is observed with coupling constants of 184 and 159 Hz, respectively.

Scheme 2.2.3. Synthesis of the homoleptic C4 coordinated NHC Ag salt 2-4
2.2.3 Ru Complexes of an Anionic Imidazol-4-ylidene

We next investigated whether transmetalation to Ru could be achieved with the anionic abnormal NHC Ag complex 2-4. It was found that stirring equimolar amounts of 2-4 and [Ru(p-cymene)Cl]$_2$ in THF for 16 h resulted in a dark red solution, which upon workup afforded crystals of dark red [Ru(IDipp-BF$_3$)(p-cymeme)Cl]$_2$ 2-5 in 63% yield (Scheme 2.2.4). Complex 2-5 is a rare example of an abnormally bound Ru NHC species, and the first example of a Ru complex bearing a $\mu^1$ bound anionic NHC. In THF-d$_8$ solution, four doublets are observed in the alkyl region of the $^1$H NMR spectrum, corresponding to the four inequivalent NHC-iPr groups (Figure 2.2.4). Broad resonances are attributable to p-cymene moiety. A single crystal X-ray analysis (Figure 2.2.3) confirmed the dimeric nature of 2-5 in which the two Ru centres are bridged by chloride atoms. The Ru–C$_{\text{NHC}}$ distance was determined to be 2.119(2) Å, slightly longer than the length of 2.084(7) Å reported for the abnormal NHC complex Ru(p-cymene)(1,3-dimethyl-2-phenylimidazol-4-yl)Cl$_2$, which we postulate is attributable to steric factors.
Scheme 2.2.4. Transmetalation of an anionic imidazol-4-ylidene to Ru

Figure 2.2.3. Molecular structure of the dimer 2-5. Thermal ellipsoids are displayed at 50% probability. iPr groups on the NHC and hydrogen atoms are removed for clarity. Colours: C, grey; Ru, magenta; Cl, green; F, yellow-green; N, blue; B, pale yellow.

Interestingly, a CD$_2$Cl$_2$ solution of 2-5 at room temperature gives rise to a broad, largely featureless $^1$H NMR spectrum (Figure 2.2.4). Upon cooling to 0 °C, the signals sharpen to reveal the presence of two species in a 1:0.66 ratio (Figure 2.2.5). Further cooling to -20 °C and -40 °C alters this ratio to 1:0.60 and 1:0.50 respectively, consistent with an equilibrium between two species. Each species
contains an $\eta^6$ p-cymene ring and a C4 bound IDipp-BF$_3$ ligand. Upon further cooling to -80 °C, signals for the minor component broaden into the baseline of the NMR spectrum, while sharper resonances are observed for the major component (Figure 2.2.5). This behavior is believed to be the result of monomer-dimer equilibrium with the dominant species being the dimer at low temperature. The observed broadening at -80 °C in the minor species is attributed to the movement of the chloride ligand in monomeric Ru(IDippBF$_3$)(p-cymene)Cl between two magnetically inequivalent positions on the NMR timescale. We cannot rule out the possibility of conformational isomers of dimeric 2-5 giving rise to the observed equilibrium, however, no such mixture is observed in the $^1$H NMR spectrum in THF-d$_8$. High temp variable temperature $^1$H NMR experiments unfortunately did not shed light on this dynamic process. A 1,1,2,2-tetrachloroethane-d$_2$ solution of 2-5 displays very broad resonances up to 80 °C, and higher temperatures result in significant decomposition to 2-1 and an unidentified Ru(p-cymene) species.
Figure 2.2.4. $^1$H NMR spectrum of 2-5 in CD$_2$Cl$_2$ (top) and THF-d$_8$ (bottom).
Figure 2.2.5. Variable temperature $^1$H NMR (CD$_2$Cl$_2$) spectra of 2-5 displaying dynamic equilibrium, aromatic region. The remaining imidazol-5-yl proton is observed at approximately 7.0 ppm.

Interestingly, if LiCl is not removed from the reaction mixture, the LiCl adduct [Li(THF)(Et$_2$O)][RuCl$_2$(IDipp-BF$_3$)(p-cymene)] 2-6 can instead be crystallized from THF/Et$_2$O solution (Figure 2.2.6). In the solid state, the Ru-C$_{\text{NHC}}$ bond length is 2.110(6) Å, similar to what was observed for 2-5. The NMR spectra of 2-5 and 2-6 in solution are indistinguishable, save for the presence of a $^7$Li resonance at -1.95 in THF-d$_8$ solution in the case of 2-6. It is probable that solvated LiCl separates from 2-6 in solution, and the same monomer-dimer equilibrium observed in CD$_2$Cl$_2$ solutions of 2-5 also exists in solutions of 2-6. Complex 2-5 can be preferentially isolated from the reaction mixture by stirring in CH$_2$Cl$_2$/toluene for two hours, during which time LiCl precipitates from solution.
Figure 2.2.6. Molecular structure of 2-6. Thermal ellipsoids are displayed at 50% probability. iPr groups on the NHC and hydrogen atoms are removed for clarity. Disordered Et₂O was modelled isotopically over two positions; one position is shown for clarity. Colours: C, grey; Ru, magenta; Cl, green; F, yellow-green; O, red; N, blue; B, pale yellow; Li, pale purple.

In an attempt to generate a Ru-hydride species, complex 2-5 was reacted with two equivalents of Et₃SiH. Upon reaction workup, a new hydride species was observed in the ¹H NMR spectrum, displaying a singlet at -11.01 ppm in THF-d₈. Signals for a C4 bound IDipp-BF₃ ligand and η⁶ coordinated p-cymene were also present in this new species. However, significant decomposition to 2-1 was also observed. Attempts at recrystallization of this material resulted in complete decomposition via further formation of 2-1, suggesting that this hydride species may be unstable. An in situ catalytic reaction was also attempted: 40 equivalents of 1-hexene were added to a CD₂Cl₂ solution of 2-5, to which was added 42 equivalents of Et₃SiH. After 1 h at 45 °C, conversion to 2-hexene and triethyl(hexyl)silane was observed, however, only resonances corresponding to 2-
1 could be identified in the aromatic region of the $^1$H NMR spectrum. From this observation it was concluded that the anionic abnormal carbene is unstable in the presence of a hydride ligand, decomposing likely via reductive elimination to form 2-1; reactivity similar to what has been observed for C4 metalated Pd imidazolylidene hydride species (Scheme 1.2.5).\textsuperscript{35} It is unclear at this point whether the catalytically active species contains the ligand, or catalysis is instead occurring via a low coordinate Ru(0) species, but given the apparent instability of the hydride species at ambient conditions, it seems likely that a Ru(0) species is the actual catalyst. Hence this was not further investigated.

The dimeric 2-5 readily reacts with monodentate ligands including PPh$_3$ and CO to give the compounds Ru(IDipp-BF$_3$)(p-cymeme)(PPh$_3$)Cl 2-7 and Ru(IDipp-BF$_3$)(p-cymeme)(CO)Cl 2-8, respectively (Scheme 2.2.5), which were characterized crystallographically (Figure 2.2.7, Figure 2.2.8) and in solution. Complexes 2-7 and 2-8 each display ten doublets in the aliphatic region of the $^1$H NMR spectrum, indicative of restricted rotation of all five iPr groups, presumably resulting from steric congestion in the ligand field. The carbonyl complex 2-8 displays a CO stretching frequency at 2008 cm$^{-1}$. Ru-C$_{\text{NHC}}$ bond lengths are 2.118(3) Å and 2.068(1) Å in 2-7 and 2-8, respectively.
Scheme 2.2.5. Synthesis of NHC-Ru complexes 2-7, 2-8 and 2-9

Figure 2.2.7. Molecular structure of 2-7. Thermal ellipsoids are displayed at 50% probability. iPr groups on the NHC and hydrogen atoms are removed for clarity. Colours: C, grey; Ru, pink; Cl, green; P, purple; F, yellow-green; N, blue; B, pale yellow.
Figure 2.2.8. Molecular structure of 2-8. Thermal ellipsoids are displayed at 50% probability. iPr groups on the NHC and hydrogen atoms are removed for clarity. Colours: C, grey; Ru, magenta; Cl, green; F, yellow-green; N, blue; B, pale yellow.

Compound 2-5 also reacts with Ag(Et₂O)[B(C₆F₅)₄] in CH₂Cl₂ (Scheme 2.2.5), resulting in an immediate colour change from dark red to orange, and precipitation of AgCl from solution. The filtered reaction mixture was layered with hexamethyldisiloxane and pale orange needles of a new species 2-9 formed overnight. A molecular structure of 2-9 (Figure 2.2.9) revealed that upon halide abstraction, proton transfer has occurred between an iPr methine positions and the C4 position on the NHC, and this new carbanionic position was now coordinated to the Ru centre. This unusual binding is stabilized by an η²-interaction with the adjacent phenyl ring and an agostic interaction with one of the adjacent CH₃ groups. In the solid state, the Ru–C distance for the deprotonated carbon centre is 2.104(3) Å, while the corresponding distances to the adjacent aryl and methyl carbons are 2.236(3) Å, 2.234(3) and 2.342(3) Å, respectively. The Caryl–Caryl bond length on the η² coordinated ring is elongated to 1.448(4) Å. The hydrogen atoms on the agostically coordinated methyl group were located in the electron density map and reveal a Ru–H distance of 1.85(5) Å. The $^{19}$F NMR
spectrum of 2-9 is consistent with the 1:1 ratio of B(C₆F₅)₄ and IDipp-BF₃ moieties. ¹H NMR spectrum in CD₂Cl₂ for 2-9 confirmed protonation of the IDipp-BF₃ ligand at the C4 position had occurred; the two backbone imidazolyl protons are inequivalent, as are all of the aryl and alkyl protons in the IDipp-BF₃ ligand, supporting C₁ symmetry of 2-9 (Figure 2.2.9). A doublet integrating to one proton corresponding to the Ru coordinated aryl IDipp methine position is observed at 2.66 ppm, and couples to a doublet of doublets at 7.61 ppm, also integrating to one proton, as indicated by a gCOSY experiment. Additionally, a broad signal integrating to three protons is observed at -3.30 ppm, which is assigned to the agostically coordinated methyl group. The deprotonated iPr-methine position coordinated to the Ru centre resonates at 69.5 ppm in the ¹³C{¹H} NMR spectrum. The ¹³C{¹H} resonance of the agostically coordinated methyl group occurs at 2.5 ppm.

Figure 2.2.9. Molecular structure of the cation of 2-9. Thermal ellipsoids are displayed at 50% probability. Selected hydrogen atoms are shown. One iPr group was disordered and was modelled isotropically over two positions; one position is shown for clarity. Colours: C, grey; H, turquoise; Ru, magenta; F, yellow-green; N, blue; B, pale yellow.
Figure 2.2.10. $^1$H NMR (CD$_2$Cl$_2$) spectrum of 2-9. The expansion shows the Ru coordinated aryl methine proton as a doublet at 2.66 ppm, which overlaps with a septet, integrating to two protons, at 2.67 ppm and corresponding to the two remaining equivalent Dipp-iPr methine protons. The agostically coordinated CH$_3$ group appears as a broad singlet at -3.30 ppm.
The formation of 2-9 suggests that upon abstraction of the halide from Ru by Ag(Et$_2$O)[B(C$_6$F$_5$)$_4$], the cationic Ru centre mediates proton migration from the iPr-methine position to the carbene carbon (Scheme 2.2.6). Presumably, this rearrangement is driven by the high basicity of the C4 position. Interestingly, Bertrand and coworkers have observed that their isolated neutral abnormal NHC decomposes by a related proton transfer reaction in the presence of lithium salts or by heating (Scheme 2.1.2).

Scheme 2.2.6. Proposed mechanism for the formation of 2-9.

2.2.4 Rh Complexes of an Anionic Imidazol-4-ylidene

Rh complexes of this ligand were also explored, as species of the formula RhCl(L)(CO)$_2$ are well established as a scale of the donor properties of the ligand L.$^{22}$ In an attempt to generate Rh(IDipp-BF$_3$)(COD)Cl, two equivalents of 2-2 were added to [Rh(COD)Cl]$_2$ in THF. However, instead of the intended product, the doubly ligated salt Li[Rh(IDipp-BF$_3$)$_2$(COD)] 2-10 was instead isolated (Scheme 2.2.7), which corresponds to reaction of two molecules of 2-2 per Rh atom. Complex 2-10 can be more appropriately made using the correct stoichiometry in 89% yield. Crystals suitable for X-ray diffraction were grown from
THF/Et₂O solution (Figure 2.2.11). Complex 2-10 crystallizes as a one dimensional linear chain, where each Li cation bridges two molecules of the anionic Rh moiety via coordination to the IDipp-BF₃ fluorides. The coordination sphere at Li is completed by two molecules of THF. In the $^{13}$C($^{1}$H) NMR spectrum of 2-10 the carbenic carbon can be observed at 159.7 ppm and displays a $^{1}$J$_{\text{Rh-C}}$ coupling constant of 51 Hz.

Scheme 2.2.7. Synthesis of 2-10.

Figure 2.2.11. Molecular structure of 2-10. Thermal ellipsoids are displayed at 50% probability. Hydrogen atoms and iPr groups on the NHCs are omitted for clarity. Colours: C, grey; Rh, teal; F, yellow-green; O, red; N, blue; B, pale yellow; Li, pale purple.
Thawing a frozen THF solution of 2-10 under CO atmosphere results in the formation of a mixture of two products by $^1$H and $^{19}$F NMR spectroscopy in an approximate 55:45 ratio. Addition of pentane to a THF solution of the mixture results in the deposition of both orange and yellow single crystals, which were analyzed by X-ray diffraction and found to be the configurational isomers [Li(THF)$_3$][cis-Rh(IDipp-BF$_3$)$_2$(CO)$_2$] 2-11a and [Li(THF)$_3$][trans-Rh(IDipp-BF$_3$)$_2$(CO)$_2$] 2-11b (Scheme 2.2.8). The molecular structure of the cis isomer 2-11a (Figure 2.2.12) reveals a square planar geometry about the Rh centre, where the two Rh-C$_{\text{NHC}}$ distances are 2.098(5) and 2.107(5) Å. However, the molecular structure of the trans isomer 2-11b (Figure 2.2.13) reveals an unusual geometry at Rh, which is best described as distorted sawhorse, where the OC-Rh-CO angle is 144.9(3)$^\circ$. This bending is likely due to the trans-influence of the strong field carbonyl ligands, which warp the structure from square planar to avoid being completely trans to one another. The C$_{\text{NHC}}$-Rh-C$_{\text{NHC}}$ angle also deviates from planarity at 165.0(2)$^\circ$. The Rh-C$_{\text{NHC}}$ distances are 2.067(4) and 2.072(4) Å.

Figure 2.2.12. Molecular Structure of 2-11a. Thermal ellipsoids are displayed at 50% probability. Hydrogen atoms and iPr groups on the NHCs are removed for clarity. Disordered THF molecules were modelled isotropically over two positions; one position is shown for clarity. Colours: C, grey; Rh, teal; F, yellow-green; O, red; N, blue; B, pale yellow; Li, pale purple.
Figure 2.2.13. Molecular structure of 2-11b. Thermal ellipsoids are displayed at 50% probability. Hydrogen atoms and iPr groups on the NHC are omitted for clarity. One BF$_3$ moiety was modelled isotropically over three positions; one position is shown. Colours: C, grey; Rh, teal; F, yellow-green; O, red; N, blue; B, pale yellow; Li, pale purple.

Heating the mixture of isomers in THF at 40 °C results in slow conversion to one product, which is believed to be the trans isomer 2-11b. This is due to the presence of an agostic interaction evident in one of the iPr CH$_3$ groups, which is observed as a very broad singlet at 0.85 ppm in the $^1$H NMR spectrum, and a close contact in the molecular structure of 2-11b between the Rh centre and one of the iPr groups, however this assignment is tentative. The carbonylation reaction likely proceeds through an intermediate three coordinate monocarbonlyated product, which partially isomerizes in the thawing THF to the sterically and electronically favoured trans isomer, before reacting with an additional equivalent of CO to form the mixture of isomers 2-11a and 2-11b (Scheme 2.2.8). With the addition of a second equivalent of CO, the trans isomer is now only slightly thermodynamically favoured, which is slowly produced by prolonged heating in THF. Unfortunately, this conversion to the trans isomer is incomplete even after 5 days at 50 °C, and is accompanied by some decomposition to 2-1. Further heating to 66 °C results in decomposition of both products. As such, neither 2-11a nor 2-11b could be exclusively isolated.
Scheme 2.2.8. Mechanism for the formation of isomers 2-11a and 2-11b
Combination of one equivalent 2-2 with a 0.5 equivalents of $[\text{Rh(CO)}_2\text{Cl}]_2$ appears to afford the product $\text{Li}[\text{cis-RhCl(IDipp-BF}_3\text{)(CO)}_2]$ 2-12 (Scheme 2.2.9). Although a molecular structure of 2-12 could not be obtained, its NMR spectra in THF-d$_8$ solution significantly differ from those of 2-11a or 2-11b, excluding the possibility that 2-12 is ligated by both two carbonyls and two IDipp-BF$_3$ units. An IR spectrum of 2-12 was obtained and strong CO absorptions are observed at 2067 and 1998 cm$^{-1}$, an average value of 2032.5 cm$^{-1}$, confirming the formulation as a cis-Rh di-carbonyl species. Somewhat surprisingly, these stretching frequencies would indicate that 2-2 is slightly less electron donating than the parent neutral C2 coordinated NHC IDipp (average vCO = 2031.5 cm$^{-1}$). It seems that the inductively electron withdrawing nature of the BF$_3$ unit trumps any additional electron richness afforded by the ligand being both anionic and C4 bound. Simultaneous to the discovery of this, Tamm and co-workers published similar conclusions with C2 deprotonated abnormal NHC-B(C$_6$F$_5$)$_3$ adducts (Scheme 1.2.8): they are no more electron donating that their parent neutral NHCs, despite being anionic.

![Scheme 2.2.9. Synthesis of 2-12.](image)

2.3 Conclusions

The data presented in this chapter clearly indicate that the anionic abnormal carbene 2-2 is an inappropriate choice as a spectator ligand for their original intended use in Ru based hydrogenation catalysis. The ligand was shown to be significantly less donating than anticipated, decomposes in the presence of a hydride ligand to form 2-1, and C-H activates the ligand backbone in the presence of coordinative unsaturation. Nevertheless, this work has demonstrated
that transmetalation of an anionic NHC ligand from Ag provides viable access to Ru complexes containing the anionic NHC ligand. Subsequent reactions with donors effect dimer scission, while abstraction of halide results in a unique binding mode of the carbene via deprotonation of the iPr fragment of the N-aryl substituent. Furthermore, an equilibrium between doubly NHC-ligated cis and trans Rh dicarbonyls reveals a delicate balance of steric and electronic influences in these complexes. This novel reactivity stands in contrast to C2 ligated NHCs and other carbene donors, and suggests that anionic NHC complexes may provide access to further unique transformations.

2.4 Experimental Section
2.4.1 Crystallographic Details

X-ray Data Collection and Reduction. Crystals were coated in Paratone-N oil in the glovebox, mounted on a MiTegen Micromount, and placed under a N\textsubscript{2} stream, thus maintaining a dry, O\textsubscript{2}-free environment for each crystal. The data were collected on a Bruker Kappa Apex II diffractometer using a graphite monochromator with Mo K\textalpha{} (\(\lambda = 0.71073\ \text{Å}\)) or Cu K\textalpha{} (\(\lambda = 1.54178\ \text{Å}\)) radiation. The data were collected at 150(2) K for all crystals. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the empirical multiscan method SADABS. In cases where non-merohedral twinning was detected, the data was indexed with CELLNOW to determine the contributions of the respective crystal domains, and the data were corrected for absorption effects using TWINABS. The heavy atom positions were determined employing the SHELXTL direct methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least squares techniques on F, minimizing the function \(\omega \ (F_o - F_c)^2\) where the weight \(\omega\) is defined as \(4F_o^2/2\sigma\ (F_o^2)\) and \(F_o\) and \(F_c\) are the observed and calculated structure factor amplitudes, respectively. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of positional disordering. The final models of twinned structures were obtained by refinement against the twinned data. C-H
atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C-H bond length of 0.95 Å. H-atom temperature factors were fixed at 1.20 times the isotropic temperature factor of the C-atom to which they are bonded. The H-atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance.

Table 2.4.1. Crystallographic information

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<th>2-4</th>
<th>2-5</th>
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<tbody>
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#### 2.4.2 Experimental Details

**General Comments:** All manipulations were carried out under an atmosphere of dry, \(O_2\)-free \(N_2\) employing a Vacuum Atmospheres glovebox or a Schlenk vacuum line. Solvents were purified with a Grubbs-type column system manufactured by Innovative Technology and dispensed into thick-walled Straus flasks equipped with Teflon-valve stopcocks. \(CD_2Cl_2\) was distilled under reduced pressure from \(CaH_2\) and degassed by successive freeze-pump-thaw cycles. Deuterated THF and benzene were distilled from purple sodium benzophenone ketyl. \(^1H\), \(^{13}C\{^1H\}\), \(^19F\), \(^{11}B\), \(^{31}P\{^1H\}\), and \(^7Li\) NMR spectra were recorded at 25 °C on Bruker 400 MHz, Agilent DD2 500 MHz or Agilent DD2 600 MHz spectrometers, unless otherwise noted. Chemical shifts are reported in parts per...
million are given relative to SiMe$_4$ and referenced to the residual solvent signal. $^{13}$C{$_1^1$H} NMR signals are reported to a precision of 0.01 ppm to avoid reporting duplicates of spatially close signals, but should be understood to be accurate to 0.1 ppm. Elemental analyses were performed in house employing a Perkin-Elmer CHN Analyzer. In some cases, elemental analyses were reproducibly low on carbon content, presumably due to the formation of metal carbides during combustion. IR spectra were collected on a Perkin-Elmer Spectrum One FT-IR instrument. [Ru(p-cymene)Cl$_2$]$_2$, nBuLi solution, BF$_3$(OEt)$_2$, PPh$_3$, and CO were purchased from Sigma-Aldrich or Strem chemicals and used without further purification. Ag(Et$_2$O)[B(C$_6$F$_5$)$_4$]$^{66}$ and IDipp$^{67}$ were synthesized according to literature procedures.

**IDippBF$_3$ 2-1**: IDipp (1.045 g, 2.69 mmol) was dissolved in Et$_2$O (10 mL) and BF$_3$(Et$_2$O) (0.362 µL, 2.93 mmol) was added to the solution in a dropwise fashion with stirring. A white crystalline precipitate formed immediately, and pentane (10 mL) was added to the mixture. After stirring for 10 min. the precipitate was collected by filtration, washed with pentane (2 x 10 mL) and dried under vacuum (1.165 g, 95%). $^1$H NMR (THF-d$_8$): 7.52 (s, 2H, NCH x 2), 7.44 (t, $^3$J$_{H-H} = 7.8$ Hz, 2H, p-Dipp), 7.29 (d, $^3$J$_{H-H} = 7.8$ Hz, 4H, m-Dipp), 2.57 (septet, $^3$J$_{H-H} = 7.0$ Hz, 4H, CH(CH$_3$_2), 1.27 (d, $^3$J$_{H-H} = 6.8$ Hz, 6H, CH(CH$_3$_2), 1.17 (d, $^3$J$_{H-H} = 6.9$ Hz, 6H, CH(CH$_3$_2). $^{19}$F NMR (THF-d$_8$): -140.0 (1:1:1:1 q, $^1$J$_{B-F} = 33$ Hz, BF$_3$). $^{11}$B NMR (THF-d$_8$): -0.9 (q, $^1$J$_{B-F} = 33$ Hz, BF$_3$). $^{13}$C{$_1^1$H} NMR (THF-d$_8$): 146.28 (ipso-iPr), 134.88 (ipso), 130.76 (p-Dipp), 124.93 (NCH), 124.27(m-Dipp), 29.70 (CH(CH$_3$)$_2$), 25.10 (CH(CH$_3$)), 23.17(CH(CH$_3$)). Anal. Calcd. for C$_{27}$H$_{36}$BF$_3$N$_2$ (456.39): C, 71.05; H, 7.95; N, 6.14. Found: C, 71.35; H, 7.93; N, 6.14.

**(THF)$_4$Li(IDippBF$_3$) 2-2**: A solution of 2-1 (1.163 g, 2.55 mmol) in THF (10 mL), was cooled to -40 °C, and a pre-cooled n-BuLi solution (1.70 mL, 1.6 M in hexane, 2.72 mmol) was added. The stirred mixture was allowed to warm to room temperature over the course of 1 h to give a white precipitate. Pentane (10 mL) was then added, the mixture was shaken and the supernatant decanted. The
white solid obtained was washed with pentane (4 x 10 mL) and dried under vacuum (1.540 g, 97%). The amount of Li-bound THF remaining is dependent on the time spent drying the solid under vacuum, the number of THF equivalents ‘x’ can be determined by 1H NMR spectroscopy and typically varies between 0.7 – 3. The product was stored in a -45 °C freezer under N₂. 1H NMR (THF-d₈): 7.27 (t, 3J_H-H = 7.6 Hz, 1H, p-Dipp), 7.20 (dd, 3J_H-H = 7.0 Hz, 8.1 Hz, 1H, p-Dipp), 7.15 (d, 3J_H-H = 7.6 Hz, 2H, m-Dipp), 7.11 (d, 3J_H-H = 7.8 Hz, 2H, m-Dipp), 6.27 (s, 1H, NCH), 2.79 (septet, 3J_H-H = 7.0 Hz, 2H, CH(CH₃)₂), 2.70 (septet, 3J_H-H = 7.0 Hz, 2H, CH(CH₃)₂), 1.22 (d, 3J_H-H = 6.9 Hz, 6H, CH(CH₃)₂), 1.21 (d, 3J_H-H = 7.0 Hz, 6H, CH(CH₃)₂), 1.13 (d, 3J_H-H = 7.0 Hz, 6H, CH(CH₃)₂), 1.10 (d, 3J_H-H = 7.0 Hz, 6H, CH(CH₃)₂). 19F NMR (THF-d₈): -141.3 (1:1:1:1 br q, 1J_B-F = 36 Hz, BF₃). 11B NMR (THF-d₈): -2.3 (q, 1J_B-F = 38 Hz, BF₃). 7Li NMR (THF-d₈): -1.25 (s). 13C{1H} NMR (THF-d₈): 146.42 (ipso Ar-lpr), 146.11 (ipso Ar-lpr), 142.30 (ipso), 137.16 (ipso), 129.80 (NCH), 128.57 (p-Dipp), 127.43 (p-Dipp), 123.14 (m-Dipp), 122.80 (m-Dipp), 28.90 (CH(CH₃)), 28.81 (CH(CH₃)), 25.46 (CH(CH₃)), 24.89 (CH(CH₃)), 23.48 (CH(CH₃)), 23.18 (CH(CH₃)). Elemental Analyses was not possible due to the extreme air sensitivity of this compound.

**Au(I)(Dipp)BF₃(PPh₃) 2-3**: Compound 2-2 (50 mg, 0.073 mmol) and AuCl(PPh₃) (40 mg, 0.080 mmol) were combined in THF (2 mL) and allowed to stir for 48 h. The solvent was then removed under vacuum and the residue was extracted with toluene (5 mL). After filtration from any insoluble material, the solution was concentrated to approximately 1 mL under vacuum, causing the precipitation of a white solid. The supernatant was decanted, and the resulting white solid was washed with pentane (2 x 3 mL) and dried under high vacuum. (53 mg, 79%). 1H NMR (C₆D₆): 7.28 (t, 3J_H-H = 7.6 Hz, 1H, p-Dipp), 7.24 (dd, 3J_H-H = 7.1 Hz, 8.3 Hz, 1H, p-Dipp), 7.17-7.15 (m, 4H, m-Dipp) (multiplicity obscured by C₆D₆H resonance), 7.05 (dm, 3J_H-H = 8.2 Hz, 3H, o-PPh₃), 7.02 (dm, 3J_H-H = 8.1 Hz, 3H, o-PPh₃), 6.95 (tm, 3J_H-H = 7.4 Hz, 3H, p-PPh₃), 6.88 (tm, 3J_H-H = 7.8 Hz, 6H, m-PPh₃), 6.83 (d, 4J_H-P = 1.1 Hz, 1H, NCH), 3.15 (septet, 3J_H-H = 6.8 Hz, 2H, CH(CH₃)₂), 3.06 (septet, 3J_H-H = 6.8 Hz, 2H, CH(CH₃)₂), 1.62 (d, 3J_H-H = 6.8 Hz,
6H, CH(CH$_3$)$_2$), 1.55 (d, $^3$J$_{H-H}$ = 6.9 Hz, 6H, CH(CH$_3$)$_2$), 1.27 (d, $^3$J$_{H-H}$ = 6.8 Hz, 6H, CH(CH$_3$)$_2$), 1.16 (d, $^3$J$_{H-H}$ = 6.9 Hz, 6H, CH(CH$_3$)$_2$). $^{19}$F NMR (C$_6$D$_6$): -138.0 p.p.m. (1:1:1:1 br q, $^1$J$_{B-F}$ = 33 Hz, BF$_3$). $^{31}$P$^{1}$H NMR (C$_6$D$_6$): 42.3 (s, PPh$_3$). $^{11}$B NMR (C$_6$D$_6$): 0.3 (br q, $^1$J$_{B-F}$ = 32 Hz, BF$_3$). $^{13}$C$^{1}$H NMR (C$_6$D$_6$): 146.37 (ipso Ar-iPr), 146.10 (ipso Ar-iPr), 139.60 (ipso), 135.18 (ipso), 134.30 (d, $^2$J$_{C-P}$ = 14 Hz, o-PPh$_3$), 131.50 (p-PPh$_3$), 130.15, 129.96 (p-PPh$_3$), 129.72 (p-PPh$_3$), 129.31 (d, $^3$J$_{C-P}$ = 11 Hz, m-PPh$_3$), 128.71 (NCH), 123.79 (m-Dipp), 123.72 (m-Dipp), 29.31 (CH(CH$_3$)), 29.21 (CH(CH$_3$)), 25.73 (CH(CH$_3$)), 25.55 (CH(CH$_3$)), 23.81 (CH(CH$_3$)), 23.54 (CH(CH$_3$)). Anal. Calcd. for C$_{45}$H$_{50}$AuBF$_3$N$_2$P (914.65): C, 59.09; H, 5.51; N, 3.06. Found: C, 58.30; H, 5.32; N, 2.90.

Li[Ag(IDippBF$_3$)$_3$] 2-4: To a suspension of 2-2 (1.180 g, 1.90 mmol) in THF (10 mL), was added anhydrous AgCl (0.245 g, 1.72 mmol) and the mixture was stirred for 16 h in the dark. The resulting suspension was filtered through Celite and the solvent was removed in vacuo. Toluene (10 mL) was added and the mixture was stirred for 10 min. The mixture was then filtered from LiCl and concentrated under vacuum. The resulting colourless oil was triturated in pentane, yielding a white solid which was dried in vacuo (0.806 g, 83%). Crystals of [(IDippBF$_3$)$_2$Ag][Li(THF)$_3$] were grown from slow diffusion of pentane into a THF solution. $^1$H NMR (THF-d$_8$): 7.30 (t, $^3$J$_{H-H}$ = 7.6 Hz, 2H, p-Dipp), 7.17 (d, $^3$J$_{H-H}$ = 7.7 Hz, 2H, m-Dipp), 7.02 (d, $^3$J$_{H-H}$ = 7.7 Hz, 2H, m-Dipp), 6.33 (d, $^1$J$_{Ag-H}$ = 1.7 Hz, 1H, NCH), 2.60 (septet, $^3$J$_{H-H}$ = 7.0 Hz, 2H, CH(CH$_3$)$_2$), 2.56 (septet, $^3$J$_{H-H}$ = 7.0 Hz, 2H, CH(CH$_3$)$_2$), 1.18 (d, $^3$J$_{H-H}$ = 6.9 Hz, 6H, CH(CH$_3$)$_2$), 1.13 (d, $^3$J$_{H-H}$ = 6.9 Hz, 6H, CH(CH$_3$)$_2$), 1.00 (d, $^3$J$_{H-H}$ = 6.8 Hz, 6H, CH(CH$_3$)$_2$). $^{19}$F NMR (THF-d$_8$): -139.5 -- -139.9 (br m, BF$_3$). $^{11}$B NMR (THF-d$_8$): 1.0 -- 1.6 (br m, BF$_3$). $^7$Li NMR (THF-d$_8$): -0.96 (s). $^{13}$C$^{1}$H NMR: 161.54 (pseudo dd, $^1$J$_{109Ag-C}$ = 184 Hz, $^1$J$_{107Ag-C}$ = 159 Hz, NCAg), 146.39 (ipso Ar-iPr), 145.92 (ipso Ar-iPr), 140.59 (ipso), 136.16 (ipso), 129.39 (pseudo d, $^2$J$_{Ag-C}$ = 15 Hz, NCH), 129.25 (p-Dipp), 128.41 (p-Dipp), 123.46 (m-Dipp), 123.13 (m-Dipp), 28.99 (CH(CH$_3$)), 28.94 (CH(CH$_3$)), 25.45 (CH(CH$_3$)), 25.27 (CH(CH$_3$)),

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23.33 (CH(CH₃)), 23.21 (CH(CH₃)). Anal calcd. for C₅₄H₇₀AgB₂F₆LiN₄ (1025.58): C, 63.24; H, 6.88; N 5.46. Found: C, 63.48; H, 6.80; N, 5.28.

[Ru(p-cymene)(IDippBF₃)Cl]₂ 2-5: To a solution of 2-4 (145 mg, 0.141 mmol) in THF was added [Ru(p-cymene)Cl₂]₂ (75 mg, 0.122 mmol), and the mixture was stirred for 16 h at 25 °C, resulting a dark red solution and the precipitation of AgCl. The solution was filtered and concentrated under vacuum (Crystals of 2-6 may be grown by recrystallizing this residue from THF/Et₂O: ⁷Li NMR (THF-d₈): -1.95 (s). Other NMR spectra are identical to those of 2-5). The red oil obtained was dissolved in toluene (10 mL) and stirred for two hours, affording a red precipitate. CH₂Cl₂ (8 mL) was added and the resultant suspension was stirred for 2 h and then the mixture filtered from precipitated LiCl. The mixture was concentrated in vacuo, and Et₂O (10 mL) added to precipitate red microcrystals. The solid was washed with Et₂O (3 x 5 mL) and dried. To remove final traces of LiCl, the solid was again dissolved in CH₂Cl₂, filtered, the product precipitated with pentane, and dried under high vacuum (124 mg, 63%). Crystals suitable for X-ray diffraction were grown from slow diffusion of pentane in to a CH₂Cl₂ solution. ¹H NMR (THF-d₈): 7.45 (t, ³J_H-H = 7.2 Hz, 1H, p-Dipp), 7.34 (d, ³J_H-H = 7.4 Hz, 2H, m-Dipp), 7.28 (t, ³J_H-H = 7.2 Hz, 1H, p-Dipp), 7.13 (d, ³J_H-H = 7.4 Hz, 2H, m-Dipp), 6.85 (br s, 1H, NCH), 5.50 (br, 2H, p-cymeneAr), 4.60 (br, 2H, cymeneAr), 2.90 (br, 2H, CH(CH₃)₂), 2.71-2.53 (br m, 3H, CH(CH₃)₂), 1.66 (s, 3H, p-cymeneMe), 1.41 (d, ³J_H-H = 6.8 Hz, 6H, CH(CH₃)₂), 1.27 (d, ³J_H-H = 6.8 Hz, 6H, CH(CH₃)₂), 1.09 (d, ³J_H-H = 6.8 Hz, 6H, CH(CH₃)₂), 0.97 (br, 6H, p-cymene CH(CH₃)₂). ¹⁹F NMR (THF-d₈): -136.4 – -137.0 (br m, BF₃). ¹¹B NMR (THF-d₈): -0.5 (br q, ¹J_B-F = 35 Hz, BF₃). ¹³C {¹H} NMR (CDCl₃): 130.05 (p-Dipp), 130.00 (p-Dipp), 124.49 (br, m-Dipp), 124.19, 124.10 (br, m-Dipp), 30.60, 29.23, 28.97, 25.15, 23.25 (br). Anal calcd. for C₇₄H₉₈B₂Cl₂F₆N₄Ru₂ •2(CH₂Cl₂) (1622.12): C, 56.27; H, 6.35, N, 3.45. Found: C, 56.12; H, 6.12; N, 3.41.
Ru(DippBF₃)(ρ-cymene)(PPh₃)Cl 2-7: PPh₃ (16 mg, 0.061 mmol) was added to a dark red solution of 2-5 (43 mg, 0.030 mmol) in CH₂Cl₂ (2 mL), resulting in an immediate color change to orange. The mixture was filtered and concentrated to 1 mL. Pentane (15 mL) was added to precipitate an orange-brown solid which was collected, washed with pentane (3 x 5 mL), and dried under high vacuum (45 mg, 76%). Crystals suitable for X-ray diffraction were grown from slow diffusion of pentane in to a CH₂Cl₂ solution.¹H NMR (CD₂Cl₂): 7.46-7.26 (m, 18H, PPh₃ + p-Dipp x 2 + m-Dipp x 1), 7.18 (dd, 3J_H-H = 7.8 Hz, 4J_H-H = 1.3 Hz, 1H, m-Dipp), 7.13 (dd, 3J_H-H = 7.8 Hz, 4J_H-H = 1.5 Hz, 1H, m-Dipp), 7.10 (dd, 3J_H-H = 7.8 Hz, 4J_H-H = 1.5 Hz, 1H, m-Dipp), 6.03 (s, 1H, NCH), 5.81 (d, 3J_H-H = 6.2 Hz, cymeneAr), 5.47 (apparent t, 3J_H-H = 5.4 Hz, cymeneAr), 4.91 (d, 3J_H-H = 6.2 Hz, cymeneAr), 3.92 (d, 3J_H-H = 5.7 Hz, cymeneAr), 2.65 (septet, 2H, 3J_H-H = 6.7 Hz, 2H, CH(CH₃)₂), 2.53 (septet, 3J_H-H = 6.9 Hz, 1H, CH(CH₃)₂), 2.32 (septet, 3J_H-H = 6.9 Hz, 1H, CH(CH₃)₂), 2.12 (s, 3H, cymeneMe), 1.61 (d, 3J_H-H = 6.7 Hz, 3H, CH(CH₃)₂), 1.33 (d, 3J_H-H = 6.7 Hz, 3H, CH(CH₃)₂), 1.31 (d, 3J_H-H = 6.8 Hz, 3H, CH(CH₃)₂), 1.24 (d, 3J_H-H = 6.8 Hz, 3H, CH(CH₃)₂), 1.09 (d, 3J_H-H = 6.9 Hz, 3H, CH(CH₃)₂), 1.08 (d, 3J_H-H = 6.9 Hz, 3H, CH(CH₃)₂), 0.96 (d, 3J_H-H = 7.0 Hz, 3H, CH(CH₃)₂), 0.92 (apparent t, 3J_H-H = 6.1 Hz, 6H, CH(CH₃)₂), 0.31 (d, 3J_H-H = 6.8 Hz, 3H, CH(CH₃)₂). ³¹P{¹H} NMR (CD₂Cl₂): 30.3 (s). ¹⁹F NMR (CD₂Cl₂): -134.0 (1:1:1:1 br q, ¹J_B-F = 33 Hz, BF₃), ¹¹B NMR (CD₂Cl₂): -0.7 (br q, ¹J_B-F = 37 Hz, BF₃). ¹³C{¹H} NMR (CD₂Cl₂): 149.20 (ipso Ar-iPr), 146.92 (ipso Ar-iPr), 146.74 (ipso Ar-iPr), 145.56 (ipso Ar-iPr), 138.40 (ipso), 134.26 (br, PPh₃), 133.70 (ipso), 130.74 (br, PPh₃), 129.63 (p-Dipp), 129.26 (p-Dipp), 128.92 (d, 3J_P-C = 8.9 Hz, NCH), 128.82 (d, 3J_P-C = 1.3 Hz, ipso cymenePr), 128.33 (br, PPh₃), 124.03 (m-Dipp), 123.49 (m-Dipp), 123.24 (m-Dipp), 122.43 (m-Dipp), 99.71 (d, 3J_P-C = 5 Hz, p-cymeneAr), 88.99 (d, 3J_P-C = 20 Hz, p-cymeneAr), 87.77 (p-cymeneAr), 79.95 (d, 3J_P-C = 13 Hz, p-cymeneAr), 31.11 (CH(CH₃)₂), 30.00 (CH(CH₃)₂), 29.54 (CH(CH₃)₂), 29.98 (CH(CH₃)₂), 28.83 (CH(CH₃)₂), 27.45 (CH(CH₃)₂), 27.25 (CH(CH₃)₂), 26.93 (CH(CH₃)₂), 24.73 (CH(CH₃)₂), 24.69 (CH(CH₃)₂), 24.24 (CH(CH₃)₂), 22.61 (CH(CH₃)₂), 22.36 (CH(CH₃)₂), 22.05 (CH(CH₃)₂), 21.26 (CH(CH₃)₂), 17.45 (p-cymeneMe). Anal
calcd. for C_{55}H_{64}BClF_{3}N_{2}Ru (988.41): C, 66.83; H, 6.53, N, 2.83. Found: C, 66.12; H, 6.24; N, 2.80.

**Ru(DippBF_{3})(p-cymene)(CO)Cl 2-8:** A deep red solution of 2-5 (53 mg, 0.036 mmol) in CH_{2}Cl_{2} (2 mL) was backfilled with 1 atm of CO, resulting in an immediate color change to orange. The mixture was filtered and concentrated to 1 mL. Pentane (15 mL) was added to precipitate the product from solution as a pale yellow solid which was collected, washed with pentane (3 x 5 mL), and dried under high vacuum (38 mg. 69%). Crystals suitable for X-ray diffraction were grown from slow diffusion of pentane in to a CH_{2}Cl_{2} solution. \(^1\)H NMR (CD_{2}Cl_{2}): 7.47 (t, \(^3\)J_{H-H} = 7.5 Hz, 2H, m-Dipp), 7.30 (d, \(^3\)J_{H-H} = 7.6 Hz, 1H, p-Dipp), 7.27 (d, \(^3\)J_{H-H} = 7.4 Hz, 1H, p-Dipp), 7.24 (d, \(^3\)J_{H-H} = 7.8 Hz, 1H, p-Dipp), 7.23 (d, \(^3\)J_{H-H} = 7.8 Hz, 1H, p-Dipp), 6.67 (s, 1H, NCH), 6.28 (d, \(^3\)J_{H-H} = 6.8 Hz, 1H, cymene\_A\_r), 5.88 (apparent t, \(^3\)J_{H-H} = 7.5 Hz, cymene\_A\_r), 5.37 (d, \(^3\)J_{H-H} = 6.3 Hz, cymene\_A\_r), 2.84 (septet, \(^3\)J_{H-H} = 6.8 Hz, 1H, CH(CH_{3})_{2}), 2.67 (septet, \(^3\)J_{H-H} = 6.8 Hz, 1H, CH(CH_{3})_{2}), 2.54-2.42 (m, 2H, 2x CH(CH_{3})_{2}), 2.31 (septet, \(^3\)J_{H-H} = 6.8 Hz, 1H, CH(CH_{3})_{2}), 2.13 (s, 3H, cymene\_Me), 1.33-1.19 (m, 18H, 6x CH(CH_{3})_{2}), 1.15 (d, \(^3\)J_{H-H} = 7.0 Hz, 3H, CH(CH_{3})_{2}), 1.12 (d, \(^3\)J_{H-H} = 7.1 Hz, 3H, CH(CH_{3})_{2}), 1.07 (d, \(^3\)J_{H-H} = 7.1 Hz, 3H, CH(CH_{3})_{2}). 19F NMR (CD_{2}Cl_{2}): -137.1 (1:1:1:1 q, \(^1\)J_{B-F} = 34 Hz, BF_{3}). \(^{11}\)B NMR (CD_{2}Cl_{2}): -0.8 (q, \(^1\)J_{B-F} = 37 Hz, BF_{3}). \(^{13}\)C{\[^1\]H} NMR (CD_{2}Cl_{2}): 193.60 (CO), 148.72 (ipso Ar-ipr), 147.30 (ipso Ar-ipr), 146.16 (ipso Ar-ipr), 145.09 (ipso Ar-ipr), 137.80 (ipso), 134.35 (ipso), 130.54 (p-Dipp), 130.16 (NCH), 130.15 (p-Dipp), 124.99 (m-Dipp), 123.94 (m-Dipp), 123.74 (m-Dipp), 123.37 (m-Dipp), 121.82 (ipso-cymene\_ipr), 116.83 (ipso-cymene\_Me), 108.49 (p-cymene\_A\_r), 99.27 (p-cymene\_A\_r), 95.05 (p-cymene\_A\_r), 90.24 (p-cymene\_A\_r), 31.84 (CH(CH_{3})_{2}), 29.17 (CH(CH_{3})_{2}), 29.14 (CH(CH_{3})_{2}), 29.01 (CH(CH_{3})_{2}), 26.84 (CH(CH_{3})_{2}), 26.30 (CH(CH_{3})_{2}), 24.73 (CH(CH_{3})_{2}), 24.63 (CH(CH_{3})_{2}), 24.16 (CH(CH_{3})_{2}), 23.90 (CH(CH_{3})_{2}), 22.81 (CH(CH_{3})_{2}), 22.70 (CH(CH_{3})_{2}), 22.63 (CH(CH_{3})_{2}), 22.49 (CH(CH_{3})_{2}), 19.52 (p-cymene\_Me). IR (KBr): 2008 (s, CO). Anal calcd. for C_{39}H_{49}BClF_{3}N_{2}ORu: C, 60.52; H, 6.55; N, 3.71. Found: C, 58.82; H, 6.16; N, 3.55.
[Ru(IDippBF₃)(p-cymene)][B(C₆F₅)₄] 2-9: Compound 2-5 (44 mg, 0.030 mmol) was dissolved in CH₂Cl₂ (2 mL) and Ag(Et₂O)[B(C₆F₅)₄] (52 mg, 0.061 mmol) was added, causing an immediate colour change to orange and the precipitation of AgCl. The mixture was stirred for 30 minutes and was filtered. The solution was concentrated in vacuo to 2 mL and HMDSO (2 mL) was layered on top. After 24 h, pale orange needles separated from solution. The solid was collected by filtration, washed with Et₂O and dried under high vacuum (36 mg, 43%). Crystals suitable for X-ray diffraction were grown from slow diffusion of Et₂O in to a CH₂Cl₂ solution. ¹H NMR (CD₂Cl₂): 7.61 (dd, 3J_H-H = 6.1, 8.9 Hz, 1H, p-Dipp), 7.59 (t, 3J_H-H = 7.8 Hz, 1H, p-Dipp), 7.47 (d, 3J_H-H = 9.1 Hz, 1H, m-Dipp), 7.39 (dd, 3J_H-H = 7.9 Hz, 4J_H-H = 1.4 Hz, 1H, m-Dipp), 7.37 (dd, 3J_H-H = 7.7 Hz, 4J_H-H = 1.4 Hz, 1H, m-Dipp), 7.29 (d, 3J_H-H = 1.8 Hz, 1H, NCH), 7.21 (d, 3J_H-H = 1.8 Hz, 1H, NCH), 6.35 (d, 3J_H-H = 6.2 Hz, 1H, p-cymeneₐᵣ), 6.29 (d, 3J_H-H = 6.0 Hz, 1H, p-cymeneₐᵣ), 4.59 (d, 3J_H-H = 6.1 Hz, 1H, p-cymeneₐᵣ), 4.51 (d, 3J_H-H = 6.2 Hz, 1H, p-cymeneₐᵣ), 2.67 (septet, 3J_H-H = 6.9 Hz, 2H, CH(CH₃)₂), 2.66 (d, 3J_H-H = 6.1 Hz, 1H, [Ru]m-Dipp), 2.53 (septet, 3J_H-H = 7.0 Hz, 1H, CH(CH₃)₂), 2.32 (septet, 3J_H-H = 7.0 Hz, 1H, CH(CH₃)₂), 2.29 (s, 3H, [Ru]CH₃), 2.05 (s, 3H, p-cymeneₐₑᵢ), 1.41 (d, 3J_H-H = 6.9 Hz, 3H, CH(CH₃)₂), 1.35 (d, 3J_H-H = 6.9 Hz, 3H, CH(CH₃)₂), 1.32 (d, 3J_H-H = 6.9 Hz, 3H, CH(CH₃)₂), 1.30 (d, 3J_H-H = 6.9 Hz, 3H, CH(CH₃)₂), 1.21 (d, 3J_H-H = 6.9 Hz, 3H, CH(CH₃)₂), 1.20 (d, 3J_H-H = 6.9 Hz, 3H, CH(CH₃)₂), 1.17 (d, 3J_H-H = 6.9 Hz, 3H, CH(CH₃)₂), 1.04 (d, 3J_H-H = 6.9 Hz, 3H, CH(CH₃)₂), 0.30 (br s, 3H, [Ru]CCH₃). ¹⁹F NMR (CD₂Cl₂): -133.1 (m, 8F, o-C₆F₅), -137.6 (1:1:1:1 q, 1J_B:F = 34 Hz, 3F, BF₃), -163.6 (t, 3J_F:F = 20 Hz, 4F, p-C₆F₅), -167.5 (t, 3J_F:F = 18 Hz, 8F, m-C₆F₅). ¹¹B NMR (CD₂Cl₂): -0.7 (q, 1J_B:F = 34 Hz, BF₃), -16.7 (s, B(C₆F₅)₄). ¹³C{¹H} NMR (CD₂Cl₂): 152.14 (ipso Ar-iPr), 148.5 (br d, 1J_C:F = 241 Hz, o-C₆F₅), 146.24 (ipso Ar-iPr), 145.29 (ipso Ar-iPr), 140.54 (p-Dipp), 138.6 (br d, 1J_C:F = 243 Hz, p-C₆F₅), 136.7 (br d, 1J_C:F = 246 Hz, m-C₆F₅), 132.85, 131.44 (p-Dipp), 127.04, 125.32 (NCH), 125.07 (NCH), 124.49 (m-Dipp), 124.45 (m-Dipp), 124.2 (br, ipso-C₆F₅), 124.03 (m-Dipp), 114.90 (ipso-cymeneᵢᵢᵢᵢ), 104.54 (ipso-cymeneᵢᵢᵢᵢ), 100.54 ([Ru]CC(CH₃)₂), 89.72 (q, J_C:F = 3 Hz, cymeneᵢᵢᵢᵢ), 86.95 (q, J_C:F = 3 Hz, p-cymeneᵢᵢᵢᵢ), 81.07 (m, p-cymeneᵢᵢᵢᵢ), 80.88 (p-cymeneᵢᵦ), 69.48
([Ru]C(CH$_3$)$_2$, 65.31 ([Ru] m-Dipp), 30.87 (CH(CH$_3$)$_2$), 29.67 (CH(CH$_3$)$_2$), 29.23 (CH(CH$_3$)$_2$), 25.34 (CH(CH$_3$)$_2$), 25.28 (CH(CH$_3$)$_2$), 24.26 (CH(CH$_3$)$_2$), 23.38 (CH(CH$_3$)$_2$), 22.61 (CH(CH$_3$)$_2$), 22.38 (CH(CH$_3$)$_2$), 22.05 (CH(CH$_3$)$_2$), 21.06 (CH(CH$_3$)$_2$), 20.88 ([Ru]CCH$_3$), 17.73 (p-cymeneMe), 2.51 ([Ru]CH$_3$). Anal. Calcd. for C$_{61}$H$_{49}$B$_2$F$_{23}$N$_2$Ru (1369.71): C, 53.49; H, 3.61; N, 2.05. Found: C, 53.31; H, 3.58; N, 2.41.

[Li(THF)$_2$][Rh(IDipp-BF$_3$)$_2$(COD)] 2-10: Compound 2-2 (100 mg, 0.141 mmol) was added to a suspension of [Rh(COD)Cl]$_2$ (17 mg, 0.034 mmol) in THF (5 mL) and the solution as allowed to stir for 1 h. After this time, the solution was concentrated to 1 mL and layered with pentane (18 mL) and allowed to crystallize for a period of 48 hours. The supernatant was decanted, and the crystals were washed with toluene (4 x 3 mL). The solid was then dissolved in CH$_2$Cl$_2$ (3 mL) and filtered of any insoluble material. The product was precipitated by addition of pentane, collected via filtration and dried under high vacuum (77 mg, 89%). $^1$H NMR (CDCl$_3$): 7.32 (t, $^3$J$_{H-H}$ = 7.7 Hz, 2H, p-Dipp), 7.24 (t, $^3$J$_{H-H}$ = 7.7 Hz, 2H, p-Dipp), 7.14 (d, $^3$J$_{H-H}$ = 7.7 Hz, 2H, m-Dipp), 7.10 (d, $^3$J$_{H-H}$ = 8.0 Hz, 2H, m-Dipp), 7.08 (d, $^3$J$_{H-H}$ = 8.1 Hz, 2H, m-Dipp), 7.02 (d, $^3$J$_{H-H}$ = 7.7 Hz, 2H, m-Dipp), 6.56 (s, 2H, NCH), 3.85-3.80 (br m, 2H, CODCH), 3.65 (br s, 8H, THFCH$_2$), 3.50-3.45 (br m, 2H, CODCH)$_2$, 2.79 (septet, $^3$J$_{H-H}$ = 6.9 Hz, 1H, CH(CH$_3$)$_2$), 2.52 (septet, $^3$J$_{H-H}$ = 6.9 Hz, 1H, CH(CH$_3$)$_2$), 2.39 (septet, $^3$J$_{H-H}$ = 6.9 Hz, 1H, CH(CH$_3$)$_2$), 2.25 (septet, $^3$J$_{H-H}$ = 6.7 Hz, 1H, CH(CH$_3$)$_2$), 1.81 (br s, 8H, THFCH$_2$), 1.76-1.66 (m, 2H, CODCH)$_2$, 1.61-1.53 (m, 2H, CODCH$_2$), 1.39-1.25 (br m, 4H, CODCH$_2$), 1.22 (d, $^3$J$_{H-H}$ = 6.9 Hz, 6H, CH(CH$_3$)$_2$), 1.19 (d, $^3$J$_{H-H}$ = 6.5 Hz, 6H, CH(CH$_3$)$_2$), 1.08 (d, $^3$J$_{H-H}$ = 6.5 Hz, 6H, CH(CH$_3$)$_2$), 1.04 (d, $^3$J$_{H-H}$ = 6.8 Hz, 12H, CH(CH$_3$)$_2$), 1.00 (d, $^3$J$_{H-H}$ = 6.7 Hz, 6H, CH(CH$_3$)$_2$), 0.94 (d, $^3$J$_{H-H}$ = 6.6 Hz, 6H, CH(CH$_3$)$_2$), 0.65 (d, $^3$J$_{H-H}$ = 6.6 Hz, 3H, CH(CH$_3$)$_2$). $^{19}$F NMR (CDCl$_3$): -138.3 - 138.6 (br, BF$_3$). $^{11}$B NMR (CDCl$_3$): -1.0 (br, BF$_3$). $^7$Li NMR (CDCl$_3$): -2.99 (s). $^{13}$C NMR (THF-d$_8$): 159.70 (d, $^1$J$_{Rh-C}$ = 51 Hz, Rh-C$_{IDippBF}_3$), 147.22 (ipso Ar-iPr), 146.95 (ipso Ar-iPr), 146.67 (2x ipso Ar-iPr), 140.48 (ipso), 135.94 (ipso), 129.26 (p-Dipp), 128.68 (NCH), 128.44 (p-Dipp), 123.60 (m-Dipp), 123.54 (m-Dipp), 123.46 (m-Dipp), 123.39 (m-Dipp),
81.54 (d, $^1J_{Rh,C} = 10$ Hz, CODCH), 76.89 (d, $^1J_{Rh,C} = 10$ Hz, CODCH), 68.03 (THF), 32.82 (CODCH), 29.81 (CODCH), 29.06 (CH(CH$_3$)$_2$), 29.04 (CH(CH$_3$)$_2$), 28.88 (CH(CH$_3$)$_2$), 28.78 (CH(CH$_3$)$_2$), 26.38 (CH(CH$_3$)$_2$), 26.20 (THF), 26.13 (CH(CH$_3$)$_2$), 26.10 (CH(CH$_3$)$_2$), 25.45 (CH(CH$_3$)$_2$), 24.57 (CH(CH$_3$)$_2$), 24.51 (CH(CH$_3$)$_2$), 23.08 (CH(CH$_3$)$_2$), 22.86 (CH(CH$_3$)$_2$). Anal. Calcd. for C$_{77}$H$_{95}$B$_2$F$_6$LiN$_4$O$_2$Rh (1271.01): C, 66.15; H, 7.61; N, 4.41. Found: C, 65.61; H, 7.52; N, 4.12.

Synthesis of a mixture of [Li(THF)$_3$][cis-Rh(IDipp-BF$_3$)$_2$(CO)$_2$] 2-11a and [Li(THF)$_3$]trans-Rh(IDipp-BF$_3$)$_2$(COD)] 2-11b: Compound 2-10 (30 mg, 0.024 mmol) was frozen in THF (2 mL) in a liquid N$_2$ bath, and backfilled with 1 atm of CO. The mixture was allowed to thaw and was stirred at room temperature for 20 minutes. The solution was layered with pentane (10 mL) and allowed to sit overnight at room temperature, causing the formation of a mixture of orange and yellow crystals of 2-11a and 2-11b in an approximate ratio of 55:45, respectively, which were collected and dried under vacuum (16 mg, 53%). Selected NMR resonances and spectra are reported. 2-11a: $^1$H NMR (THF-d$_8$): 7.32 (t, $^3J_{H-H} = 7.6$ Hz, 2H, p-Dipp), 7.25 (t, $^3J_{H-H} = 7.6$ Hz, 2H, p-Dipp), 7.18 (d, $^3J_{H-H} = 7.9$ Hz, 4H, m-Dipp), 7.11 (d, $^3J_{H-H} = 8.0$ Hz, 4H, m-Dipp), 6.39 (s, 2H, NCH), 2.67 (septet, $^3J_{H-H} = 6.7$ Hz, 4H, CH(CH$_3$)$_2$), 2.63 (septet, $^3J_{H-H} = 6.7$ Hz, 4H, CH(CH$_3$)$_2$), 2.63 (septet, $^3J_{H-H} = 6.9$ Hz, 12H, CH(CH$_3$)$_2$), 1.20 (d, $^3J_{H-H} = 6.9$ Hz, 12H, CH(CH$_3$)$_2$), 1.18 (d, $^3J_{H-H} = 6.9$ Hz, 12H, CH(CH$_3$)$_2$), 1.10 (d, $^3J_{H-H} = 6.9$ Hz, 12H, CH(CH$_3$)$_2$). $^{19}$F NMR (THF-d$_8$): -139.4 - -139.7 (br m, BF$_3$). 2-11b: $^1$H NMR (THF-d$_8$): 7.28 (t, $^3J_{H-H} = 7.6$ Hz, 2H, p-Dipp), 7.27 (t, $^3J_{H-H} = 7.6$ Hz, 2H, p-Dipp), 7.12 (d, $^3J_{H-H} = 7.6$ Hz, 8H, m-Dipp), 6.57 (s, 2H, NCH), 2.77 (septet, $^3J_{H-H} = 6.7$ Hz, 4H, CH(CH$_3$)$_2$), 2.59 (septet, $^3J_{H-H} = 6.7$ Hz, 4H, CH(CH$_3$)$_2$), 1.20 (d, $^3J_{H-H} = 6.8$ Hz, 12H, CH(CH$_3$)$_2$), 1.16 (d, $^3J_{H-H} = 6.9$ Hz, 24H, CH(CH$_3$)$_2$), 0.85 (br, 12H, CH(CH$_3$)$_2$). $^{19}$F NMR (THF-d$_8$): -138.7 - -139.0 (br m, BF$_3$). Anal. Calcd. for C$_{68}$H$_{91}$B$_2$F$_6$LiN$_4$O$_2$Rh (1298.95): C, 63.32; H, 7.11; N, 4.43. Found: C, 61.27; H, 7.09; N, 4.20.

Li(THF)$_x$[Rh(IDipp-BF$_3$)(CO)$_2$] 2-12: Compound 2-2 (177 mg, 0.258 mmol (x = 3)) in 5 mL THF was combined with [Rh(CO)$_2$Cl]$_2$ (50 mg, 0.129 mmol) and
stirred overnight. The solvent was removed under vacuum to yield an orange solid, which was washed with pentane and dried under vacuum. (170 mg, 93%). By NMR spectroscopy it is evident that 0.7 equiv. of THF remains bound to the product. $^1$H NMR (THF-d$_8$): 7.33 (t, $^3$J$_{H-H} = 7.8$ Hz, 1H, p-Dipp), 7.31 (t, $^3$J$_{H-H} = 7.8$ Hz, 1H, p-Dipp), 7.26 (s, 2H, NCH), 7.20 (d, $^3$J$_{H-H} = 7.8$ Hz, 2H, m-Dipp), 7.17 (d, $^3$J$_{H-H} = 7.8$ Hz, 4H, m-Dipp), 2.80 (septet, $^3$J$_{H-H} = 6.7$ Hz, 2H, CH(CH$_3$)$_2$), 2.65 (septet, $^3$J$_{H-H} = 6.7$ Hz, 2H, CH(CH$_3$)$_2$), 2.13 (d, $^3$J$_{H-H} = 6.8$ Hz, 12H, CH(CH$_3$)$_2$), 1.19 (d, $^3$J$_{H-H} = 6.8$ Hz, 12H, CH(CH$_3$)$_2$), 1.14 (d, $^3$J$_{H-H} = 6.8$ Hz, 12H, CH(CH$_3$)$_2$). $^{19}$F NMR (THF-d$_8$): -141.2 - -141.7 (br m) (BF$_3$). $^{11}$B NMR (THF-d$_8$): -1.0 - -3.2 (br, BF$_3$). $^7$Li NMR: -2.65 (s). IR(KBr): 2067 (vCO), 1998 (vCO).

2.5 References


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Chapter 3. Cyclic Bent Allene Complexes as Catalysts for Homogeneous Hydrogenation

3.1 Introduction

3.1.1 Motivation

The motivation of this research project is a continuation of the efforts described in Chapter 2, relating to the synthesis of a highly active and selective Ru based catalyst for the hydrogenation of olefins, in particular for the hydrogenation of the olefinic residues of nitrile butadiene rubber (NBR)\(^1\) in conjunction with our industrial partners LANXESS (Scheme 3.1.1). Current industrial methods for this hydrogenation employ Wilkinson’s catalyst, RhCl(PPh\(_3\))\(_3\). Given that Rh is one of the most expensive metals on the periodic table, even the substitution for a Ru catalyst of comparable activity would represent a significant savings. Ru based catalysts for the hydrogenation of olefins, such as RuHCl(PPh\(_3\))\(_3\) and RuHCl(CO)(NHC)(PR\(_3\)), have been known for some time,\(^2\)-\(^7\) but in general have marginal activity compared to systems based on Rh and Ir. However, it has been observed in Ru based systems that the incorporation of more electron donating ligands, such as NHCs, results in an increase in the catalytic activity.\(^8\) This effect is thought to be due to the stabilization of low coordinate Ru species formed during catalysis. Therefore, in an attempt to generate a more highly active Ru based catalyst, we have synthesized a family of Ru-hydrido complexes bearing strongly electron donating carbodicarbene ligands.

\[ \text{NBR} \xrightarrow{\text{H}_2, \text{catalyst}} \text{HNBR} \]

Scheme 3.1.1. The hydrogenation of nitrile-butadiene rubber (NBR) to hydrogenated nitrile butadiene rubber (HNBR)
3.1.2 Carbones

Since their discovery over two decades ago, N-heterocyclic carbenes (NHCs) have earned a prominent position in the toolbox of the organometallic chemist.\textsuperscript{9-18} Their high $\sigma$-donating ability and steric bulk have proven functional in stabilizing low-coordinate transition metal complexes, and have found numerous applications in catalysis. More recently, a number of novel divalent carbon species have been synthesized based on other heterocycles,\textsuperscript{19-30} offering new avenues to alter the $\sigma$ and/or $\pi$-donor characteristics of the carbene.

![Chemical structures of Carbones](image)

\textbf{Figure 3.1.1.} Members of the “Carbon(0)” family: \textbf{A},\textbf{B}: Carbodiphosphoranes. \textbf{C}: Carbodicarbene. \textbf{D}-\textbf{F}: Cyclic Bent Allenes. \textbf{G}: Tetraaminoallene.

In 2008, Bertrand and coworkers reported the synthesis of stable pyrazol-4-ylidenes that featured heteroatoms at the 3,5 positions of the ring, termed ‘cyclic bent allenes’ (CBAs) (Figure 3.1.1. \textbf{D}, \textbf{E}).\textsuperscript{31} It has been shown computationally and experimentally that the introduction of these heteroatoms delocalizes the ring $\pi$ electrons exocyclicly,\textsuperscript{32-34} rendering the central carbon atom of the CBA both strongly $\sigma$ and $\pi$-basic, and the heterocycle weakly aromatic. CBAs are members of the carbodicarbene family, and are part of a growing class of nominally
carbon(0) compounds (Figure 3.1.1)\textsuperscript{35-62} The isolation of a Rh-bis(carbonyl) complex bearing this ligand revealed its significantly greater donating power relative to NHCs; the Tolman Electronic parameter (TEP) of D is 2034.9 cm\textsuperscript{-1}\textsuperscript{31,63} Additionally, the CBAs can be isolated in high yields on a large scale, and are thermally stable in pure form up to 95 °C under inert atmosphere\textsuperscript{31} Despite these attractive properties, only a small number of CBA metal complexes have been described\textsuperscript{31,64} and no examples of catalysis with such systems had been reported prior to this work. Catalysis employing carbodicarbene ligands also remains very rare, and has so far been limited to chelated systems\textsuperscript{65,66}

3.1.3 Ru based Olefin Hydrogenation

Since the beginnings of organometallic chemistry in the 1960s, homogeneous catalytic olefin hydrogenations have been largely the domain of Rh and Ir based systems\textsuperscript{67} two of the most expensive transition metals. Significantly cheaper Ru has been used for olefin hydrogenation catalysis, although highly active catalysis is usually restricted to monosubstituted olefins\textsuperscript{68,69} or systems where a directing group is present\textsuperscript{70-73} It has long been known that the complex Ru(PCy\textsubscript{3})\textsubscript{2}(CO)HCl will catalyze the hydrogenation of unactivated olefins\textsuperscript{2-7} Nolan and Fogg have synthesized mixed NHC-phosphine variants of the type Ru(NHC)(PR\textsubscript{3})(CO)HCl, and found that the use of labile phosphines in combination with strongly donating NHCs had a positive effect on rates of catalysis at elevated temperatures\textsuperscript{8} Berke and others have also demonstrated that abstracting or substituting a halide for a weakly coordinating anion in related Re catalysts can also increase the rates of hydrogenation\textsuperscript{74,75} Based on this precedent, we reasoned that the even more strongly donating nature of CBAs, coupled with their ability to act as four electron donors, should impart greater stability to a coordinatively unsaturated cationic active species (Scheme 3.2.2). Herein, we describe the synthesis of a family of hydrido carbonyl Ru complexes featuring CBAs, and demonstrate their superior activity in hydrogenation catalysis of both functionalized and unfunctionalized olefins, as well as their utility in diastereoselective reductions. Chiral modifications of the ligand are also explored.
Scheme 3.1.2. Catalyst Pre-equilibrium

3.2 Results and Discussion

3.2.1 Ligand Synthesis

CBAs are accessed by deprotonation of the corresponding 1,2-diphenyl-3,5-bis(aryloxy)pyrazolium salts. The salts are prepared by the method of Bertrand and coworkers and may be isolated on scales as large as 0.25 kg. The synthesis of the 3,5-bis(2,6-dimethylphenyl) derivative and its deprotonation to form the free CBA 3-1 is detailed in Scheme 3.2.1. While the original report of the synthesis of 3-1 yielded the product as a mixture with KBF₄ in a 47% yield, we have refined this methodology to allow the isolation of pure 3-1 in yields approaching 90% and quantities as high as 0.5 g. The free CBA 3-1 is highly reactive and air sensitive pale yellow microcrystalline solid; samples stored in a -45 °C freezer under N₂ for as little as 24 h become dark brown in colour. Compound 3-1 is best used immediately upon isolation.
3.2.2 Initial Metalation Attempts

Our initial foray into the chemistry of CBAs involved examination of direct reaction of compound 3-1 with various Ru starting materials. Unfortunately, direct reaction with RuCl$_2$(PPh$_3$)$_3$, RuHCl(PPh$_3$)$_3$, RuHCl(NHC)(PPh$_3$)$_2$, [RuCl$_2$(p-cymene)$_2$]$_2$, RuCl$_2$(DMSO)$_4$, RuCpCl(PPh$_3$)$_2$, RuHCl(H$_2$)(PCy$_3$)$_2$, and RuH$_2$(PPh$_3$)$_3$ all afforded inseparable mixtures of products. Subsequently, we attempted the transmetalation of the CBA via an Ag complex, a methodology which has been extensively applied to NHC ligands.$^{76}$

Combination of one equivalent of 3-1 with one equivalent of AgOTf affords the adduct (CBA)AgOTf 3-2 as a colourless crystalline solid (Scheme 3.2.2). Unfortunately, 3-2 crystallizes only as extremely fine needles unsuitable for X-ray diffraction. However, the complex was characterized by solution NMR spectroscopy, and its formulation was supported by elemental analysis.
Interestingly, the use of an excess of AgOTf afforded the doubly metalated cyclic bent allene species (CBA)(AgOTf)$_2$ 3-3 in 53% yield (Scheme 3.2.2). Crystals of 3-3 suitable for X-ray diffraction were obtained from CH$_2$Cl$_2$/Et$_2$O solution (Figure 3.2.1). In the solid state, the central carbon of the cyclic bent allene is bound to both Ag centres with identical bond lengths of 2.163(4) Å, as imposed by crystallographic symmetry. There is an argentophilic interaction present between the two Ag centres, with an Ag-Ag bond length of 2.7826(6) Å. The Ag-C-Ag angle is 80.1(2)°. While it has been predicted that carbodicarbenes such as 3-1 can serve as a four electron donor and bind to two metal centres, complex 3-3 is the first example of the isolation of such a species. The significantly differing $^1$H and $^{13}$C NMR spectra of 3-2 and 3-3 in CD$_2$Cl$_2$ suggest that the double ligation of the central carbon atom is maintained in solution.

Scheme 3.2.2. Synthesis of Ag-CBA complexes 3-2 and 3-3.
We examined the reaction of complexes 3-2 and 3-3 with Ru starting materials. Reactions with RuHCl(PPh₃)₃, RuCl₂(PPh₃)₃, RuHCl(NHC)(PPh₃)₂, and [RuCl₂(p-cymene)₂]₂ were attempted. Unfortunately, transmetalation was never observed. The addition of chloride sources such as tetraethlyammonium chloride, as well as heating the reactions did not productively affect the reaction outcomes. We hypothesize that the relative electron richness of the CBA, when compared to
NHCs, results in robust CBA-Ag complexes, which are unable to deliver the organic substrate to another metal centre.

3.2.3 Synthesis of Ru CBA Complexes

In the course of our trials with various Ru starting materials, the reaction of 3-1 and RuHCl(CO)(PPh₃)₃ was the last to be examined. After stirring at room temperature in toluene for 16 hours, the reaction mixture was filtered and concentrated, resulting in the precipitation of single crystals of beige RuHCl(CO)(CBA)(PPh₃)₂ 3-4 which was isolated in 47% yield (Scheme 3.2.3). The molecular structure of 3-4 reveals a distorted octahedral geometry where the CBA and hydride are mutually cis, and both mutually trans to a PPh₃ ligand (Figure 3.2.2). Steric crowding forces both of the pendant aryloxy groups on the CBA to bend away from the metal centre, as has been previously observed by Bertrand and coworkers.⁶⁴

Scheme 3.2.3. Synthesis of Ru-CBA complexes 3-4 – 3-6
The Ru-P bond length trans to the hydride is notably elongated (2.475(1) Å) compared to the other trans to the CBA (2.361(1) Å), likely due to steric congestion. Concordantly, upon dissolution of complex 3-4 in CD$_2$Cl$_2$, dissociation of PPh$_3$ trans to hydride is observed, and two signals are observed in the $^{31}$P{$^1$H} NMR spectrum; one at 44.6 ppm corresponding to the Ru-monophosphine species, and the other corresponding to free PPh$_3$ at -5.2 ppm. The $^1$H NMR spectrum of 3-4 displays a doublet in the hydride region at -24.22 ppm with a $^2J_{\text{H-P}}$ coupling constant of 26 Hz, further supporting dissociation of
PPh\textsubscript{3} from 3-4, and indicating the \textit{cis} configuration of the hydride and PPh\textsubscript{3} in the product Ru monophosphine species. In very concentrated NMR samples, a low intensity doublet of doublets can be observed in the hydride region at -6.32 ppm with \(^2J_{H-P}\) coupling constants of 23 and 130 Hz, attributable to the crystallographically characterized bisphosphine species 3-4.

![Molecular structure of 3-5](image)

**Figure 3.2.3.** Molecular structure of 3-5. Thermal ellipsoids are drawn at 50% probability. All hydrogen atoms except hydride are omitted for clarity. Colours: C, grey; H, turquoise; Ru, magenta; Cl, green; P, purple; O, red; N, blue.

Treatment of a solution of 3-4 with one equivalent of BH\textsubscript{3}(THF) sequesters the labile phosphine as the adduct H\textsubscript{3}B-PPh\textsubscript{3} and allows the for isolation of pure RuHCl(CO)(CBA)(PPh\textsubscript{3}) 3-5 as a bright yellow solid (Scheme 3.2.3). The
formulation of 3-5 was confirmed by a single crystal X-ray diffraction study (Figure 3.2.3). While the pendant xylyl groups are now canted toward the metal, the Ru-C_{CBA} distances (2.122(4) Å in 3-4 and 2.128(2) Å in 3-5) remain quite similar. There is no evidence for interaction of the pendant xylyl groups with the open coordination site on Ru. Interestingly, the {^1H} NMR signals attributable to the CBA ligand are significantly broadened at room temperature (Figure 3.2.4), implying fluxionality. Upon cooling to -60 °C, signals in the methyl region coalesce into four singlets, each integrating to three protons. The upfield aryl signals observed in Figure 3.2.4 are consistent with a close contact of a xylyl arm with a phenyl group on PPh₃, which is also observed in the molecular structure (Figure 3.2.3). The IR spectrum of 3-5 displays a CO stretch at 1892 cm⁻¹, significantly lower than that observed for the analogous NHC complex RuHCl(CO)(SIMes)(PPh₃) (1911 cm⁻¹),⁸ revealing the greater electron donating power of the CBA in these systems. The central carbon of the CBA is observed as a doublet at 106.4 ppm in CD₂Cl₂ in the {^{13}C}{^1H} NMR spectrum, with 83 Hz \(^2\)J_{P,C} coupling.
Substitution of the phosphine ligand for the more strongly donating NHC, SIMes, can be achieved by refluxing complex 3-4 with 3.5 equivalents of the NHC in THF for 24 h (Scheme 3.2.3). An excess of the NHC is required to drive the reaction to completion, indicating that an associative substitution mechanism is likely operating, where the incoming NHC initially binds to the vacant site cis to the CBA. The isolated bright yellow-orange RuHCl(CO)(CBA)(SIMes) 3-6 displays similar broad resonances for the CBA arms as observed for 3-5 (Figure 3.2.8). A molecular structure confirmed a similar geometry to complex 3-5 where SIMes is trans to the CBA (Figure 3.2.5). Interestingly, the steric environment of the metal centre causes one of the xylyl arms of the CBA to bend away from the metal centre while the other is bent towards. This ‘semi open’ conformation of the CBA has not been previously observed. The Ru-C_{SIMes} bond length of 2.134(3) Å is elongated compared to distances reported for Ru(Ph)Cl(CO)(PCy₃)(SIMes)⁷⁷ and RuCl₂(CO)(PCy₃)(SIMes),⁷⁸ consistent with the greater donating power of the CBA. The IR spectrum displays a CO stretch at 1881 cm⁻¹, among the lowest

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**Figure 3.2.4.** Variable temperature $^1$H NMR (CD₂Cl₂) spectra of 3-5.
reported for complexes of this type.\textsuperscript{8,79} The $^{13}\text{C}^1\text{H}$ NMR chemical shift of the central carbon in the CBA in CD$_2$Cl$_2$ is 114.1 ppm.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{Molecular structure of 3-6. Thermal ellipsoids are drawn at 50\% probability. All hydrogen atoms except hydride are omitted for clarity. Colours: C, grey; H, turquoise; Ru, magenta; Cl, green; O, red; N, blue.}
\end{figure}

A strategy that has been successfully employed in increasing catalytic activity in related hydrogenation catalysis is to replace a strongly bound halide with a weakly coordinating anion.\textsuperscript{74,75,79} To this end, equimolar combinations of either complex 3-5 or 3-6 and TMSOTf (Scheme 3.2.4) resulted in instantaneous
reactions in CH$_2$Cl$_2$ at room temperature, generating the species RuH(OTf)(CO)(CBA)(L) (3-7, L= PPh$_3$; 3-8, L= SIMes), respectively. These species were fully characterized by spectroscopic and analytical methods, and the molecular structures have been confirmed by single crystal diffraction studies (Figure 3.2.6, Figure 3.2.7). Metric parameters of complexes 3-5 and 3-6 and their respective triflate salts 3-7 and 3-8 are similar, where the Ru-C$_{CBA}$ distances are 2.110(3) and 2.120(4) Å in 3-7 and 3-8, respectively. The compounds 3-7 and 3-8 give rise to infrared CO stretches at 1919 and 1886 cm$^{-1}$, respectively. These absorptions are slightly blue-shifted comparatively to those observed for 3-5 and 3-6, reflecting the more electropositive nature of the Ru centres when the electron poor OTf anion is incorporated. In the $^{13}$C{$^1$H} NMR spectrum in CD$_2$Cl$_2$ the central CBA carbon atoms appear at 103.1 (d, $^2$J$_{C-P}$ = 77 Hz) and 109.6 (s) ppm in the complexes 3-7 and 3-8, respectively.

Scheme 3.2.4. Halide abstraction by TMSOTf yielding 3-7 and 3-8.

Interestingly, in the case of 3-8, extremely broad signals in $^1$H NMR spectrum were observed for both the SIMes and CBA ligands at room temperature (Figure 3.2.8). This significant broadening is not observed complex 3-6, suggesting that the implied dynamic nature is the result of triflate dissociation in CD$_2$Cl$_2$ solution and NMR timescale rotation about the Ru-SIMes and Ru-CBA bonds. In addition, the $^1$H NMR spectrum of 3-7 is much sharper and very similar to that of 3-5, suggesting that dissociation of triflate occurs in the more electron rich environment of 3-8. Upon cooling a CD$_2$Cl$_2$ solution of 3-8 to -80°C, ten singlets
integrating to three protons each are observed in the aliphatic region of the $^1$H NMR spectrum (Figure 3.2.9). This is consistent with inhibited rotation of both the CBA and SIMes ligands about the metal centre, and a $C_1$ symmetric complex at reduced temperature.

Figure 3.2.6. Molecular structure of 3-7. Thermal ellipsoids are drawn at 50% probability. All hydrogen atoms except hydride are omitted for clarity. Colours: C, grey; H, turquoise; Ru, magenta; Cl, green; P, purple; S, yellow; F, yellow-green; O, red; N, blue.
Figure 3.2.7. Molecular structure of 3-8. Thermal ellipsoids are drawn at 50% probability. Disordered triflate was modeled isotropically over two positions and one position is shown for clarity. All hydrogen atoms except hydride are omitted for clarity. Colours: C, grey; H, turquoise; Ru, magenta; Cl, green; S, yellow; F, yellow-green; O, red; N, blue.
Figure 3.2.8. $^1$H NMR spectra of 3-6 (bottom) in C$_6$D$_6$ and 3-8 (top) in CD$_2$Cl$_2$ at room temperature.
Figure 3.2.9. Variable temperature $^1$H NMR (CD$_2$Cl$_2$) spectra of 3-8; detail of aliphatic region. Protonated CBA is identifiable as a minor impurity (approx 5 mol%)
3.2.4 Catalytic Hydrogenation of Olefins

Catalytic olefin hydrogenation reactions were performed under 20 bar H₂ pressure at 25 °C employing 10 M olefin solutions in CH₂Cl₂, using catalysts 3-5 – 3-8 (Table 3.2.1). Hydrogenation of 1-hexene proceeded rapidly under these conditions at very low loadings with catalysts 3-6, 3-7, and 3-8. Catalyst 3-8 proved to be the most active, where quantitative conversion can be achieved in 15 minutes at 0.01 mol% loading. At 0.005 mol% loading, 3-8 is capable of 92% conversion to n-hexane in 15 minutes (Table 3.2.1, Entry 8), corresponding to an average TOF of 20.4 s⁻¹. Further reduction of the reaction time to only 5 minutes (Table 3.2.1, Entry 9) reveals 47% conversion and an average TOF of 31.3 s⁻¹.

The quantitative hydrogenation of cyclohexene also proceeded in 30 minutes when catalyst 3-8 was employed at 0.02 mol% loading (Entry 18). Lowering the catalyst loading to 0.01 mol% resulted in 93% conversion to cyclohexane in 30 minutes (Table 3.2.1, Entry 19), giving an average TOF of 5.2 s⁻¹. Compounds 3-5 – 3-7 showed little to no activity under identical conditions. The contrast in the catalytic activity of 3-8 and 3-7 is attributed to the lesser lability of triflate in more electron deficient complex 3-7 (vida supra).

The tertiary olefin 2-methyl-2-butene is also hydrogenated to 91% completion in 30 minutes and to complete conversion within 60 minutes at a loading of 0.1 mol% of 3-8 (Table 3.2.1, Entries 25, 26). Quantitative conversion can also be achieved at 0.05 mol% after 120 minutes (Table 3.2.1, Entry 28). However, poor conversion is observed for 2,3-dimethyl-2-butene at a relatively high loading of 0.5 mol% (Table 3.2.1, Entry 31). In addition, entries 2, 3, 4, 5, 6, 9, 18, and 20 from Table 3.2.1 were repeated in the presence of excess elemental Hg; in all cases, no effect on catalytic turnover was observed, excluding the possibility of heterogeneous Ru(0) acting as a catalyst. Lower pressure hydrogenation runs (5.0 mol% catalyst, 4 atm H₂) in J-Young NMR tubes in 0.5 mL CD₂Cl₂ were carried out on 0.1 mmol of 1-hexene, cyclohexane, and styrene for catalyst 3-6 and 3-8. During catalysis, only hydride resonances corresponding to the isolated complexes were observed, suggesting that these species are the catalyst resting states. No catalytic intermediates could be detected under these conditions.
<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate/Product</th>
<th>Catalyst (mol%)</th>
<th>t(min)</th>
<th>Conv. (%)(^a)</th>
<th>TON</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bu—CH=CHBu</td>
<td>3-5 (0.01)</td>
<td>30</td>
<td>8(10(^b))</td>
<td>800</td>
</tr>
<tr>
<td>2</td>
<td>Bu—CH=CHBu</td>
<td>3-6 (0.01)</td>
<td>30</td>
<td>97(3)</td>
<td>9,700</td>
</tr>
<tr>
<td>3</td>
<td>Bu—CH=CHBu</td>
<td>3-7 (0.01)</td>
<td>30</td>
<td>64(35)</td>
<td>6,400</td>
</tr>
<tr>
<td>4</td>
<td>Bu—CH=CHBu</td>
<td>3-8 (0.01)</td>
<td>30</td>
<td>100</td>
<td>10,000</td>
</tr>
<tr>
<td>5</td>
<td>Bu—CH=CHBu</td>
<td>3-8 (0.01)</td>
<td>15</td>
<td>100</td>
<td>10,000</td>
</tr>
<tr>
<td>6</td>
<td>Bu—CH=CHBu</td>
<td>3-8 (0.01)</td>
<td>5</td>
<td>68(29)</td>
<td>6,800</td>
</tr>
<tr>
<td>7</td>
<td>Bu—CH=CHBu</td>
<td>3-8 (0.005)</td>
<td>30</td>
<td>92(6)</td>
<td>18,400</td>
</tr>
<tr>
<td>8</td>
<td>Bu—CH=CHBu</td>
<td>3-8 (0.005)</td>
<td>15</td>
<td>92(4)</td>
<td>18,400</td>
</tr>
<tr>
<td>9</td>
<td>Bu—CH=CHBu</td>
<td>3-8 (0.005)</td>
<td>5</td>
<td>47(18)</td>
<td>9,400</td>
</tr>
<tr>
<td>10</td>
<td>Bu—CH=CHBu</td>
<td>Ru(PCy(_3))(_2)(CO)HCl (0.01)</td>
<td>30</td>
<td>79(2)</td>
<td>7,900</td>
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<td>11</td>
<td>Bu—CH=CHBu</td>
<td>Ru(SIMes)(PPh(_3))(CO)HCl (0.01)</td>
<td>30</td>
<td>35(5)</td>
<td>3,500</td>
</tr>
<tr>
<td>12</td>
<td>Bu—CH=CHBu</td>
<td>[Ir(COD)(py)(PCy(_3))]([PF_6]) (0.01)</td>
<td>30</td>
<td>100</td>
<td>10,000</td>
</tr>
<tr>
<td>13</td>
<td>Bu—CH=CHBu</td>
<td>[Ir(COD)(py)(PCy(_3))]([PF_6]) (0.005)</td>
<td>30</td>
<td>86(14)</td>
<td>17,200</td>
</tr>
<tr>
<td>14</td>
<td>Cyclic olefin</td>
<td>3-5 (0.05)</td>
<td>30</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Cyclic olefin</td>
<td>3-6 (0.05)</td>
<td>30</td>
<td>11</td>
<td>220</td>
</tr>
<tr>
<td>16</td>
<td>Cyclic olefin</td>
<td>3-7 (0.05)</td>
<td>30</td>
<td>6</td>
<td>120</td>
</tr>
<tr>
<td>17</td>
<td>Cyclic olefin</td>
<td>3-8 (0.05)</td>
<td>30</td>
<td>100</td>
<td>2,000</td>
</tr>
<tr>
<td>18</td>
<td>Cyclic olefin</td>
<td>3-8 (0.02)</td>
<td>30</td>
<td>100</td>
<td>5,000</td>
</tr>
<tr>
<td>19</td>
<td>Cyclic olefin</td>
<td>3-8 (0.02)</td>
<td>15</td>
<td>71</td>
<td>3,550</td>
</tr>
<tr>
<td>20</td>
<td>Cyclic olefin</td>
<td>3-8 (0.01)</td>
<td>30</td>
<td>93</td>
<td>9,300</td>
</tr>
<tr>
<td>21</td>
<td>Cyclic olefin</td>
<td>Ru(PCy(_3))(_2)(CO)HCl (0.05)</td>
<td>30</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>Cyclic olefin</td>
<td>Ru(SIMes)(PPh(_3))(CO)HCl (0.05)</td>
<td>30</td>
<td>&lt;1</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>Cyclic olefin</td>
<td>RhCl(PPh(_3))(_3) (0.05)</td>
<td>30</td>
<td>18</td>
<td>360</td>
</tr>
<tr>
<td>24</td>
<td>Cyclic olefin</td>
<td>[Ir(COD)(py)(PCy(_3))]([PF_6]) (0.05)</td>
<td>30</td>
<td>96</td>
<td>9,600</td>
</tr>
<tr>
<td>25</td>
<td>Cyclic olefin</td>
<td>3-8 (0.1)</td>
<td>30</td>
<td>91</td>
<td>910</td>
</tr>
<tr>
<td>26</td>
<td>Cyclic olefin</td>
<td>3-8 (0.1)</td>
<td>60</td>
<td>100</td>
<td>1,000</td>
</tr>
<tr>
<td>27</td>
<td>Cyclic olefin</td>
<td>3-8 (0.05)</td>
<td>30</td>
<td>56</td>
<td>1,120</td>
</tr>
<tr>
<td>28</td>
<td>Cyclic olefin</td>
<td>3-8 (0.05)</td>
<td>120</td>
<td>100</td>
<td>2,000</td>
</tr>
<tr>
<td>29</td>
<td>Cyclic olefin</td>
<td>[Ir(COD)(py)(PCy(_3))]([PF_6]) (0.1)</td>
<td>30</td>
<td>86</td>
<td>860</td>
</tr>
<tr>
<td>30</td>
<td>Cyclic olefin</td>
<td>[Ir(COD)(py)(PCy(_3))]([PF_6]) (0.05)</td>
<td>30</td>
<td>59</td>
<td>1,180</td>
</tr>
<tr>
<td>31(^b)</td>
<td>Cyclic olefin</td>
<td>3-8 (0.5)</td>
<td>30</td>
<td>6</td>
<td>12</td>
</tr>
</tbody>
</table>

**Conditions:** x mol\% catalyst and 10 mmol olefin in 1.00 mL CH\(_2\)Cl\(_2\), 20 bar. H\(_2\), 25°C.

\(^a\)Conversion determined by \(^1\)H NMR spectroscopy. Number in parentheses indicates isomerization to 2-hexene. \(^b\)1.0 mmol substrate in 1.00 mL CH\(_2\)Cl\(_2\) was used.

For comparative purposes, hydrogenation catalysis was carried out under the same conditions with the known Ru based active catalysts Ru(PCy\(_3\))\(_2\)(CO)HCl and Ru(SIMes)(PPh\(_3\))(CO)HCl (Table 3.2.1, Entries 10, 11, 21, 22).\(^8\) These
catalysts exhibited significantly lower degrees of hydrogenation of 1-hexene, and no activity in the hydrogenation of cyclohexene under the same conditions. In addition, Wilkinson’s catalyst, RhCl(PPh₃)₃, performed poorly in the hydrogenation of cyclohexene at 0.05 mol% (Table 3.2.1, Entry 23). In contrast, Crabtree’s highly active catalyst,²⁰ [Ir(COD)(py)(PCy₃)][PF₆], showed activity comparable to 3-8 under identical conditions for 1-hexene (Entries 12, 13), cyclohexene (Entry 24) and 2-methyl-2-butene (Table 3.2.1, Entries 29, 30).

Hydrogenations were also conducted with various vinylarene derivatives (Table 3.2.2). While 3-8 was found to effect the hydrogenations of various substituted styrenes at very low loadings, Crabtree’s catalyst was found to achieve only partial or marginal conversions under identical conditions. The early stages of hydrogenation of styrene to ethylbenzene by 0.005 mol% of catalyst 3-6, 3-8, and Crabtree’s catalyst was examined (Figure 3.2.10). While Crabtree’s catalyst has the highest initial turnover frequency at the one minute mark, it abruptly plateaus at this stage, indicating that catalyst deactivation is occurring. Crabtree’s catalyst is outperformed by both 3-6 and 3-8 over the course of the 10 minute run with 3-8 achieving 98% conversion in this time. Taken together, these data clearly demonstrate that catalyst 3-8 among the most active hydrogenation catalysts for unactivated olefins.
Table 3.2.2. Hydrogenation of styrene derivatives.

<table>
<thead>
<tr>
<th></th>
<th>Catalyst (mol%)</th>
<th>Substrate/ Product</th>
<th>T(°C)/ t(h)</th>
<th>P (bar)</th>
<th>Conv (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3-8 (0.005)</td>
<td>![Styrene]</td>
<td>25/0.5</td>
<td>20</td>
<td>97</td>
</tr>
<tr>
<td>2</td>
<td>[Ir] (0.005)</td>
<td>![Styrene]</td>
<td>25/0.5</td>
<td>20</td>
<td>63</td>
</tr>
<tr>
<td>3</td>
<td>3-8 (0.02)</td>
<td>![Styrene]</td>
<td>25/1</td>
<td>20</td>
<td>95</td>
</tr>
<tr>
<td>4</td>
<td>[Ir] (0.02)</td>
<td>![Styrene]</td>
<td>25/1</td>
<td>20</td>
<td>57</td>
</tr>
<tr>
<td>5</td>
<td>3-8 (0.05)</td>
<td>![Styrene]</td>
<td>25/1</td>
<td>20</td>
<td>95</td>
</tr>
<tr>
<td>6</td>
<td>[Ir] (0.05)</td>
<td>![Styrene]</td>
<td>25/1</td>
<td>20</td>
<td>16</td>
</tr>
<tr>
<td>7</td>
<td>3-8 (0.05)</td>
<td>![Styrene]</td>
<td>80/16</td>
<td>50</td>
<td>100&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>8</td>
<td>[Ir] (0.05)</td>
<td>![Styrene]</td>
<td>80/16</td>
<td>50</td>
<td>56</td>
</tr>
<tr>
<td>9&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3-8 (0.5)</td>
<td>![Styrene]</td>
<td>80/16</td>
<td>50</td>
<td>98</td>
</tr>
<tr>
<td>10&lt;sup&gt;b&lt;/sup&gt;</td>
<td>[Ir] (0.5)</td>
<td>![Styrene]</td>
<td>80/16</td>
<td>50</td>
<td>29</td>
</tr>
</tbody>
</table>

<sup>a</sup>Conversion determined by <sup>1</sup>H NMR spectroscopy. <sup>b</sup>1.0 mmol substrate in 0.10 mL C<sub>6</sub>H<sub>5</sub>Cl. <sup>c</sup>Isolated yield.

Figure 3.2.10. The hydrogenation of styrene to ethylbenzene. Conditions: 0.005 mol% catalyst with 3.0 mmol styrene in 0.30 mL CH<sub>2</sub>Cl<sub>2</sub>. 23 bar H<sub>2</sub>, 25 °C. Blue = 3-8; Green = 3-6; Red = [Ir(COD)(py)(PCy<sub>3</sub>)][PF<sub>6</sub>] “Crabtree’s catalyst”.
Catalyst 3-8 was also used to hydrogenate several olefins containing functional groups (Table 3.2.3). These reactions were carried out at 80°C under 50 bar H₂ pressure in neat substrate. Importantly, substrates were not rigorously dried, but were only degassed under vacuum prior to catalysis. The catalytic data demonstrates that 3-8 tolerates ester, carbonyl, nitro, and alcohol functional groups without difficulty. For example, isophorone is hydrogenated selectively to 3,3,5-trimethylcyclohexanone at 0.001 mol% loading (Table 3.2.3, Entry 4), with no traces of ketone reduction. Similarly, 3-nitrosytrene is selectively hydrogenated to 3-ethyl-nitrobenzene at 0.002 mol% loading (Table 3.2.3, Entry 6).

Table 3.2.3. Hydrogenation of functionalized Olefins with 3-8

<table>
<thead>
<tr>
<th>Substrate/Product</th>
<th>t(h) b</th>
<th>Loading (mol%)</th>
<th>Conv. (%) a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>0.01</td>
<td>100 (&gt;99)</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>0.005</td>
<td>81</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>0.004</td>
<td>100 (87)</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>0.001</td>
<td>94</td>
</tr>
<tr>
<td>5</td>
<td>16</td>
<td>0.005</td>
<td>100 (&gt;99)</td>
</tr>
<tr>
<td>6</td>
<td>16</td>
<td>0.002</td>
<td>98</td>
</tr>
<tr>
<td>7 e,f</td>
<td>13</td>
<td>0.02</td>
<td>100(92) de: 99</td>
</tr>
<tr>
<td>8 e,f</td>
<td>13</td>
<td>0.01</td>
<td>93 de: 97</td>
</tr>
<tr>
<td>9 f</td>
<td>3</td>
<td>0.05</td>
<td>95 de: 44</td>
</tr>
<tr>
<td>10 f</td>
<td>3</td>
<td>0.02</td>
<td>72 de: 54</td>
</tr>
</tbody>
</table>

Conditions: 50 bar H₂, 80 °C, 3.0 mmol neat olefin. a Conversion was determined by ¹H NMR spectroscopy and/or GC MS. b Reaction times are unoptimized. c 10 mmol of neat olefin was used. d Identity of directed isomer established by comparison with literature NMR spectra and/or X-ray crystallography. e Isolated yield.
We have also explored the utility of catalyst 3-8 in functional group directed diastereoselective olefin reductions.\textsuperscript{81-86} Given the implied four coordinate nature of the active species in catalyst 3-8 (Scheme 3.1.2), it seemed reasonable 3-8 should be able to bind a directing group for preferential delivery of hydrogen to one face of an olefin. To this end, it was found that catalyst 3-8 was capable of the directed reduction of terpinen-4-ol with loadings as low as 0.02 mol\% while achieving a d.e. of 99\% (Table 3.2.3, Entry 10; Figure 3.2.11). This diastereoselectivity implies loss of triflate in the catalytic cycle, so the directing group may bind to the metal centre. A proposed catalytic cycle is detailed in Scheme 3.2.5. Low pressure hydrogenation catalysis in J-Young NMR tubes have indicated that the isolated complex 3-8 is the only observable organometallic species in solution during catalysis (vida supra), so it is postulated here as the catalytic resting state (however, it should be noted that the catalytic mixtures have never been analyzed under the high pressure (≥ 20 bar) conditions used in Tables 3.2.1 – 3.2.3, due to the inherent technical challenges of such an experiment). The geometry of the substrate, terpinen-4-ol, requires a facial orientation of the olefin, directing group, and the metal hydride in order for olefin insertion to proceed, therefore isomerization to a cis CBA/NHC species upon substrate coordination is required. Ligand loss may also be an operative pathway in this case. However, such an isomerization is not required for olefin insertion to occur for non-directing substrates, so it is probable that catalysis proceeds through a trans CBA/NHC complex in other catalytic reactions (or perhaps both pathways operate).

Methylated terpinen-4-ol could also be hydrogenated effectively, although with more modest diastereoselectivity (Table 3.2.3, Entry 9, 10). Presumably, the weaker coordination of the more sterically encumbered ether functionality limits its utility as a directing group.
Figure 3.2.11. The crystallographically characterized major diastereomer from Table 3.2.3, Entries 7 & 8. Hydrogen atoms on carbons removed for clarity.

Scheme 3.2.5. Proposed mechanism for the hydrogenation of terpinen-4-ol by 3-8.
The Ru-CBA catalysts were also evaluated in the hydrogenation of nitrile butadiene rubber (NBR). Catalysis was performed at 80 °C under 50 bar hydrogen pressure over a 5.0% w/w solution of NBR in PhCl (Table 3.2.4). It was found that use of catalysts 3-5 and 3-7 resulted in significant cross linking of the polymer, as indicated by the formation of insoluble gels. However, catalysts 3-6 and 3-8 were found to be efficient in the hydrogenation of NBR, achieving conversion to HNBR with loadings as low as 0.1 and 0.05 µmol. IR spectroscopy indicated that the product HNBR is identical with a commercial sample supplied by LANXESS. GPC analysis of the HNBR revealed polydispersities (PDI) ranging from about 2.2 to 2.7, which is typical for HNBR. Lower catalyst loadings generally resulted in smaller values of M_n and M_w, but higher PDI. CBA catalysts 3-6 and 3-8 also outperform the known active NBR hydrogenation catalysts RhCl(PPh_3)_3 and RuHCl(IEtOMe)(SIMes)(PPh_3) (Table 3.2.4, Entries 16 - 19).
Table 3.2.4. Hydrogenation of NBR by cyclic bent allene catalysts 3-5 – 3-8.

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<th>Catalyst Loading</th>
<th>Degree of Hydrogenation</th>
<th>GPC Analysis of HNBR (1.0 mg/mL in THF)</th>
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<td>(mg)</td>
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Conditions: 5.00 mL of 5.0% w/w NBR in dry PhCl. 50 bar H₂ pressure at 80 °C for 20 h. a10.00 mL of 5.0% w/w NBR in dry PhCl. 50 bar H₂ pressure at 80 °C for 20 h. b400 equivalents of PPh₃ added. [Ru] = RuHCl((EtOMe)(SIMes)(PPh₃). [Rh] = RhCl(PPh₃)₃. Conversion was determined by the method of Marshall and coworkers. Entries 16 – 19 were reproduced from ref 87.

3.2.5 Further Variations of the Catalytic System

To further optimize the activity of CBA hydrogenation catalysts, ligand variation was attempted. Similar to the ion effect observed for the Crabtree catalysts, it was hypothesized that the incorporation of an anion less coordinating than triflate would result in an increase in catalytic activity. In this vein, reactions of 3-6 were attempted with NaPF₆, AgBF₄, KB(C₆F₅)₄, and [(Et₃Si)₂H][B(C₆F₅)₄]. In all cases, mixtures of products were obtained. We hypothesize that the four coordinate species formed upon triflate dissociation of 3-8 is unstable in the absence of rapid anion recombination or coordination to a substrate, and cannot be stabilized by less coordinating anions.

[127]
The nature of the NHC was next varied. It is observed in Table 3.2.1, Entry 31 that catalyst 3-8 is marginally active in the room temperature hydrogenation of an unfunctionalized tetrasubstituted olefin, among the most challenging substrates for hydrogenation. We rationalized that the use of a less sterically encumbered NHC would open up the coordination sphere of the metal, possibly resulting in an increase in catalytic activity. Reactions of the NHCs Me2IiMe, iPr, ICy, Ip-tol and well as Me2CAAC and bis(diisopropylamino)cyclopropenylidene were attempted with 3-5. In all cases mixtures, of products were obtained. However, in the cases of ICy and Ip-tol, small crops of crystals were obtained from the reaction mixtures, which were analyzed by X-ray diffraction. In both cases, the crystals were formed in amounts insufficient for characterization by spectroscopic methods (<1 mg). Nevertheless, the structures obtained have shed light on the challenges faced in substitution reactions of 3-5.

![Scheme 3.2.6](image)

**Scheme 3.2.6.** Reaction of 3-5 with the NHC ICy

Combination of an excess of ICy with 3-5 in THF results in the formation of a complex mixture of products (Scheme 3.2.6). Pentane was added to the reaction mixture, and was allowed to sit under nitrogen atmosphere at ambient temperature for several weeks. After this time a few red crystals deposited on the vessel wall. X-ray analysis identified the product unambiguously as the 4-pyrazolin-3-one-4-yl Ru aryl species 3-9 (Figure 3.2.12). It is likely that 3-9 is formed from oxidative addition of the CBA C-O linkage in the Ru(0) complex, Ru(CO)(CBA)(ICy)2. The Ru(0) species could potentially be formed by deprotonation of the metal hydride by ICy. Protonated ICy was also observed in
the reaction mixture. This observation indicates that with more basic NHCs, reduction of the metal hydride is a competing pathway to substitution. As all of the additional carbenes studied (except Ip-tol) are more electron donating than SIMes, the failure of these reactions can be rationalized by this mechanism.

Figure 3.2.12. Molecular structure of 3-9. Thermal ellipsoids are drawn at 50% probability. All hydrogen atoms are omitted for clarity. Colours: C, grey; Ru, magenta; O, red; N, blue.

The reaction of 3-5 with an excess of Ip-tol in THF also afforded a mixture of products (Scheme 3.2.7). Pentane was added to the mixture, which after standing under N₂ atmosphere at ambient temperature for one week afforded a few beige crystals. X-ray analysis identified the product as the 6-coordinate doubly cyclometalated species 3-10 (Figure 3.2.13), where the CBA has been lost from the metal centre. While the sequence of steps leading to the formation
of 3-10 is ambiguous (several possible mechanisms may be drawn), it highlights ortho-metalation as another potential side reaction when attempting ligand substitution with N-aryl substituted NHCs.

Scheme 3.2.7. Reaction of 3-5 with the NHC Ip-tol.

Figure 3.2.13. Molecular structure of 3-10. Thermal ellipsoids are drawn at 50% probability. All hydrogen atoms are omitted for clarity. Colours: C, grey; Ru, magenta; P, purple; O, red; N, blue.
As none of the reactions yielded any isolable products of catalytic interest, the derivatization of the Ru CBA family of catalysts by NHC variation was not further pursued.

3.2.6 Chiral Variations of the CBA – Ligand Synthesis

Given the success of CBA catalysts at olefin hydrogenation, we next investigated whether enantioselective versions of the Ru-CBA catalysts could be obtained. Enantioselective olefin hydrogenations have been studied extensively since the 1960s, modern hydrogenation methods often use chiral analogues of Crabtree’s catalyst.\textsuperscript{90,91} To construct a chiral cyclic bent allene, we envisioned a system where one arm of the CBA was substituted with an enantiopure 1,1’-bi(naphth-2-ol) (BINOL) derived moiety, where the BINOL linker may subsequently be cyclometalated at the 2’ position, to enforce a rigid 9-membered metallacycle (Figure 3.2.14).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{chiral_cyclo.png}
\caption{A chiral cyclometalated cyclic bent allene}
\end{figure}

Due to the facile construction of the 3,5-diaryloxy pyrazolium salts, assembling this asymmetric framework represents only a modest synthetic challenge. Bertrand and coworkers have reported that 1,2-diphenyl-3,5-dichloropyrazolium salts may be selectively mono-aryloxylated to yield the corresponding 1,2-diphenyl-3-chloro-5-(aryloxy)pyrazolium salts,\textsuperscript{92} where further nucleophilic substitution may be subsequently carried out on the remaining aryl chloride to produce non-symmetrical pyrazolium salts. Accordingly, addition of a 0.91 equivalents of 1,2-diphenyl-3-chloro-5-(2,6-dimethylphenoxy)pyrazolium tetrafluoroborate to (S)-(-)-2’-(t-butyldimethylsiloxy)-1,1’-binaphth-2-ol in the presence of triethylamine cleanly produces the corresponding enantiopure
pyrazolium salt 3-11 (Scheme 3.2.8). Compound 3-11 may be synthesized on a multigram scale in an 83% yield, and has been characterized by NMR spectroscopy and elemental analysis. Two $^1$H NMR signals assignable to the diastereotopic TBDMS methyl groups are observed at -0.19 and -0.32 ppm in CD$_2$Cl$_2$ solution, and the corresponding $^{13}$C{$^1$H} resonances are observed at -4.3 and -4.6 ppm. The central pyrazolium C-H resonance is observed at 5.00 ppm in the $^1$H NMR spectrum.

Deprotonation of the pyrazolium salt 3-11 proved to be challenging. The use of bases such as KHMDS, nBuLi, NaH, or NaNH$_2$ in Et$_2$O solution at -45 °C resulted in mixtures of products, however, a major species observed in the KHMDS and NaNH$_2$ reaction mixtures was consistent with resonances anticipated for the deprotonated product, offering encouragement that suitable conditions for isolation of such a species might be found. Eventually, it was discovered that the use of LiHMDS as the base in 1:1 Et$_2$O/pentane solution at -45 °C allowed the isolation of an off white solid with NMR spectra consistent with the deprotonated product 3-12a in 23% yield (Scheme 3.2.8). The $^1$H NMR spectrum of 3-12a in THF-d$_8$ revealed the absence of a pyrazolium C-H resonance. The phenoxy methyl protons are observed as a singlet at 2.08 ppm. The diastereotopic TBDMS methyl groups are observed at -0.09 and -0.33 ppm. From heteronuclear NMR experiments, it is evident that 3-12a is isolated as an adduct with the LiBF$_4$ generated in the reaction mixture; a strong $^7$Li resonance is observed at -2.38 ppm, and $^{19}$F and $^{11}$B resonances corresponding to a BF$_4$ counterion are also observed. No $^{13}$C{$^1$H} NMR signal for the central carbon atom could be detected, possibly due to coupling to the quadrupolar $^7$Li atom. Otherwise, the $^1$H and $^{13}$C{$^1$H} NMR spectra of 3-12a are similar to those of 3-11. Bertrand and coworkers have also reported the isolation of a LiBF$_4$ adduct of a related 3,5-bis(pyrrolidine) substituted CBA.$^{31}$
Scheme 3.2.8. Synthesis of the chiral CBA-Li complexes 3-12a and 3-12b
The use of a mixed Et$_2$O/pentane solvent is surprisingly critical to the success of the deprotonation, as no product can be isolated if either solely Et$_2$O or pentane are used, nor does the reaction proceed cleanly in THF. Further reaction optimization revealed that 3:1 Et$_2$O/pentane was the ideal solvent mixture, which allowed for the isolation of 100 – 140 mg quantities of **3-12a** in yields consistently ranging from 59-64%. Increasing the scale of the reaction in an attempt to isolate more product resulted in a reduction in yield.

Complex **3-12a** is isolated by concentrating the Et$_2$O/pentane soluble components of the reaction mixture, followed by washing with pentane to remove (TMS)$_2$NH and any unreacted LiHMDS. Interestingly, when these pentane washes were combined and concentrated, a second CBA containing product precipitated from solution, with resonances consistent with the complex CBA-LiN(TMS)$_2$ **3-12b**. In THF-d$_8$ solution, $^1$H NMR spectra of **3-12a** and **3-12b** are nearly identical, save for the presence of a singlet at -0.16 ppm, corresponding to the coordinated LiHMDS in **3-12b** and integrating to eighteen protons. A $^7$Li NMR signal at 0.72 ppm is also observed. Single crystals of **3-12b** suitable for X-ray diffraction were obtained from a pentane solution maintained at -45 °C for several months (Figure 3.2.15). Complex **3-12b** crystallizes in the chiral space group P1, supporting the enantiopurity of the complex. The Flack parameter refined to a value of -0.03(3), indicating that the correct S configuration of **3-12b** has been determined. Unusually, three molecules of **3-12b** are present in an asymmetric unit. In the solid state the C-Li distances are 2.09(1), 2.13(1), and 2.12(1) Å and the respective N-Li distances are 1.90(1), 1.88(1) and 1.89(1) Å. The formation of **3-12b** is consistent with the observation that the deprotonation of **3-11** appears to slow as the reaction proceeds, as **3-12b** is likely less active for further deprotonation of **3-11** than is free LiHMDS.
Complex 3-12a is clearly the more desirable product for subsequent metalation reactions, and as this compound could be reliably isolated in appreciable quantities, attempts were made to isolate a metal complex of this chiral carbodicarbene. Similar to 3-1, complex 3-12a is highly reactive and air-sensitive and is best used immediately after isolation for any subsequent manipulations.

3.2.7 Metal Complexes of a Chiral CBA

Given the success of CBA-Ru hydrido carbonyl based hydrogenation catalysts, metalation reactions with Ru sources were first explored. Reactions with RuHCl(CO)(PPh₃)₃, RuHF(CO)(PPh₃)₃, RuHCl(CO)(PCy₃), RuHCl(PPh₃)₃, and [RuCl₂(p-cymene)]₂ were attempted under various conditions - unfortunately, in
no case could any ligated product be isolated from the reaction mixtures. Our attention next turned to the isolation of Ag derivatives, with the goal of capturing and transmetalating the chiral cyclic bent allene to Ru.

**Scheme 3.2.9.** Synthesis of a chiral CBA-Ag complex

It was discovered that addition of an equimolar amount of AgOTf to 3-12a in \( \text{Et}_2\text{O} \), followed by stirring with an excess of [Ph₄P]Cl resulted in the formation of the AgCl adduct of the chiral bent allene, 3-13 (Scheme 3.2.9). Although crystals of 3-13 suitable for X-ray diffraction could not be obtained, 3-13 was characterized by NMR spectroscopy and its formulation supported by elemental analysis. The \(^1\text{H}\) NMR spectrum in \( \text{CD}_2\text{Cl}_2 \) revealed restricted rotation about the xyloxy group; two resonances were observed at 2.11 and 1.78 ppm each integrating to three protons. We attribute this new inequivalence to the additional steric bulk attained upon coordination of the C4 position of the chiral bent allene to the Ag centre. The diastereotopic TBDMS methyl resonances are observed at -0.17 and -0.37 ppm. The central carbon atom was observed as a low intensity broad doublet at 94.5 ppm in the \(^{13}\text{C}\{^1\text{H}\}\) NMR spectrum, with a \(^1\text{J}_{\text{Ag-C}}\) coupling constant of 217 Hz. Individual coupling constants to \(^{107}\text{Ag}\) and \(^{109}\text{Ag}\) could not be discerned. Heteronuclear NMR experiments confirmed the absence of any Li, F, B, or P containing moieties in this compound.

Complex 3-13 was reacted with RuHCl(CO)(PPh₃)₃, RuHF(CO)(PPh₃)₃, RuHCl(CO)(PCy₃), RuHCl(PPh₃)₃, and [RuCl₂(p-cymene)]₂ in an attempt to afford transmetalation of the chiral carbodicarbene to Ru. Unfortunately, no reaction was observed in any case, similar to results obtained with the aforementioned symmetrical bent allene Ag complex 3-2. It would seem that the high electron
releasing ability of the cyclic bent allene results in robust Ag-CBA complexes, which unlike NHC-Ag complexes, cannot be used to deliver the organic ligand to another metal centre.

Direct metalation of other metal complexes was next attempted. It was discovered that combination of 3-12a with 0.5 equivalents of [Ir(COD)Cl]₂ in toluene results in the formation of the metalated product Ir(CBA)(COD)Cl 3-14, which was isolated in 60% yield (Scheme 3.2.10). Crystals of 3-14 suitable for X-ray diffraction were grown from CH₂Cl₂/Et₂O at ambient temperature (Figure 3.2.16). Complex 3-14 crystallizes in the chiral orthorhombic space group P2₁2₁2₁, supporting the enantiopurity of the complex. The Flack parameter refined to a value of -0.004(2), indicating that the correct absolute configuration of 3-14 has been determined. Inversion of the crystal and re-refinement resulted in a Flack parameter of 1.020(15), concomitant with a significant increase in the values of R₁ and wR₂.

![Scheme 3.2.10. Synthesis of chiral CBA-Ir complexes](image)

In the solid state, the complex 3-14 adopts a square planar geometry typical for Ir(I). The Ir-CBA bond length is 2.068(3) Å. The BINOL derived moiety
displays an $S$ configuration, as anticipated from the chirality of the starting material. The $^1$H NMR spectrum of a CD$_2$Cl$_2$ solution of 3-14 reveals that the xyloxy methyl groups are split into two inequivalent resonances at 2.62 and 1.61 ppm, each integrating to three protons; similar to what was observed for 3-13. The diastereotopic TBDMS methyl groups are observed at -0.10 and -0.60 ppm. A resonance at 107.1 ppm is assigned to the central bent allene carbon atom in the $^{13}$C{^1}H NMR spectrum, similar to resonances observed for Ru cyclic bent allene complexes 3-5 – 3-8.

![Molecular structure of 3-14.](image)

**Figure 3.2.16.** Molecular structure of 3-14. Thermal ellipsoids are drawn at 50% probability. All hydrogen atoms are omitted for clarity. The COD ligand is disordered over two positions and was modelled isotropically. One position is shown for clarity. Colours: C, grey; Ir, dark teal; Cl, green; Si, pale yellow; O, red; N, blue.

Interestingly, a minor organometallic component is also present in the NMR spectra of this compound (ca. 10 mol%), which we tentatively assign to a rotomer
of 3-14, perhaps resulting from the inversion of the chloride and COD positions with respect to the chiral bent allene. In the minor component, $^1$H NMR signals for the olefinic cyclooctadiene protons are observed at 5.65, 5.09, 5.03 and 4.67 ppm. Despite the rather downfield shift of these resonances, an Ir-toluene complex can be ruled out by a gCOSY experiment, which reveals coupling between the resonances at 5.09 and 5.65 and an aliphatic multiplet centred at 3.13 ppm integrating to two protons, which is consistent with coordinated cyclooctadiene. The diastereotopic TBDMS methyl resonances are observed at 0.12 and -0.30 ppm. Inequivalent phenoxy methyl groups are also observed in this minor component, resonating at 2.42 and 1.69 ppm. Complex 3-14 conforms to the expected elemental analysis with variance less than ±0.30 % for each of the C, H and N components. Recrystallization of 3-14 does not alter the apparent composition of these two species (approx. 9:1).

Compound 3-14 cleanly reacts with an excess of CsF in THF to form the cyclometalated derivative 3-15 (Scheme 3.2.10), which was isolated in 72% yield. In CD$_2$Cl$_2$ solution, the $^1$H and $^{13}$C{$^1$H} NMR spectra (Figure 3.2.18) reveals the absence of the TBDMS protecting group. The xyloxy methyl groups are inequivalent and display equal resonances in the $^1$H NMR spectrum at 2.71 and 1.91 ppm. The $^{13}$C{$^1$H} NMR spectrum displays a resonance at 108.3 which we assign to the central bent allene carbon atom. The molecular structure of 3-15 was obtained from crystals grown from CH$_2$Cl$_2$/Et$_2$O (Figure 3.2.17). Complex 3-15 crystallizes in the chiral space group P2$_1$2$_1$2$_1$, supporting the enantiopurity of the complex. The solid state structure confirmed the formulation of complex 3-15 as the 9-membered metallacycle, with S configuration maintained in the BINOL moiety. In the solid state the Ir-O bond length is 2.068(2) Å and the Ir-C$_{CBA}$ bond length is 2.086(4) Å. The Flack parameter is -0.014(3), confirming the correct absolute configuration of the molecule has been determined. Inversion of the crystal and re-refinement results in a Flack parameter of 1.032(4), concomitant with a significant increase in the values of $R_1$ and $wR_2$. 
Figure 3.2.17. Molecular structure of 3-15. Thermal ellipsoids are drawn at 50% probability. All hydrogen atoms are omitted for clarity. Colours: C, grey; Ir, dark teal; O, red; N, blue.
Figure 3.2.18. $^1$H NMR (top) and $^{13}$C($^1$H) NMR (bottom) spectra of complex 3-15 in CD$_2$Cl$_2$. 
3.2.7 Electronic Structure of Metal Coordinated CBA

Does the CBA ligand confer one or two sets of electrons to the metal centre? In the geminally dimetalated 3-3, the CBA clearly functions as a four electron donor, however, in the saturated 18 electron Ru complex 3-4, it must be a two electron donor. It was noted in the series of crystallographically characterized CBA complexes that the degree of pyramidalization of the endocyclic nitrogen atoms varies considerably between the structures, from 343.6(5)° to 360.0(4)° (Table 3.2.5). Upon examination of this parameter, it seems that a qualitative relationship can be made between the average degree of pyramidalization at the N centres and the π-accepting ability of the complex to which it is bound, with more strongly accepting complexes yielding more planar environments about nitrogen. For example, the 18 electron Ru-species 3-4 is not π-accepting, and yields an strongly pyramidalized average angle sum at N of 345.9(9)°, while the geminally dimetallated species 3-3 gives N atoms which are perfectly planar. This trend is also clear in the Ru-CBA series 3-5 – 3-8. Loss of phosphine from 3-4 to form 3-5 gives coordinative unsaturation to the metal centre, and the pyramidalization at N decreases to 351.6(3)°. Substitution of chloride for triflate in 3-7 further increases the π-acidity of the complex and yields an average N angle sum of 356.4(4)°. Likewise, the more electron rich SIMes complexes 3-6 and 3-8 give relatively more pyramidalized N atoms, at 350.8(5)° and 354.2(5)°, respectively. Additionally, the CBA-LiHMDS complex 3-12b had significantly pyramidalized nitrogens with an average angle sum of 349.9(7)°. Similarly, substitution of chloride for a more nucleophilic aryloxide moiety in Ir complexes 3-14 and 3-15 also results in an increase in average pyramidalization at the endocyclic N atoms from 358.2(5)° to 355.9(5)°.
Table 3.2.5. N-pyramidalization in CBA complexes

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This effect can be rationalized by considering the possible electronic structures of metal coordinated CBA (Figure 3.2.19). Planar N atoms suggest delocalization of the N $\pi$-electrons to the adjacent endocyclic carbon centres, and donation of both pairs of electrons from the central carbone atom to the metal centre, which would be expected in cases of germinal dimetalation, or coordination to highly electron poor metal centres. Conversely, pyramidalized nitrogens suggest delocalization of the electrons in the filled carbone $\pi$-type orbital onto the ligand (Figure 3.2.19), which allows the weakly aromatic<sup>32</sup> heterocycle to localize a lone pair of electrons on N, thus adopting a more pyramidalized configuration.

**Figure 3.2.19.** Electronic structure of CBA-metal complexes

While the observed pyramidalization at N is certainly impacted by crystallographic packing effects, it is nevertheless suggestive that this trend is...
maintained through all nine crystallographically characterized CBA complexes described in this chapter, at least in a qualitative sense. This data suggests a variable binding mode of the CBA, where the carbon centre may alternatively donate two or four electrons depending on the requirements of the coordination centre.

3.3 Summary and Conclusions

In summary, we have described the synthesis and characterization of a series of CBA-Ru complexes, and demonstrated that a strongly donating CBA in combination with an NHC is capable of stabilizing an isolable species 3-8 with a labile OTf anion. This yields a catalyst exhibiting very high activity for the hydrogenation of unactivated olefins, chemoselective olefin hydrogenation, and functional group directed diastereoselective olefin hydrogenation. Comparative catalytic runs indicated the CBA-Ru species is significantly more active than similar NHC-Ru and phosphine complexes, and displays activity rivalling Crabtree’s catalyst in the hydrogenation of unactivated olefins, while outperforming it in styrene derivative reductions. Collectively, these data also illustrate that the exceptional donor abilities of CBA ligands provide a resource for catalyst design that has seen limited use to date.

Although catalytic applications of chiral Ir species 3-14 and 3-15 have not been explored, we have nevertheless demonstrated that an asymmetric cyclic bent allene can be readily accessed via use of a TBDMS protecting group. The CBA can subsequently be cyclometalated to a metal halide to form a rigid chiral 9-membered metallacycle.

While the construction of the asymmetric ligand 3-11 is facile, the deprotonation is inadequate, as only a very narrow range of conditions yielded any isolable CBA 3-12a, and some product is still lost as an adduct with LiHMDS 3-12b, which further slows the reaction. In contrast to NHCs, CBAs seem to have a much more limited scope of metal precursors with which they react productively, and only two successful metalations with 3-12a have so far been achieved. What is required to advance this chemistry is a reliable reagent for transmetalation of the CBA, ideally one which can be generated by direct reaction.
of complex 3-11 with a metal base, circumventing the need to find suitable conditions for deprotonation of the CBA.

3.4 Experimental Section
3.4.1 Crystallographic Details

X-ray Data Collection and Reduction. Crystals were coated in Paratone-N oil in the glovebox, mounted on a MiTegen Micromount, and placed under a N₂ stream, thus maintaining a dry, O₂-free environment for each crystal. The data were collected on a Bruker Kappa Apex II diffractometer using a graphite monochromator with Mo Kα (λ = 0.71073 Å) radiation. The data were collected at 150(2) K for all crystals. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the empirical multiscan method SADABS. In cases where non-merohedral twinning was detected, the data was indexed with CELLNOW to determine the contributions of the respective crystal domains, and the data were corrected for absorption effects using TWINABS. The heavy atom positions were determined employing the SHELXTL direct methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least squares techniques on F, minimizing the function ω (F₀-F_c)² where the weight ω is defined as 4F₀²/2σ (F₀²) and F₀ and F_c are the observed and calculated structure factor amplitudes, respectively. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of positional disordering. The final models of twinned structures were obtained by refinement against the twinned data. C-H atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C-H bond length of 0.95 Å. H-atom temperature factors were fixed at 1.20 times the isotropic temperature factor of the C-atom to which they are bonded. The H-atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance.
Table 3.4.1. Crystallographic information

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3.4.2 Experimental Details

**General Remarks**: All manipulations were carried out under an atmosphere of dry, O₂-free N₂ employing a Vacuum Atmospheres glovebox or a Schlenk vacuum line. Solvents were purified with a Grubbs-type column system manufactured by Innovative Technology and dispensed into thick-walled Straus flasks equipped with Teflon-valve stopcocks. CD₂Cl₂ was distilled under reduced pressure from CaH₂ and degassed by successive freeze-pump-thaw cycles. Deuterated benzene was distilled from purple sodium benzophenone ketyl. ¹H, ⁷Li, ¹¹B, ¹³C{¹H}, ¹⁹F, and ³¹P{¹H} NMR spectra were recorded at 25°C on Bruker 400 MHz spectrometers, unless otherwise noted. Chemical shifts are reported in parts per million relative to SiMe₄ and referenced to the residual solvent signal. ¹³C{¹H} NMR signals are reported to a precision of 0.01 ppm to avoid reporting
duplicates of close signals, but should be understood to be accurate to 0.1 ppm. Combustion analyses were performed in house employing a Perkin-Elmer CHN Analyzer. IR spectra were collected on a Perkin-Elmer Spectrum One FT-IR instrument. RuHCl(CO)(PPh$_3$)$_3$ and TMSOTf were purchased from Strem Chemicals and used without subsequent purification. All commercially available substrates were purchased from Aldrich or Acros and were degassed prior to catalysis, but were not dried or further purified. Nitrile butadiene rubber was provided by LANXESS. 1,2-diphenyl-3,5-(2,6-dimethylphenoxy)pyrazolium tetrafluoroborate,¹² O-Methylated terpinen-4-ol,⁸⁶ 1,2-diphenyl-3-chloro-5-(2,6-dimethylphenoxy)pyrazolium tetrafluoroborate,⁹² and (S)-(−)-2′-(t-butyldimethylsiloxy)-1,1′-binapth-2-ol⁹³ were prepared according to literature procedures. CsF was dried at 100 °C under vacuum for 24 h before use.

1,2-diphenyl-3,5-bis(2,6-dimethylphen)pyrazol-4-ylidine 3-1: The cyclic bent allene 3-1 was synthesized by a slightly modified literature procedure.²² Finely powdered 1,2-diphenyl-3,5-(2,6-dimethylphenoxy)pyrazolium tetrafluoroborate (800 mg, 1.46 mmol) was combined with potassium hexamethyldisilazide (292 mg, 1.46 mmol) and the mixture was cooled to -45 °C. Et$_2$O (10 mL) was added at this temperature and the stirred mixture was allowed to warm to room temperature over the course of 50 min. Et$_2$O (15 mL) was then added and the resultant suspension was filtered through a fine porosity glass frit. The solution was concentrated under high vacuum until light yellow crystals just began to form (approx. 5 mL) and pentane (10 mL) was added. The solution was re-concentrated to 5 mL resulting in the precipitation of a large crop of light yellow crystals. This process was repeated once more to effect complete precipitation of the product. The remaining supernatant was decanted and the light yellow precipitate was washed with pentane (2 x 10 mL) and dried under high vacuum to yield pure 3-1 (525 mg, 88%). Spectroscopic data are identical to those previously reported.²²
CBA(AgOTf) 3-2: AgOTf (140 mg, 0.54 mmol) was dissolved in anhydrous DMF (2 mL). 3-1 (253 mg, 0.55 mmol) was added and the mixture stirred for 5 min. Et₂O (10 mL) was added to precipitate the product, which was trititated and washed further with Et₂O (4 x 10 mL) and was isolated as an off white solid (151 mg, 39%). ¹H NMR (CD₂Cl₂): 7.50 – 7.42 (m, 10H, Ar), 7.13 – 7.05 (m, 6H, Ar), 2.10 (s, 12H, OXyl).

13C{¹H} NMR (CD₂Cl₂): Very broad low intensity signals are observed. 130.19, 130.03, 129.88, 127.52, 126.96, 16.57 (C₃H₃Ar). Anal. Calcd. for C₃₂H₂₈AgF₃N₂O₅S (717.51): C, 53.57; H, 3.93; N, 3.90. Found: C, 53.31; H, 4.24; N, 3.88.

CBA(AgOTf)₂·1.5DMF 3-3: AgOTf (300 mg, 1.17 mmol) was dissolved in DMF (2 mL). 3-1 (195 mg, 0.42 mmol) was added and the mixture stirred for 5 min. Et₂O (10 mL) was added to precipitate the product, which was trititated and washed further with Et₂O (4 x 10 mL) and was isolated as an off white solid (243 mg, 53%). Crystals suitable for X-ray diffraction were grown from CH₂Cl₂/Et₂O ¹H

NMR (CD₂Cl₂): 7.87 (s, 1.5 H, HCO₃DMF), 7.70 – 7.67 (m, 4H, Ar), 7.52 – 7.49 (m, 6H, Ar), 7.18 – 7.13 (m, 6H, Ar), 2.97 (s, 4.5H, NMe₃DMF), 2.86 (s, 4.5H, NMe₃DMF), 2.31 (s, 12 H, OXyl). ¹³C{¹H} NMR (CD₂Cl₂): 168.98 (NCO₃B₃A), 165.27 (NCO₃DMF), 150.51, 131.79, 131.22, 131.02, 130.38, 129.52, 128.96, 127.98, 120.81 (q, ¹JC-F = 321 Hz, OTf), 37.29 (NMe₃DMF), 31.97 (NMe₃DMF), 16.99 (CH₃Ar). ¹⁹F NMR (CD₂Cl₂): -78.0 (s, OTf). Anal. Calcd. for C₃₆H₃₅Ag₂F₃N₃O₉S₂ (1046.98) ·1.5(C₃H₇NO): C, 41.47; H, 3.76; N, 4.51. Found: C, 41.64; H, 3.84; N, 4.74.

Ru(CBA)(PPh₃)₂(CO)HCl 3-4: 3-1 (271 mg, 0.588 mmol) was added to a suspension of Ru(PPh₃)₃(CO)HCl (504 mg, 0.529 mmol) in toluene (10 mL) and the mixture was stirred for 16 h. The suspension was then filtered through a plug of celite and the solvent was removed under vacuum without stirring, causing X-ray quality crystals of the product to precipitate in a red-brown oil. The residue was trititated with small successive portions of Et₂O until the supernatant became yellow in colour. The crystalline beige solid obtained was further washed with pentane (2 x 5 mL) and dried under high vacuum (289 mg, 47%). No NMR
spectra could be obtained as the complex readily dissociates triphenylphosphine in solution, forming compound **3-5**. IR(KBr): 1899 cm\(^{-1}\) (vCO). Anal. Calcd. for C\(_{50}H_{44}ClN_2O_3PRu\) (1150.67): C, 70.98; H, 5.17; N, 2.43. Found: C, 71.24; H, 5.15; N, 2.45.

**Ru(CBA)(PPh\(_3\))(CO)HCl** 3-5: To a solution of **3-4** (168 mg, 0.146 mmol) in THF (5 mL) was added BH\(_3\) (1.0 M in THF, 146 μL, 0.146 mmol). The solution was concentrated to approximately 1 mL and pentane (15 mL) was added to precipitate the product. The bright yellow solid was collected by filtration and dried under high vacuum (121 mg, 93%). \(^1\)H NMR (CD\(_2\)Cl\(_2\)): 7.49 (d, \(^3\)J\(_{H-H}\) = 8.0 Hz, 4H, o-Ph), 7.42 (t, \(^3\)J\(_{H-H}\) = 8.0 Hz, 4H, m-Ph), 7.37-7.21 (m, 17H, PPh\(_3\) & p-Ph), 7.01 (br s, 2H, m-OAr), 6.74 (br s, 2H, m-OAr), 6.44 (br s, 2H, p-OAr), 2.28 (br s, 6H, OArCH\(_3\)), 2.09 (br s, 6H, OArCH\(_3\)), -24.21 (d, \(^2\)J\(_{H-P}\) = 26.3 Hz, 1H, RuH). \(^13\)C\(^{1}\)H NMR (CD\(_2\)Cl\(_2\)): 201.27 (CO), 151.02, 136.92 (d, \(^1\)J\(_{C-P}\) = 36.4 Hz, ipso-PPh\(_3\)), 134.96, 134.66 (d, \(^3\)J\(_{C-P}\) = 11.3 Hz, o-PPh\(_3\)), 129.84, 129.17 (d, \(^4\)J\(_{C-P}\) = 10.0 Hz, m-PPh\(_3\)), 127.67 (d, \(^5\)J\(_{C-P}\) = 9.1 Hz, p-PPh\(_3\)), 126.68, 125.93, 106.38 (d, \(^2\)J\(_{C-P}\) = 83.2 Hz, C\(_{CBA}\)), 17.48 (br, CH\(_3\)). \(^31\)P NMR (CD\(_2\)Cl\(_2\)): 44.6 (d, \(^2\)J\(_{H-P}\) = 26.3 Hz, 1H, RuH). IR(KBr): 1892 cm\(^{-1}\) (vCO). Anal. Calcd. for C\(_{50}H_{44}ClN_2O_3PRu\) (888.39): C, 67.60; H, 4.99; N, 3.15. Found: C, 67.87; H, 5.34; N, 2.93.

**Ru(CBA)(SIMes)(CO)HCl** 3-6: To a solution of **3-4** (150 mg, 0.130 mmol) in THF (5 mL) was added SIMes (140 mg, 0.457 mmol) and the solution was refluxed for 24 hours. The solution was cooled to room temperature and concentrated to approximately 1 mL. Pentane (15 mL) was added to precipitate the product as a bright yellow-orange solid, which was washed with pentane (3 x 10 mL) and dried under high vacuum (111 mg, 92%). \(^1\)H NMR (C\(_6\)D\(_6\)): 6.88 (br s, 2H, Mes), 6.86 - 6.77 (m, 6H), 6.75 (d, \(^3\)J\(_{H-H}\) = 8.0 Hz, 4H, m-OAr), 6.65 (br s, 2H, Mes), 6.60 - 6.57 (m, 6H), 3.30 (m, 4H, NCH\(_2\)CH\(_2\)N), 2.73 (br s, MesCH\(_3\), 6H), 2.51 (br s, MesCH\(_3\), 6H), 2.15 (br s, OArCH\(_3\), 12H), 2.05 (br s, MesCH\(_3\), 6H), -26.04 (s, 1H, Ru-H). \(^13\)C\(^{1}\)H NMR (CD\(_2\)Cl\(_2\)): 221.40 (NCN), 203.37 (CO), 171.39 (NCO), 152.38, 137.71, 137.64, 137.11, 136.81, 134.91, 130.38, 129.33, 129.30,
129.18, 128.93, 128.76 (br), 127.71, 125.39, 114.08 (C\(_{\text{CBA}}\)), 51.18 (NCCN), 20.96 (MesCH\(_3\)), 19.20 (MesCH\(_3\)), 19.15 (MesCH\(_3\)), 16.76 (br, XylCH\(_3\)). IR (KBr): 1881 cm\(^{-1}\) (\(v\)CO). Anal. Calcd. for C\(_{53}\)H\(_{55}\)ClN\(_4\)O\(_3\)Ru (932.55): C, 68.26; H, 5.94; N, 6.01. Found: C, 68.22; H, 5.38; N, 5.83.

**Ru(CBA)(PPh\(_3\))(CO)H(O\(\text{Tf}\)) 3-7**: Employing silylated glassware, compound 3-5 (50 mg, 0.056 mmol) was dissolved in THF (2 mL) and TMSOTf (10.5 μL, 0.058 mmol) was added. Solvent was removed under high vacuum and yellow solid was washed with pentane (3 x 5 mL) and dried under high vacuum (54 mg, 96%). Small amounts (~5 mol%) of inseparable \([\text{CBAH}]\)[OTf] are also observed. 

\(^1\)H NMR (CD\(_2\)Cl\(_2\)): 7.53 (d, \(^3\)J\(_{\text{H-H}}\) = 8.0 Hz, 4H, o-Ph), 7.45 - 7.31 (m, 15H, o-PPh\(_3\), p-PPh\(_3\), m-Ph & p-Ph), 7.23 (t, \(^3\)J\(_{\text{H-H}}\) = 8.0 Hz, 6H, m-PPh\(_3\)), 7.01 (br s, 2H, m-OAr), 6.78 (br s, 2H, m-OAr), 6.09 (br s, 2H, p-OAr), 2.41 (br s, 6H, OArCH\(_3\)), 2.14 (br s, 6H, OArCH\(_3\)), -23.38 (d, \(^2\)J\(_{\text{H-P}}\) = 23.3 Hz, 1H, RuH). 

\(^{13}\)C{\(^1\)H} NMR (CD\(_2\)Cl\(_2\)): 204.37 (d, \(^2\)J\(_{\text{C-P}}\) = 15.3 Hz, CO), 158.77, 150.38, 135.39 (d, \(^1\)J\(_{\text{C-P}}\) = 37.3 Hz, ipso-PPh\(_3\)), 134.19 (d, \(^3\)J\(_{\text{C-P}}\) = 11.7 Hz, o-PPh\(_3\)), 133.80 (br), 130.06, 129.99, 129.80, 129.62 (d, \(^5\)J\(_{\text{C-P}}\) = 1.9 Hz, p-PPh\(_3\)), 129.02, 128.17 (br), 128.11 (d, \(^5\)J\(_{\text{C-P}}\) = 9.0 Hz, m-PPh\(_3\)), 103.05 (d, \(^1\)J\(_{\text{C-P}}\) = 77.5 Hz, C\(_{\text{CBA}}\)), 17.25 (br, Me). 

\(^{19}\)F NMR (CD\(_2\)Cl\(_2\)): -78.7 (s) (O\(\text{Tf}\)). 

\(^{31}\)P NMR (CD\(_2\)Cl\(_2\)): 43.2 (d, \(^2\)J\(_{\text{H-P}}\) = 23.5 Hz, PPh\(_3\)). IR (KBr): 1919 cm\(^{-1}\) (\(v\)CO). Anal. Calcd. for C\(_{54}\)H\(_{55}\)F\(_3\)ClN\(_4\)O\(_6\)PRuS (1002.01): C, 61.13; H, 4.43; N, 2.80. Found: C, 61.23; H, 4.84; N, 2.72.

**Ru(CBA)(SIMes)(CO)H(O\(\text{Tf}\)) 3-8**: This was synthesized in an exactly analogous manner to 3-7 using compound 3-6. The product was obtained as an orange solid (87%). Small amounts (~5 mol%) of inseparable [CBAH][OTf] are also observed. 

\(^1\)H NMR (CD\(_2\)Cl\(_2\)): 7.46 - 6.48 (br m, 20H, Ar), 3.90 - 3.73 (m, 4H, NCH\(_2\)CH\(_2\)N), 2.66 - 1.54 (br m, 24H, ArCH\(_3\)) 2.34 (s, 6H, ArCH\(_3\)), -26.56 (s, 1H, RuH). 

\(^{13}\)C{\(^1\)H} NMR (CD\(_2\)Cl\(_2\)): Very broad low intensity signals are observed, select resonances are reported: 217.96 (NCN), 205.83 (CO), 137.41(br), 131.0-128.5 (br m), 127.7 (br), 125.3 (br), 109.58 (C\(_{\text{CBA}}\)), 51.31 (br, NCCN), 20.85 (br, Me), 18.34 (br, Me), 18.14 (br, Me), 16.7 (br, Me). 

\(^{19}\)F NMR (CD\(_2\)Cl\(_2\)): -77.9 (s)
Hydrogenation procedure; Table 3.2.1, Table 3.2.2: Entries 1-6: Under an inert atmosphere, x mmol of catalyst was weighed into a Parr vessel and dissolved in 1.00 mL or 0.30 mL CH$_2$Cl$_2$. 10 mmol or 3.0 mmol of the appropriate substrate was then added, the vessel was sealed, and rapidly purged three times with 20 bar H$_2$. The vessel was then filled to 20 bar H$_2$ pressure and allowed to stir at ambient temperature. The pressure was vented after the allotted time, and the vessel was opened in air. The solution was filtered through a small plug of Celite, and conversion was determined by $^1$H NMR spectroscopy by integration of the respective product and starting material resonances.

Hydrogenation procedure; Table 3.2.3, Table 3.2.2: Entries 7-10: Under an inert atmosphere, x mmol of catalyst was weighed into a Parr vessel and 3.0 mmol of the appropriate substrate was added. The vessel was sealed, rapidly purged three times with 40 bar H$_2$, filled to 40 bar H$_2$ pressure, and placed in an 80 °C oil bath with rapid stirring for a thermal equilibration period of 15 minutes. After this time, pressure was adjusted to 50 bar, and the reactor was allowed to stir at this temperature for the allotted time. Upon completion, the reactor was allowed to cool to room temperature over a period of 30 minutes, the pressure was vented, and the vessel was opened in air. The solution was filtered through a small plug of Celite, and conversion was determined $^1$H NMR spectroscopy and/or GC MS.

Hydrogenation Procedure; Table 3.2.4: Under an inert atmosphere, x mmol of catalyst was weighed into a Parr vessel and 5.00 mL of a 5.0% w/w solution of NBR in dry PhCl was added. The vessel was sealed, rapidly purged three times with 40 bar H$_2$, filled to 40 bar H$_2$ pressure, and placed in an 80 °C oil bath with rapid stirring for a thermal equilibration period of 15 minutes. After this time, pressure was adjusted to 50 bar, and the reactor was allowed to stir at this

temperature for the allotted time. Upon completion, the reactor was allowed to cool to room temperature over a period of 30 minutes, the pressure was vented, and the vessel was opened in air. The polymer solutions were coagulated by the addition of excess MeOH, and the polymer was collected and dried overnight in a vacuum oven set at 50 °C. The polymer was analyzed by GPC (1.0 mg/mL in THF) and IR spectroscopy (neat). The conversion to HNBR was determined by the method of Marshall and coworkers.

3-11: 1,2-diphenyl-3-chloro-5-(2,6-dimethylphenoxy)pyrazolium tetrafluoroborate (1.18 g, 2.55 mmol) and (S)-(−)-2′-(t-butyldimethylsiloxy)-1,1′-binapth-2-ol (1.13 g, 2.81 mmol) were dissolved in CH₂Cl₂ (15 mL). Triethylamine (0.41 mL, 5.58 mmol) was added and the mixture was stirred overnight. The mixture was concentrated under high vacuum, and pentane (100 mL) was added to precipitate the product. The residue was further triturated and washed with pentane (3 x 50 mL). The solid obtained was absorbed on silica, which was washed with CH₂Cl₂ to elute nonpolar impurities. The product was eluted with 1:1 CH₂Cl₂/acetone. The solution obtained was concentrated under high vacuum, and pentane (100 mL) was added to precipitate the product as a white solid, which was collected and dried under high vacuum (1.79 g, 83%). ¹H NMR (CD₂Cl₂): 8.07 (d, J_H-H = 8.6 Hz, 1H, Ar), 8.00-7.94 (m, 3H, Ar), 7.74 (d, J_H-H = 8.8 Hz, 1H, Ar), 7.52 (d, J_H-H = 7.9 Hz, 1H, Ar), 7.48-7.06 (m, 16H, Ar), 6.91 (d, J_H-H = 8.6 Hz, 1H, Ar), 8.80 (d, J_H-H = 7.7 Hz, 2H, Ar), 5.00 (s, 1H, pyr-H), 2.03 (s, 6H, OXyl), 0.29 (s, 9H, tBu-Si), -0.19 (s, 3H, Me-Si), -0.32 (s, 3H, Me-Si). ¹³C{¹H} NMR (CD₂Cl₂): 158.88 (NCO), 158.37 (NCO), 151.98, 150.25, 148.76, 133.95, 133.91, 132.91, 132.12, 131.66, 131.50, 130.77, 130.47, 130.19, 130.08, 130.07, 129.85, 129.57, 129.44, 128.81, 128.76, 128.64, 128.49, 128.06, 127.70, 127.18, 127.04, 126.84, 126.10, 124.58, 124.37, 121.17, 119.48, 118.36, 76.18 (pyr-H), 24.92 (CH₃CSi), 17.61 (CH₃CSi), 16.08 (CH₃Ar), -4.28 (MeSi), -4.62 (MeSi). ¹⁹F NMR (CD₂Cl₂): -152.8 (BF₄). ¹¹B NMR (CD₂Cl₂): -1.0 (BF₄). Anal. Calcd. For C₄₉H₄₇BF₄N₂O₃Si (826.81): C, 71.19; H, 5.73; N, 3.39. Found: C, 70.92; H, 5.55; N, 3.39.
3-12a/3-12b: To a suspension of 3-11 (151 mg, 0.183 mmol) in Et₂O/pentane (3 mL/1 mL) at -45°C was added LiHMDS (31 mg, 0.185 mmol). The mixture was allowed to warm to room temperature with stirring over a period of 30 min. The mixture was filtered of any insoluble material and the residue was further extracted with Et₂O (3 x 1 mL). The combined filtrate was concentrated to dryness, and was washed with small portions of pentane (3 x 3 mL). The product 3-12a is a beige solid (97 mg, 64%). The combined pentane washes were concentrated to 1 mL, and cooled to -45°C overnight, affording a white precipitate of 3-12b (12 mg, 7%). Crystals of 3-12b suitable for X-ray diffraction were grown from a pentane solution maintained at -45°C for 3 months.

3-12a: ¹H NMR (THF-d₈): 8.24 (d, ³J₇₋₅ = 8.9 Hz, 1H, Ar), 7.88 – 7.79 (m, 4H, Ar), 7.39 (d, ³J₇₋₅ = 8.1 Hz, 1H, Ar), 7.32 (t, ³J₇₋₅ = 7.8 Hz, 2H, Ar), 7.26 – 7.07 (m, 9H, Ar), 6.96 – 6.86 (m, 6H, Ar), 6.45 (d, ³J₇₋₅ = 6.5 Hz, 2H, Ar), 2.08 (s, 6H, OXyl), 0.37 (s, 9H, tBu-Si), -0.09 (s, 3H, Me-Si), -0.33 (s, 3H, Me-Si). ¹³C{¹H} NMR (THF-d₈): 173.24 (NCO), 172.85 (NCO), 152.56, 151.68, 151.11, 137.13, 135.66, 134.97, 134.18, 132.27, 131.10, 130.42, 129.95, 129.49, 129.09, 128.95, 128.43, 128.37, 127.95, 127.21, 127.07, 126.80, 126.61, 126.27, 125.97, 125.59, 125.39, 125.32, 124.32, 124.10, 123.64, 121.82, 121.47, 25.30 (CH₃Si), 17.96 (CH₃CSi), 16.89 (CH₃Ar), -4.17 (MeSi), -4.73 (MeSi). ⁷Li NMR (THF-d₈): -2.38 (s). ¹⁹F NMR (THF-d₈): -158.4 (s, BF₄). 3-12b: ¹H NMR (THF-d₈): 8.25 (d, ³J₇₋₅ = 9.2 Hz, 1H, Ar), 7.88 – 7.77 (m, 4H, Ar), 7.39 (d, ³J₇₋₅ = 7.8 Hz, 1H, Ar), 7.31 (t, ³J₇₋₅ = 7.6 Hz, 2H, Ar), 7.25 – 7.06 (m, 9H, Ar), 6.96 – 6.86 (m, 6H, Ar), 6.45 (d, ³J₇₋₅ = 7.0 Hz, 2H, Ar), 2.07 (s, 6H, OXyl), 0.37 (s, 9H, tBu-Si), -0.09 (s, 3H, Me-Si), -0.16 (s, 18H, N(TMS)₂), -0.33 (s, 3H, Me-Si). ⁷Li NMR (THF-d₈): 0.72 (s). Elemental analysis was not performed on these complexes due to their extreme sensitivity.

3-13: To a solution of 3-12a (48 mg, 0.058 mmol) in Et₂O (5 mL) was added AgOTf (15 mg, 0.058 mmol). The mixture was stirred for 10 minutes in the dark and filtered of the LiBF₄ precipitate. To the filtrate was added Ph₄PCI (66 mg, 0.176 mmol) and the mixture was stirred for 2 h in the dark. The mixture was again filtered and concentrated to 1 mL, Pentane was added to precipitate the
product. This was collected and dried, and then extracted into CH$_2$Cl$_2$ and filtered of any insoluble material. The filtrate was concentrated and pentane (10 mL) was added to precipitate the product as an off white solid, which was collected and dried under high vacuum (35 mg, 69%). $^1$H NMR (CD$_2$Cl$_2$): 7.99 (d, $^3$J$_{H-H}$ = 8.5 Hz, 1H, Ar), 7.94 (d, $^3$J$_{H-H}$ = 8.5 Hz, 1H, Ar), 7.86 (t, $^3$J$_{H-H}$ = 8.5 Hz, 2H, Ar), 7.61 (d, $^3$J$_{H-H}$ = 8.7 Hz, 1H, Ar), 7.48 – 6.97 (m, 18H, Ar), 6.64 (d, $^3$J$_{H-H}$ = 8.7 Hz, 2H, Ar), 2.11 (s, 3H, OXyl), 1.78 (s, 3H, OXyl), 0.35 (s, 9H, tBu-Si), -0.17 (s, 3H, Me-Si), -0.37 (s, 3H, Me-Si). $^{13}$C($^1$H) NMR (CDCl$_3$): 169.04 (NCO), 168.30 (NCO), 151.24, 149.80, 148.52, 133.95, 133.77, 132.80, 132.51, 130.82, 129.73, 129.63, 129.58, 129.51, 129.35, 129.24, 129.19, 128.89, 128.72, 127.55, 127.20, 126.91, 126.78, 126.32, 126.14, 125.93, 125.30, 123.94, 121.32, 120.76, 120.18, 94.51 (br d, $^1$J$_{Ag-C}$ = 217 Hz, Ag-C), 25.01 (CH$_3$CSi), 17.56 (CH$_3$CSi), 16.71 (CH$_3$Ar), -4.14 (MeSi), -4.65 (MeSi). Anal. Calcd. for C$_{49}$H$_{46}$AgClN$_2$O$_3$Si (882.32): C, 66.70; H, 5.26; N, 3.18. Found: C, 66.70; H, 5.32. N, 3.09.

3-14: Compound 3-12a (109 mg, 0.131 mmol), and [Ir(COD)Cl]$_2$ (43 mg, 0.064 mmol) were combined in toluene (5 mL) at -45 °C. The mixture was allowed to warm to room temperature and stirred for 2 hours, resulting in the gradual formation of a yellow precipitate. The solution was concentrated, and Et$_2$O (10 mL) was added to fully precipitate the product, which was washed further with Et$_2$O (3 x 10 mL). The solid obtained was extracted with CH$_2$Cl$_2$ (5 mL) and filtered of any insoluble material. The filtrate was concentrated, and pentane was added to precipitate the product as a yellow solid, which was collected and dried (85 mg, 60%). Crystals suitable for X-ray diffraction were grown from CH$_2$Cl$_2$/Et$_2$O. $^1$H NMR (CDCl$_3$) [Major Rotomer, approx. 90%]: 9.20 (d, $^3$J$_{H-H}$ = 9.3 Hz, 1H, Ar), 8.04 (d, $^3$J$_{H-H}$ = 9.0 Hz, 1H, Ar), 7.95 – 7.92 (m, 2H, Ar), 7.88 (d, $^3$J$_{H-H}$ = 8.0 Hz, 1H, Ar), 7.68 – 7.63 (m, 1H, Ar), 7.41 (t, $^3$J$_{H-H}$ = 7.1 Hz, 1H, Ar), 7.34 (t, $^3$J$_{H-H}$ = 7.4 Hz, 1H, Ar), 7.31 (t, $^3$J$_{H-H}$ = 7.6 Hz, 1H, Ar), 7.21 – 7.06 (m, 10H, Ar), 7.00 – 6.95 (m, 3H, Ar), 6.79 – 6.71 (m, 3H, Ar), 4.00 (dt, $^3$J$_{H-H}$ = 7.6 Hz, 5.3Hz, 1H, CH$_{COD}$), 3.92 (t, $^3$J$_{H-H}$ = 7.6 Hz, 1H, CH$_{COD}$), 2.82 (t, $^3$J$_{H-H}$ = 6.6 Hz, 1H, CH$_{COD}$), 2.62 (s, 3H, OXyl), 2.33 – 2.27 (m, 1H, CH$_{COD}$), 1.61 (s, 3H, OXyl), 1.58
- 1.48 (m, 1H, CH₂COD), 1.37 – 1.24 (m, 3H, CH₂COD), 1.02 – 0.95 (m, 1H, CH₂COD), 0.76 – 0.67 (m, 1H, CH₂COD), 0.67 – 0.59 (m, 1H, CH₂COD), 0.58 – 0.47 (m, 1H, CH₂COD), 0.06 (s, 9H, tBu-Si), -0.10 (s, 3H, Me-Si), -0.60 (s, 3H, Me-Si).
[Minor Rotomer, approx. 10%, selected resonances]: 5.67 – 5.63 (m, 1H, CH COD), 5.12 – 5.06 (m, 1H, CH COD), 5.06 – 5.00 (m, 1H, CH COD), 4.69 – 4.65 (m, 1H, CH COD), 3.19 – 3.08 (2H, CH₂COD), 2.42 (s, 3H, OXyl), 1.69 (s, 3H, OXyl), 0.60 (s, 9H, tBu-Si), 0.12 (s, 3H, Me-Si), -0.30 (s, 3H, Me-Si).

{13}C{¹H} NMR (CDCl₃)

[Major Rotomer]: 165.30 (NCO), 162.47 (NCO), 152.29, 151.81, 150.27, 134.71, 134.12, 133.49, 133.02, 131.91, 129.40, 129.29, 129.18, 129.08, 128.91, 128.68, 128.58, 128.35, 128.05, 127.89, 126.42, 126.38, 125.99, 125.77, 125.40, 124.75, 123.84, 121.49, 121.13, 120.81, 120.69, 107.09 (Ir-C CBA), 72.38 (CH₂COD), 51.91 (CH COD), 48.39 (CH₂COD), 34.95 (CH₂COD), 31.21 (CH₂COD), 30.65 (CH₂COD), 27.12 (CH₂COD), 24.78 (CH₃CSi), 18.28 (CH₃Ar), 17.77 (CH₃Ar), 17.30 (CH₃CSi), -3.11 (MeSi), -5.22 (MeSi). Anal. Calcd. for C₅₇H₅₈IrN₂O₃Si (1039.40): C, 63.69; H, 5.44; N, 2.61. Found: C, 63.41; H, 5.48; N, 2.54.

3-15: Compound 3-14 (74 mg, 0.069 mmol) was stirred in THF (3 mL) overnight in the presence of an excess of CsF (300 mg, 1.97 mmol). The reaction mixture was filtered, concentrated, and the product precipitated with pentane as a yellow solid, which was collected and dried (46 mg, 72%). Crystals suitable for X-ray diffraction were grown from CH₂Cl₂/Et₂O. {¹H} NMR (CD₂Cl₂): 8.10 (d, ³J_H-H = 9.1 Hz, 1H, Ar), 7.96 (d, ³J_H-H = 8.4 Hz, 1H, Ar), 7.75 (d, ³J_H-H = 9.1 Hz, 1H, Ar), 7.71 (d, ³J_H-H = 8.0 Hz, 1H, Ar), 7.49 (d, ³J_H-H = 8.8 Hz, 1H, Ar), (t, ³J_H-H = 6.9 Hz, 1H, Ar), 7.34 – 7.28 (m, 2H, Ar), 7.25 – 7.20 (m, 3H, Ar), 7.18 – 7.13 (m, 2H, Ar), 7.09 (t, ³J_H-H = 7.8 Hz, 1H, Ar), 7.04 – 6.96 (m, 4H, Ar), 6.91 (br s, 1H, Ar), 6.86 – 6.82 (m, 2H, Ar), 6.79 (t, ³J_H-H = 7.2 Hz, 1H, Ar), 6.45 (d, ³J_H-H = 8.4 Hz, 1H, Ar), 6.25 (d, ³J_H-H = 7.2 Hz, 2H, Ar), 3.77 (apparent t, J_H-H = 7.4 Hz, 1H, CH COD), 2.71 (s, 3H, OXyl), 2.44 (apparent t, J_H-H = 7.1 Hz, 1H, CH COD), 1.91 (s, 3H, OXyl), 1.85 – 1.78 (m, 2H, CH₂COD), 1.65 – 1.57 (m, 2H, CH₂COD), 1.05 (apparent t, J_H-H = 7.1 Hz, 1H, CH COD), 0.94 (apparent t, J_H-H = 7.1 Hz, 1H, CH COD), 0.87 (apparent q, J_H-H = 10.0 Hz, 1H, CH₂COD), 0.66 (apparent t, J_H-H = 11.3 Hz, 1H, CH₂COD),

[158]
0.47 – 0.37 (m, 2H, CH<sub>2</sub>COD). <sup>13</sup>C<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 171.44 (NCO), 165.53, 165.35, 152.30, 152.02, 134.87, 134.82, 134.30, 132.61, 132.01, 129.78, 129.66 (br) 129.40, 129.18, 129.10 (br), 128.99, 128.11, 127.93, 127.31, 127.21, 127.03, 126.99, 126.79, 126.74, 126.02, 125.88, 125.59, 125.31, 123.69, 120.74, 119.77, 114.69, 108.27 (C<sub>CBa-Ir), 77.60 (CH<sub>COD</sub>), 73.01 (CH<sub>COD</sub>), 46.48 (CH<sub>COD</sub>), 42.37 (CH<sub>COD</sub>), 34.91 (CH<sub>COD</sub>), 32.12 (CH<sub>COD</sub>), 30.23 (CH<sub>COD</sub>), 27.13 (CH<sub>COD</sub>), 17.79 (CH<sub>3</sub>Ar), 17.23 (CH<sub>3</sub>Ar). Anal. Calcd. for C<sub>51</sub>H<sub>43</sub>IrN<sub>2</sub>O<sub>3</sub> (924.13): C, 66.28; H, 4.69; N, 3.03. Found: C, 65.89; H, 4.67; N, 3.00.

3.5 References

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Chapter 4. Carbone Complexes of Fe

4.1 Introduction

4.1.1 Cyclic Bent Allenes & Carbodiphosphoranes

N-heterocyclic carbenes (NHCs) have found widespread use as ligands in a number of transition metal catalyzed transformations. Their strong \( \sigma \)-donating ability can facilitate oxidative addition, increase metal back donation to \( \pi \)-acidic ligands, and assist in ancillary ligand dissociation; important steps in many catalytic cycles. Recently, interest has expanded to include divalent carbon donors other than the first explored imidazol-2-ylidines. Metal bound mesoionic carbenes based on imidazol-4-ylidine,\(^{10-12}\) triazole,\(^{13-15}\) and pyrazole,\(^{16-19}\) as well as cyclic alkylamino carbenes\(^{20}\) have been prepared and have been shown to exhibit different \( \sigma \)-donor and \( \pi \)-acceptor properties than NHCs, allowing refined electronic tuning of the metal centre.

In 2008, Bertrand and coworkers reported the isolation of pyrazol-4-ylidenes featuring heteroatomic substitution at the 3,5 positions, which were termed cyclic bent allenes (CBAs).\(^{21}\) The very strong donating nature of this ligand was evidenced by the average \( \nu_{CO} \) of Rh(CO)\(_2\)Cl(CBA), which was among the lowest ever reported; the Tolman electronic parameter (TEP) of this ligand has been determined to be 2034.9 cm\(^{-1}\).\(^{22}\) Additionally, computational and experimental data has confirmed that CBAs are dibasic, and are capable of behaving as four electron donors at the central carbon atom.\(^{23-25}\) This ability stems from the introduction of heteroatoms at the 3,5 positions on pyrazole ring; exocyclic delocalization of the ring \( \pi \) electrons through these positions significantly reduces aromaticity of the heterocycle, and localizes two lone pairs of electrons on the central carbon atom (Figure 4.1.1). CBAs can be equivalently described as a linked bis-carbene ligating a carbon(0) atom. Despite their unique properties, only a very small number of reports describing their coordination chemistry have appeared in the literature.\(^{21,26}\)
Carbodiphosphoranes (CDPs) are another unique subclass of the carbone family displaying high $\sigma$ and $\pi$-basicity (Scheme 4.1.1), and include the strongest electron donor ligands ever measured.\textsuperscript{27-40} CDPs are arguably the most explored members of the carbone family, and many complexes of the 2\textsuperscript{nd} and 3\textsuperscript{rd} row metals have been accessed, including complexes where CDP is bound to two metal centres at the central carbon atom.\textsuperscript{27,41} Despite these advances, few complexes of CDPs have been explored within the first row metals, and no examples have insofar been reported with Fe.

![Figure 4.1.1. Resonance forms of 3,5-bis(aryloxy)pyrazol-4-ylidine (CBA)](image)

**Scheme 4.1.1.** The synthesis of hexaphenylcarbodiphosphorane

4.1.2 NHC Fe Chemistry

Fe is the most abundant terrestrial element, it is non-toxic, and is orders of magnitude less expensive than noble metals upon which many catalytic processes are based.\textsuperscript{42} Biologically, Fe is often found in catalytic roles as in the active sites of enzymes such as hydrogenase, nitrogenase, and cytochrome P450. However, for many decades the potential of Fe in homogeneous catalysts was underexplored. Fe complexes are often paramagnetic, highly $O_2$ sensitive, and in general bind ligands more weakly than their heavier analogues Ru and Os, altogether posing more significant challenges to the organometallic chemist. Nevertheless, in the past decade, new powerful Fe based catalysts have
emerged for transformations including hydrogenation,\textsuperscript{43,44} hydrosilylation,\textsuperscript{45} and N-heterocycle synthesis.\textsuperscript{46}

NHCs have been extensively applied to the 2\textsuperscript{nd} and 3\textsuperscript{rd} row transition elements due to their ability to stabilize highly unsaturated complexes by donating electron density to the metal centre, a configuration which is favourable to many catalytic reactions.\textsuperscript{47} Fe-NHC chemistry has begun to be explored more intensely in recent years; several reports have described the isolation of Fe complexes featuring chelating NHC ligands,\textsuperscript{42,48-58} as well as a handful of four coordinate species featuring monodentate NHCs.\textsuperscript{59-63} Combinations of sterically demanding NHCs and anionic ligands have been utilized to access highly unsaturated three coordinate trigonal planar species including Fe(NHC)X\textsubscript{2} (X = Bn, N(SiMe\textsubscript{3})\textsubscript{2}, Mes, OSiPh\textsubscript{3}, NH(DiPP)),\textsuperscript{62-65} and Fe(NHC)Cl(R) (R= Bn, N(SiMe\textsubscript{3})\textsubscript{2}, CH\textsubscript{2}TMS).\textsuperscript{64} Fe-NHC complexes have been applied in catalytic reactions including Kumada coupling,\textsuperscript{66-68} hydrogenation,\textsuperscript{57} and C-H borylation.\textsuperscript{69,70}

We have shown in Chapter 3 that the incorporation of extremely electron releasing ligands, such as CBAs, into the coordination sphere of Ru based complexes affords highly active olefin hydrogenation catalysts. In this vein, we have also explored some coordination chemistry of Fe with these strongly donating ligands to gain further insights into their influence on the reactivity of the Fe centre. Herein, the first Fe complexes of CBAs and CDPs are described, and some fundamental organometallic reactions are explored.

4.2 Results and discussion
4.2.1 Fe CBA Complexes

Reaction of FeCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} with a slight excess of the CBA 4-1 (Scheme 4.2.1) in toluene over the course of two hours resulted in the formation of a white precipitate 4-2. Upon purification, the \textsuperscript{1}H NMR spectrum of 4-2 displayed six paramagnetically shifted resonances (Figure 4.2.1), integrating appropriately for the heterotopic protons present in the ligand. A single crystal X-ray diffraction study of 4-2 identified the complex as monomeric three-coordinate Fe(CBA)Cl\textsubscript{2} (Figure 4.2.3). The ligands are disposed in a trigonal planar geometry about the metal centre where the sum of the angles about Fe is 359.9(2)°. The Fe-C\textsubscript{CBA}
bond length is 2.065(4) Å, shorter than distances typically reported for three coordinate Fe-NHC complexes.\textsuperscript{62,64} The pendant xylyl groups are canted toward the Fe centre, however, there is no evidence for interaction of the metal centre with these pendant groups. The average angle sum about the nitrogen atoms is 358.9(5)\(^\circ\), suggesting that the CBA is acting as a four electron donor to the highly unsaturated Fe centre (See section 3.2.7). The magnetic moment of 4-2 was determined to be 5.2 \(\mu\)B by the Evans method,\textsuperscript{71} indicative of an \(S = 2\) spin state. Complex 4-2 was also characterized by Mössbauer spectroscopy. At 80 K in zero field, a doublet was observed with a quadrupole splitting of 1.06 mm/sec and an isomer shift of 0.65 mm/sec, close to what has been previously reported for three coordinate Fe(II) where \(S = 2\) (Figure 4.2.2).\textsuperscript{72-74} To our knowledge, this is the first example of a monomeric three-coordinate Fe-dihalide species, as related NHC-Fe complexes are chloride bridged dimers.\textsuperscript{64}  

\begin{center}
\textbf{Scheme 4.2.1.} Synthesis of Fe-CBA complexes 4-2 - 4-4
\end{center}
Figure 4.2.1. $^1$H NMR spectrum of 4-2. $s =$ residual CHCl$_2$, $x =$ solvent impurities

Figure 4.2.2. Mossbauer spectrum of solid 4-2 obtained at 80 K in zero field
Attempts to reduce 4-2 by treatment with KC₈, Na/Hg, or sources of hydride resulted in intractable mixtures. However, treatment of a suspension of 4-2 at -45 °C with two equivalents of BnMgCl in Et₂O resulted in an immediate colour change to red. Within minutes, highly air sensitive golden brown crystals 4-3 suitable for X-ray diffraction separated from solution and were isolated in a 64% yield (Scheme 4.2.1). The ¹H NMR spectrum displays additional paramagnetically shifted resonances at +32.5, -36.8, and -68.4 ppm which can be assigned to the meta, ortho and para protons of the benzyl moiety, respectively. The ortho signals are broadened, likely due to their proximity to the metal centre, and signals for the phenylmethylene protons are absent, typical for protons alpha to high spin Fe(II). The magnetic moment of 4-3 was determined to be 5.3 µB.
similar to that measured for 4-2 and corresponding to an $S = 2$ spin state. Single crystal X-ray diffraction confirmed the identity of the complex as three coordinate Fe(CBA)(Bn)$_2$ 4-3 (Figure 4.2.4). The Fe-C$_{CBA}$ distance is 2.1059(2) Å and the Fe-C$_{Bn}$ distances are 2.082(2) and 2.092(2) Å, respectively. The Fe-C$_{CBA}$ distance is contracted and the Fe-benzyl distances slightly elongated compared to the three-coordinate bis-benzyl NHC complex Fe(SIDipp)(Bn)$_2$, possibly reflective of the greater donating power of the CBA.$^{64}$ The average angle sum about the nitrogen atoms in 4-3 is 355.1(2)$^\circ$, smaller that that observed in 4-2 and reflecting the relatively more electron rich metal centre upon incorporation of the benzyl ligands.

Figure 4.2.4. Molecular structure of 4-3. Thermal ellipsoids shown at 50% probability. Hydrogen atoms omitted for clarity. Colours: C, grey; Fe, orange; O, red; N, blue.
Somewhat surprisingly, 4-3 does not react with hydrogen. However, compound 4-3 does react with one atmosphere of CO resulting in the immediate reductive elimination of 1,3-diphenylacetone, confirmed by GC-MS, and formation of the pale yellow diamagnetic complex Fe(CBA)(CO)$_4$ 4-4. This insertion-elimination mechanism is not unprecedented; Deng and coworkers have isolated (Mes)$_2$CO from the reaction of Fe(Me$_2$IPr)(Mes)$_2$ with CO. Despite its high degree of coordinative unsaturation, complex 4-2 does not react with CO.

The $^{13}$C$_{\{1^H}\} \text{NMR}$ spectrum of 4-4 displays a single peak for the carbonyl ligands at 219.6 ppm, implying fast rearrangement between axially and equatorially disposed CO ligands on the NMR timescale. The central carbon of the CBA ligand resonates at 103.3 ppm. IR bands assignable to $A_1$ CO stretches were observed at 2026 and 1950 cm$^{-1}$, lower frequency than those reported for Fe(IMe)(CO)$_4$ of 2043 and 1962 cm$^{-1}$. Interestingly, the degenerate E mode CO stretch is split into a doublet with peaks at 1905 and 1893 cm$^{-1}$, presumably due to a structural perturbation in the $C_{3v}$ symmetry by inhibited rotation about the Fe-C$_{\text{CBA}}$ bond. This splitting has been previously observed in the related species (1,4-dimethyltetrazol-5-ylidene)Fe(CO)$_4$. A crystallographic study of 4-4 confirmed the formulation and reveals that the aryl-oxide substituents are oriented away from the Fe(CO)$_4$ fragment, (Figure 4.2.5). The Fe-C$_{\text{CBA}}$ distance is 2.026(2) Å, slightly longer than that reported for the sterically unhindered Fe(IMe)(CO)$_4$. However, the $\text{trans}$ C-O distance (1.151(3) Å) is also longer than that reported for Fe(IMe)(CO)$_4$, consistent with the stronger donating nature of the CBA ligand. The nitrogen atoms in 4-4 are significantly pyramidalized, with an average angle sum of of 350.3(2)$^\circ$, as would be anticipated for an 18e coordination centre (see section 3.2.7).
While the isolation these low coordinate Fe-CBA species are of fundamental interest, complexes 4-2 and 4-3 are extremely oxygen sensitive and fragile, and are prone to decomposition. To potentially form more robust Fe species, we next turned our attention to the synthesis of Fe CDP complexes.

4.2.2 Carbodiphosphorane Complexes of Fe

The transition metal chemistry of hexaphenylcarbodiphosphorane is dominated by ortho-metalation reactions,\textsuperscript{31,32,35,36,80} where the use of a basic metal starting material or simply an excess of the CDP affords the cyclometalated product (Scheme 4.2.2), as the steric attributes of the CDP ligand place the o-Ph protons near to the metal centre. Cyclometalated Fe complexes of CDPs would be anticipated to be much more stable than their monodentate CBA analogues, and
therefore may be more amenable to catalytic reactions. Homogeneous Fe catalysts are frequently based on chelated ligand systems.\textsuperscript{43-46}

\begin{align*}
\text{Ph}_3\text{P} & \quad \text{PPh}_3 \\
& \quad \text{Ph}_3\text{P} \quad \text{PPh}_3 \\
\text{2Br} & \quad \text{THF, rt} \quad \text{Ph}_3\text{P} \quad \text{PPh}_3 \\
& \quad \text{FeCl}_2(\text{PPh}_3)_2 \\
\text{Fe} & \quad \text{Cl} \\
\text{Cl} & \quad \text{PPh}_3 \\
\end{align*}

\textbf{Scheme 4.2.2.} ortho-metalation of hexaphenylcarbodiphosphorane

Hexaphenylcarbodiphosphorane 4-5 was synthesized by a novel simplified procedure, involving room temperature deprotonation of the corresponding methylene diphosphonium salt with two equivalents of KHMDS, and was isolated in an 88% yield (Scheme 4.2.3). This procedure is significantly safer and more convenient than established methods,\textsuperscript{81,82} as it circumvents the need for refluxing the pyrophoric and peroxide-forming NaNH\textsubscript{2} in THF, or utilizing the toxic greenhouse agent CCl\textsubscript{4}, and can be conveniently performed in a drybox in approximately 90 minutes on a gram scale.

\begin{align*}
\text{Ph}_3\text{P}^+ & \quad \text{PPh}_3 \\
& \quad 2.0 \text{ KHMDS} \\
& \quad \text{THF, rt} \\
\text{FeCl}_2(\text{PPh}_3)_2 & \quad -2 \text{ PPh}_3 \\
\end{align*}

\textbf{Scheme 4.2.3.} Synthesis of hexaphenylcarbodiphosphorane 4-5 and Fe complex 4-6.
Combination of 4-5 with an equimolar amount of FeCl₂(PPh₃)₂ in toluene results in the gradual formation of a yellow precipitate of (CDP)FeCl₂ 4-6, which was isolated in a 83% yield (Scheme 4.2.3). Single crystals suitable for X-ray diffraction were grown from CH₂Cl₂/Et₂O solution. Remarkably, both monomeric three coordinate trigonal planar (CDP)FeCl₂ and dimeric four coordinate tetrahedral [(CDP)FeCl₂]₂ are present in the same asymmetric unit (Figure 4.2.6, Figure 4.2.7). This implies that dimerization energy of 4-6 is quite small and is on the order of crystallographic packing effects. Interestingly, a second unsolvated molecular structure of 4-6 was obtained from CH₂Cl₂/pentane consisting solely of dimer, while the mixed monomer/dimer structure from CH₂Cl₂/Et₂O contains co-crystallized CH₂Cl₂ and Et₂O molecules. The C₉D₉-Fe bond lengths in the solid state in the monomeric and dimeric 4-6 are 2.055(8) Å and 2.043(7)/2.079(13)/2.095(13) Å respectively. In CD₂Cl₂ solution, ¹H NMR signals for one paramagnetically shifted phenyl environment are observed with ortho, meta and para resonances at 10.0, 5.1 and -1.3 ppm, respectively (Figure 4.2.8). However, no ³¹P NMR signal could be detected. The magnetic moment of 4-6 is 5.1 μB, implying an S = 2 ground state.

A Mössbauer spectrum of powdered and dried 4-6 was obtained, and clean doublet was observed with an isomer shift of 0.92 mm/s and quadrupole splitting of 2.63 mm/s (Figure 4.2.9). These values are typical for 4-coordinate Fe(II) and are outside the range that has been observed for 3-coordinate Fe(II) (isomer shift 0.48 – 0.71 mm/s; quadrupole splitting 0.81 – 1.74 mm/s), providing further evidence that that the dimer is the energetically preferred coordination environment of the molecule in the solid state. This observation is interesting considering the high degree of steric bulk of the CDP ligand, and is also curious considering that the monomeric ground state of complex 4-2 with can be stabilized by a CBA with flexible xyloxy flanking groups. It seems likely in both cases that their dimerization energies are quite small.
Figure 4.2.6. Molecular structure of monomeric 4-6 with thermal ellipsoids shown at 50% probability. Hydrogen atoms are omitted for clarity. Colours: C, grey; Fe, orange; P, purple; Cl, green.

Figure 4.2.7. Molecular structure dimeric 4-6 with thermal ellipsoids shown at 50% probability. Hydrogen atoms are omitted for clarity. Colours: C, grey; Fe, orange; P, purple; Cl, green.
Figure 4.2.8. $^1$H NMR (CD$_2$Cl$_2$) spectrum of 4-6.

Figure 4.2.9. Mossbauer spectrum of 4-6 obtained at 80 K in zero field.
Scheme 4.2.4. Synthesis of Fe-CDP dibenzyl complex 4-7.

The use of an excess of CDP in the synthesis of 4-6 does not result in a cyclometalated product. Substitution reactions of 4-6 were next investigated in an effort to induce ortho-metalation of the CDP ligand. Combination of 4-6 with two equivalents of BnMgCl in Et₂O solution at -45 °C results in the formation of the three coordinate dibenzyl derivative 4-7 as a highly air sensitive red solid (Scheme 4.2.4), which was characterized crystallographically and in solution. Crystals suitable for X-ray diffraction were grown from THF/pentane at -45 °C (Figure 4.2.10). In the solid state, the Fe-C_{CDP} bond length is 2.097(5) Å and the Fe-C_{Bn} bond lengths are both 2.062(5) Å. The benzyl arms of 4-7 are highly paramagnetically shifted in the ¹H NMR spectrum, with signals at -41.8, +29.6 and -75.4 ppm for the ortho, meta, and para positions, respectively, similar to resonances observed for the CBA analogue 4-3. No signals for the benzylic CH₂ protons could be observed in the window of +150 to -150 ppm. Despite the proximity of the basic Fe-Bn moieties to the ortho positions of the CDP ligand, no indication of cyclometalation is observed. Gentle heating of a THF solution of 4-7 results only in decomposition. Compound 4-7 is notably more fragile than the CBA analogue 4-3, and decomposes quickly at room temperature in non-ethereal solvents including benzene and toluene, forming black solutions. Reaction of 4-7 with one atmosphere of CO in THF also results in decomposition to a mixture of products.
Substitution reactions may also be carried out with bases such as KHMDS. While combination of 4-6 with two equivalents of KHMDS leads to decomposition of the complex and formation of the free ligand 4-5, the use of one equivalent of LiHMDS lead to the isolable complex (CDP)Fe(N(TMS)2)Cl 4-8 (Scheme 4.2.5). While 4-8 crystallizes only as extremely fine needles unsuitable for X-ray diffraction, it was characterized in solution, and its formulation was supported by elemental analysis. In addition to the ortho, meta and para CDP resonances at 19.7, 8.1 and 2.3 ppm in the $^1$H NMR spectrum, an additional signal for the N(TMS)$_2$ resonance was observed at -5.6 ppm in C$_6$D$_6$ solution. The magnetic moment of 4-8 is 5.0 $\mu_B$, revealing an $S = 2$ spin state. Similar to 4-7, no traces of cyclometalation or halodesilylation were observed upon heating 4-8. Again,
gentle heating of a THF solution of 4-8 results only in decomposition. 4-8 is quite fragile and decomposes in the solid state at -45 °C over a period of weeks.

Scheme 4.2.5. Synthesis of CDP Fe-amido complexes 4-8 and 4-9

The formation of 4-8 was further confirmed by subsequent reaction with TMSOTf, which yielded the extremely sensitive triflate derivative (CDP)Fe(N(TMS)₂)(OTf) 4-9 (Scheme 4.2.5), of which X-ray quality crystals were obtained (Figure 4.2.11). In the solid state, the Fe-C<sub>CDP</sub> bond length is 2.040(3) Å. The C-Fe-N angle is notably distorted from trigonal planar at 135.6(1)°, likely due to the steric repulsion of the bulky CDP and N(TMS)<sub>2</sub> substituents. The <i>ortho</i>, <i>meta</i> and <i>para</i> CDP resonances are observed at 19.9, 6.3 and 2.0 ppm in the <sup>1</sup>H NMR spectrum in C<sub>6</sub>D<sub>6</sub> solution, with an additional signal for the N(TMS)<sub>2</sub> resonances was observed at -1.2 ppm. The magnetic moment of 4-9 is 5.1 μ<sub>B</sub>, revealing an S = 2 spin state. Similar to 4-8, no signs of cyclometalation were obtained upon heating a THF solution of 4-9. Like 4-8, complex 4-9 decomposes in the solid state at -45 °C over a period of weeks.
Figure 4.2.11. Molecular structure of 4-9 with thermal ellipsoids shown at 50% probability. Hydrogen atoms are omitted for clarity. Colours: C, grey; Fe, orange; Cl, green; S, yellow; P, purple; Si, pale yellow; F, yellow-green; O, red; N, blue.

While Fe-CDP complexes were initially investigated as potentially more stable analogues of the Fe-CBA complexes, it was instead observed that the complexes synthesized are more fragile and sensitive than the Fe-CBA systems. As no traces of cyclometalation was observed with 4-6, 4-7, 4-8 or 4-9, and given the difficulties in handling these species, this project was not further pursued.

4.3 Summary and Conclusions

In summary, we have demonstrated that the strongly donating CBA and CDP ligands can shield the metal centre providing access to low valent Fe complexes 4-2 and 4-6. The corresponding dibenzyl species 4-3 and 4-7 can be obtained by reaction with BnMgCl, and in the case of the CBA derivative 4-3, this species can further react with CO to form the complex (CBA)Fe(CO)$_4$ 4-4. This latter species features a ‘bent back’ orientation of the pendant aryl-oxide substituents of the
CBA. Further modification of the ligand field of Fe(CDP)Cl₂ 4-6 can be achieved with LiHMDS and TMSOTf forming CDP Fe-amido complexes 4-8 and 4-9, although these species are highly sensitive and fleeting.

While the greater lability of Fe complexes has rendered these monodentate species rather fragile, we are confident that the incorporation of such strong donor ligands into chelating frameworks will result in more robust complexes with potential catalytic applications, as has been observed in NHC-Fe species.

4.4 Experimental
4.4.1 Crystallographic Details

X-ray Data Collection and Reduction. Crystals were coated in Paratone-N oil in the glovebox, mounted on a MiTegen Micromount, and placed under a N₂ stream, thus maintaining a dry, O₂-free environment for each crystal. The data were collected on a Bruker Kappa Apex II diffractometer using a graphite monochromator with Mo Kα (λ = 0.71073 Å) radiation. The data were collected at 150(2) K for all crystals. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the empirical multiscan method SADABS. In cases where non-merohedral twinning was detected, the data was indexed with CELLNOW to determine the contributions of the respective crystal domains, and the data were corrected for absorption effects using TWINABS. The heavy atom positions were determined employing the SHELXTL direct methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least squares techniques on F, minimizing the function \( \omega (F_o-F_c)^2 \) where the weight \( \omega \) is defined as \( 4F_o^2/2\sigma (F_o^2) \) and \( F_o \) and \( F_c \) are the observed and calculated structure factor amplitudes, respectively. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of positional disordering. The final models of twinned structures were obtained by refinement against the twinned data. C-H atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C-H bond length of 0.95 Å. H-atom temperature factors were fixed at 1.20 times the
isotropic temperature factor of the C-atom to which they are bonded. The H-atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance.

Table 4.4.1. Crystallographic information

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4.4.2 Experimental Details

**General Remarks:** All air sensitive manipulations were carried out under an atmosphere of dry, O\(_2\)-free N\(_2\) employing a Vacuum Atmospheres glovebox. Solvents were purified with a Grubbs-type column system manufactured by Innovative Technology and dispensed into thick-walled Straus flasks equipped with Teflon-valve stopcocks. Et\(_2\)O and toluene were stored over potassium mirrors. CD\(_2\)Cl\(_2\) was distilled under reduced pressure from CaH\(_2\) and degassed by successive freeze-pump-thaw cycles. C\(_6\)D\(_6\) and THF-d\(_8\) were distilled from purple sodium benzophenone ketyl. Combustion analyses were performed in house employing a Perkin-Elmer CHN Analyzer. \(^1\)H and \(^{13}\)C\{\(^1\)H\} NMR spectra were collected on Bruker Advance III 400 MHz, Agilent DD2 500 MHz, or Agilent DD2 600 MHz spectrometers. Chemical shifts are reported in parts per million are given relative to SiMe\(_4\) and referenced to the residual solvent signal. \(^{13}\)C\{\(^1\)H\} NMR
signals are reported to a precision of 0.01 ppm to avoid reporting duplicates of spatially close signals, but should be understood to be accurate to 0.1 ppm. IR spectra were collected on a Perkin-Elmer Spectrum One FT-IR instrument. Zero-field $^{57}$Fe Mössbauer spectra were recorded on a SEE Co. Mössbauer spectrometer (MS4) at 80 K in constant acceleration mode. $^{57}$Co/Rh was used as the radiation source. WMOSS software was used for the quantitative evaluation of the S5 spectral parameters (least-squares fitting to Lorentzian peaks). The minimum experimental line widths were 0.23 mm/s. The temperature of the sample was controlled by a Janis Research Co. CCS-850 He/N$_2$ cryostat within an accuracy of 0.3 K. Potassium hexamethyldisilazide, benzyl magnesium chloride, and carbon monoxide were purchased from Aldrich in the highest available grade and used without subsequent purification. FeCl$_2$(PPh$_3$)$_2$, and methylenebis(triphenylphosphonium) dibromide were synthesized according to literature procedures. 4-1 was synthesized according to the procedure detailed in Chapter 3.

**Fe(CBA)Cl$_2$ 4-2:** Cyclic bent allene 4-1 (241 mg, 0.523 mmol) was added to a suspension of FeCl$_2$(PPh$_3$)$_2$ (307 mg, 0.471 mmol) in 10 mL toluene. The mixture was stirred for 2 h to give an off white suspension. The precipitate (Fe(CBA)Cl$_2$•tol) was collected by filtration, and washed with toluene until the washes became colourless, followed by Et$_2$O (3 x 10 mL). The white precipitate was dissolved in a minimum of CH$_2$Cl$_2$, and precipitated with excess pentane. The supernatant was decanted, and the colourless solid dried under high vacuum (248 mg, 85%). Crystals suitable for X-ray diffraction were grown from an unstirred reaction mixture. $^1$H NMR (CD$_2$Cl$_2$): 14.4 (12H, ArCH$_3$), 6.9 (4H, m-Ph), 5.7 (4H, o-Ph), 4.5 (2H, p-Ph), -32.9 (4H, m-OAr), -47.0 (2H, p-OAr). $\mu_{\text{eff}} = 5.2$ $\mu_B$ (Evans). Anal. Calcd. for C$_{31}$H$_{28}$Cl$_2$FeN$_2$O$_2$ (587.32): C, 63.40. H, 4.81. N, 4.77. Found: C, 62.80. H, 5.17. N, 4.49.

**Fe(CBA)(Bn)$_2$ 4-3:** Compound 4-2 (100 mg, 0.170 mmol) was suspended in Et$_2$O (10 mL) and cooled to -45 °C. Benzyl magnesium chloride (1.0 M in Et$_2$O,
370 μL, 0.370 mmol) was added producing an immediate colour change to red. The mixture was quickly filtered and allowed to stand at room temperature whereupon golden brown crystals suitable for single crystal X-ray diffraction separated from solution. The crystals were washed with Et₂O (2 x 5 mL) and dried under high vacuum (86 mg, 64%). ¹H NMR (C₆D₆): 32.5 (4H, m-Bn), 14.1 (12H, ArCH₃), 5.0 (4H, m-Ph), 2.4 (2H, p-Ph), 1.0 (4H, o-Ph), -28.4 (4H, m-OAr), -36.8 (4H, o-Bn), -39.1 (2H, p-OAr), -68.4 (2H, p-Bn). μₑₑ = 5.3 μB (Evans). Anal. Calcd for C₄₅H₄₂FeN₂O₂ (698.67): C, 77.36. H, 6.06. N, 4.01. Found: C, 76.02. H, 5.96. N, 3.87.

Fe(CBA)(CO)₄ 4-4: Compound 4-3 (22 mg, 0.035 mmol) was dissolved in toluene (4 mL), frozen in liquid nitrogen, and evacuated. Approximately 1 atm of CO was condensed in the flask which was warmed to room temperature to give a yellow solution. The solution was filtered of any precipitate, concentrated to approximately 1 mL and pentane (18 mL) was layered on top. Cooling to -45 °C overnight yielded pale yellow crystals, which were collected and dried (13 mg, 75%). Single crystals suitable for X-ray diffraction were grown from a benzene/pentane solution. ¹H NMR: 6.53-6.45 (m, 4H, p-OAr & p-Ph), 6.40 (d, ³J_H-H = 7.6 Hz, 4H, m-OAr), 6.33 (t, ³J_H-H = 7.6 Hz, 4H, m-Ph), 6.17 (d, ³J_H-H = 7.6 Hz, 4H, o-Ph), 2.09 (s, 12H, ArCH₃). ¹³C{¹H} NMR (C₆D₆): 219.36 (CO), 170.14 (ipso-OAr), 152.96 (ipso-NAr), 133.62, 129.34, 129.10, 128.67, 128.57, 125.62, 103.26 (C_CBA), 17.09 (CH₃). IR(KBr): 2026(m), 1950(m), 1905(s), 1893(s), 1413(m), 1154(m), 891(w), 635(m) cm⁻¹. Anal. Calcd. for C₃₅H₂₆FeN₂O₂ (628.45): C, 66.89. H, 4.49. N, 4.46. Found: C, 67.06. H, 4.40. N, 4.43.

Hexaphenylcarbodiphosphorane 4-5: In a 20 mL vial methylenebis(triphenylphosphonium) dibromide (784 mg, 0.52 mmol) and potassium bis(trimethylsilyl)amide (450 mg, 1.29 mmol) were combined in THF (10 mL). The reaction mixture immediately became yellow in colour, and was stirred for one hour at room temperature. The mixture was the filtered through a pad of celite to remove KBr, and volatiles were removed under high vacuum. The
yellow residue was washed with Et₂O (3 x 2 mL) and pentane (3 x 5 mL) and the yellow solid obtained was dried under high vacuum (530 mg, 88%). Spectroscopic data are identical to those previously reported.⁸¹

**(CDP)FeCl₂ 4-6:** Hexaphenylcarbodiphosphorane 4-5 (232 mg, 0.43 mmol) and FeCl₂(PPh₃)₂ (276 mg, 0.41 mmol) were combined in toluene (5 mL) and stirred for two hours at room temperature, forming a yellow precipitate. The precipitate was collected, washed with toluene (3 x 5 mL), and Et₂O (3 x 5 mL). The yellow solid was then dissolved in CH₂Cl₂ (3 mL), and precipitated by the addition of pentane (17 mL). The yellow solid obtained was washed with pentane (2 x 5 mL) and dried under high vacuum (238 mg, 83%). Crystals of Fe(CDP)Cl₂•0.5[Fe(CDP)Cl₂]₂•0.5Et₂O•CH₂Cl₂ were grown by slow diffusion Et₂O into a CH₂Cl₂ solution of 4-6. Crystals of [Fe(CDP)Cl₂]₂ were grown from CH₂Cl₂/pentane. ¹H NMR (CD₂Cl₂): 10.0 (12H, o-Ph), 5.1 (12H, m-Ph), -1.3 (6H, p-Ph). μₑffective = 5.1 μₜ (Evans). Anal. Calcd. for C₃₇H₃₀Cl₂FeP₂ (663.34): C, 67.00; H, 4.56; N, 0.00. Found: C, 66.41; H, 4.53; N, 0.00.

4-7: Complex 4-6 (89 mg, 0.23 mmol) was suspended in Et₂O (5 mL) and cooled to -45 °C. Benzyl magnesium chloride (0.27 mL, 1.0 M in Et₂O, 0.27 mmol) was added at this temperature, and the mixture was stirred for 1 h, gradually warming to room temperature. The solution was filtered of any insoluble material, and the red filtrate was placed in a -45 °C freezer, and allowed to sit overnight, resulting in the deposition of a crop of red crystals. The supernatant was decanted, and the crystals obtained were washed with pentane (35 mg). Crystals suitable for X-ray diffraction were grown from THF/pentane at -45 °C. ¹H NMR (THF-d₈): 29.6 (4H, m-Bn), 4.6 (12H, m-PPh₃), -1.0 (6H, p-PPh₃), -9.6 (12H, o-PPh₃), -41.8 (4H, o-Bn), -75.4 (2H, p-Bn). The present procedure obtains 4-7 as a mixture with MgCl₂(Et₂O)₂, which cannot readily be separated due to the fast decomposition of 4-7 in non-ethereal solutions. Magnetic moment and elemental analysis of this complex were not possible.
**4-8:** Complex 4-6 (73 mg, 0.110 mmol) was dissolved in THF (5 mL) and cooled to -45 °C. LiHMDS (18 mg, 0.108 mmol) was added at this temperature and the mixture was allowed to warm to room temperature over a period of one hour with stirring. The solvent was removed under high vacuum, and the residue was stirred with Et₂O (5 mL) for 1 h. Insoluble material was removed by filtration, and the filtrate was concentrated under high vacuum. Pentane (10 mL) was added to precipitate the product as a very pale yellow microcrystalline solid, which was collected and dried under vacuum (60 mg, 71%). \(^1\)H NMR (C\(_6\)D\(_6\)): 19.7 (12H, o-Ph), 8.1 (12H, m-Ph), 2.3 (6H, p-Ph), -5.6 (18H, NTMS\(_2\)). \(\mu_{\text{eff}} = 5.0 \mu_B\) (Evans). Anal. Calcd. for C\(_{43}\)H\(_{48}\)ClFeNSi\(_2\)P\(_2\) (788.28): C, 65.52; H, 6.14; N, 1.78. Found: C, 65.93; H, 6.37; N, 1.56.

**4-9:** Complex 4-8 (46 mg, 0.058 mmol) was dissolved in toluene (3 mL) and TMSOTf (10.5 µL, 0.058 mmol) was added, resulting in a clear colourless solution. The solution was concentrated, and the product precipitated with pentane (10 mL) as a white crystalline solid, which was collected and dried under vacuum (33 mg, 63%). Crystals suitable for X-ray diffraction were grown from CH\(_2\)Cl\(_2\)/pentane. \(^1\)H NMR (C\(_6\)D\(_6\)): 19.9 (12H, o-Ph), 6.3 (12H, m-Ph), 2.0 (6H, p-Ph), -1.2 (18H, NTMS\(_2\)). \(\mu_{\text{eff}} = 5.1 \mu_B\) (Evans). Anal. Calcd. for C\(_{44}\)H\(_{48}\)F\(_3\)FeNO\(_3\)P\(_2\)SSi\(_2\) (901.89): C, 58.60; H, 5.36; N, 1.55. Found: C, 58.98; H, 5.23; N, 1.34.

**4.5 References**


(17) Han, Y.; Huynh, H. V. *Dalton Trans.* **2011**, *40*, 2141.


(64) Danopoulos, A. A.; Braunstein, P.; Wesolek, M.; Monakhov, K. Y.; Rabu, P.; Robert, V. Organometallics 2012, 31, 4102.
(81) Zybill, C.; Mueller, G. Organometallics 1987, 6, 2489.

Chapter 5. Carbodicyclopropenylidenes

5.1 Introduction

5.1.1 Carbodicarbenes

Carbodicarbenes (CDCs) are an emerging family of strongly electron donating divalent carbon ligands that can be broadly defined as a carbon atom bound to two singlet carbenes to form complexes L→C←L. The electronic nature of the central carbon atom is greatly influenced by the π-accepting nature of the flanking carbenes. Weakly π-accepting carbenes, such as unsaturated N-heterocyclic carbenes (NHCs) yield CDCs with strong σ and π-basicity, and significantly bent L-C-L angles (Figure 5.1.1; A). The incorporation of more strongly π-acidic carbenes, such as acyclic di-amino carbenes, and alkylamino carbenes results in a nearly linear allene like L-C-L configuration. However, these ‘masked carbodicarbene’ species have low bending energies and can bind to transition metals via η¹ coordination through the central carbon atom (Figure 5.1.1; D, DAu). Cyclic systems have also been used to enforce a bent ground state and comprise a subclass of CDCs known as ‘cyclic bent allenes’ (Figure 5.1.1, B,C). These species have recently been reported to be highly effective spectator ligands in transition metal catalyzed hydrogenation (see Chapter 3), hydroarylation, and hydroamination reactions. While representative CDCs of many of the major classes of singlet carbenes have been accessed, there have been no reports of such systems stabilized by cyclopropenylidenes.

Figure 5.1.1. Representative members of the carbodicarbene ligand family. A: Acyclic bent allenes. B,C: Cyclic bent allenes. D. Tetraaminoallenes.
5.1.2 Cyclopropenylidenes

The isolation of free 1,2-diaminocyclopropenylidene was reported by Bertrand and coworkers in 2006.\textsuperscript{37} The stability of this system is derived from the amino groups at the 1,2 positions, which stabilize the carbenoid carbon via charge delocalization.\textsuperscript{38,39} A related species is the singlet 1,2-diphenylcylopropenylidene. While this carbene is an effective spectator ligand in cross coupling catalysts,\textsuperscript{40-44} in free form it has only been observed in an Ar matrix at 10 K.\textsuperscript{45} Although 1,2-diaminocyclopropenylidene is not $\pi$ accepting,\textsuperscript{46} 1,2-diphenylcyclopropenylidenes are good $\pi$ acceptors, as evidenced by the downfield shift of their Se adducts (See section 1.2.2),\textsuperscript{47,48} and their small singlet-triplet gap.\textsuperscript{49} We rationalized that the CDC derived from this latter system should yield a stable electronic structure similar to that of the 'masked carbone' D (Scheme 5.1.1). In this chapter we report the first example of a CDC stabilized by flanking cyclopropenylidenes. Additionally, this species is the first example of a CDC based entirely on carbon. The free carbodicyclopropenylidene was characterized in solution and has been captured by main group fragments and transition metal complexes.

5.2 Results and Discussion

5.2.1 Ligand Precursor Synthesis

The synthesis of 1,2-diphenyl-3-(1,2-diphenyltriafulvene-4-yl)cyclopropenium perchlorate (the perchlorate salt of 5-1) was reported in 1982 by Okamoto and co-workers in the course of their extensive studies on hydrocarbon salts.\textsuperscript{50} By an analogous method (Scheme 5.2.1), we have prepared the tetrafluoroborate derivative 5-1 by the addition of two equivalents of trityl tetrafluoroborate to bis(1,2-diphenylcyclopropan-3-yl)methane. As was observed by Okamoto and coworkers, the transiently produced dicyclopropenium salt spontaneously loses a proton from the central carbon atom in CH\textsubscript{2}Cl\textsubscript{2}/Et\textsubscript{2}O solution to form 5-1, which was isolated in 78\% yield. The pale yellow salt is stable to air and moisture and single crystals can be grown from slow diffusion of Et\textsubscript{2}O into a CH\textsubscript{2}Cl\textsubscript{2} solution of this compound (Figure 5.2.1). In the solid state, the three membered rings are canted 16.5(3)$^\circ$ with respect to each other due to the steric interaction of the axially disposed phenyl groups. The distances of the central carbon atom to the
adjacent rings are 1.378(3) Å and 1.381(3) Å respectively, supporting the presence of a 3-centre-2-electron (3c-2e) π bond. The backbone 1,2-cyclopropene C-C distances are 1.350(3) Å and 1.356(3) Å, indicating localized double bonds at these positions. These observations support a ground state resonance structure as depicted in Scheme 5.2.1. Restricted rotation about the 3c-2e bond is observed in the room temperature $^1$H and $^{13}$C($^1$H) NMR spectra, as evidenced by the presence of two inequivalent phenyl environments.

**Scheme 5.2.1.** Synthesis of the precursor salt 5-1.
Figure 5.2.1. Molecular structure of the cation 5-1 with thermal ellipsoids drawn at 50% probability. Hydrogen atoms on phenyl groups are removed for clarity. Colours: C, grey; H, turquoise.

5.2.2 Synthesis and Characterization of Tetraphenylcarbodicyclopentadiene

Combination of 5-1 with an equimolar portion of KHMDS at -45 °C in Et₂O resulted in immediate consumption of the starting material and formation of a deep red solution (Scheme 5.2.2). However, upon extended stirring at -45 °C, or upon warming to room temperature the solution blackened, and room temperature ¹H NMR analysis revealed the presence of numerous decomposition products. Nevertheless, when the reaction was performed in a J-Young NMR tube in THF-d₈ and maintained at -60 °C (Figure 5.2.2), the red colour persisted, and a single product was observed in the NMR spectra, which were consistent with the formulation of 5-2. A single set of phenyl resonances are observed in the ¹H NMR spectrum collected at -60 °C in THF-d₈, suggesting an allene like conformation. Seven signals are observed in the ¹³C(¹H) NMR spectrum at -60 °C (Figure 5.2.4). HSQC and DEPTQ-135 experiments indicated that three of the signals correspond to aryl C-Hs, and the other four to quaternary centres, as would be anticipated for compound 5-2 (Figure 5.2.3).
Scheme 5.2.2. Synthesis of tetraphenylcarbodicyclopentadienyldiene 5-2

Figure 5.2.2. (left) A solution of 5-2 in THF-\textit{d}_8 in a -78 °C dry ice/acetone bath. (right) Computed molecular geometry (M06-2X/Def2-SVP) of 5-2.

Figure 5.2.3. Left: HOMO of 5-2; Right: LUMO of 5-2
Figure 5.2.4. DEPTQ-135 (top) and $^{13}\text{C}^{[1}\text{H}]$ NMR spectra (bottom) of 5-2 generated in situ collected at -60 °C in THF-d$_8$. Antiphase signals in the top spectrum indicate quaternary carbon atoms. Calculated $^{13}\text{C}$ NMR resonances (GIAO-B97-2/Def2-TZVP//M06-2X/Def2-SVP) are indicated in the structural diagram of 5-2, and observed resonances are indicated in parentheses.

The molecular structure of 5-2 was investigated computationally (Figure 5.2.2). Density functional theory calculations at the M06-2X/Def2-SVP level of theory reveal that the central carbon is in an almost linear environment (C2-C1-C2a angle of 179.9°). The C1-C2 (1.308 Å) and C1-C2a (1.308 Å) distances are shorter than those in 5-1 (1.378 and 1.381 Å) indicating localized double bonds at these positions. Furthermore, the Wiberg bond indices (WBIs) of the central C-C bonds from natural bond orbital (NBO) calculations (M06-2X/TZVP//M06-2X/Def2-SVP) are both 1.77, indicating C-C double bond character. The highest occupied molecular orbital (HOMO) and HOMO-1 of 5-2 are degenerate and correspond approximately to the π orbitals of the C2-C1-C2a fragment (Figure 5.2.3). The LUMO largely comprises the backbone cyclopropene C=C $\pi^*$ orbitals, but is also delocalized onto the ortho- and para- positions of the phenyl rings.
The C1 atom (-0.19 a.u.) is more negatively charged than C2 (-0.04 a.u.) or C2a (-0.04 a.u.), suggesting nucleophilicity of the C1 centre. The first and second proton affinities of 5-2 were determined to be 282.7 and 153.3 kcal/mol, respectively, similar to those calculated for compound B (Figure 5.1.1).

The bending potential of the central allenic moiety of 5-2 was also investigated. It was found that while the potential is generally shallow (6.6 kcal/mol to 140° and 10.0 kcal/mol to 130°), it is somewhat deeper than that calculated for B (5.6 kcal/mol to 136.9°).

13C NMR prediction was also performed (GIAO-B97-2/Def2-TZVP//M06-2X/Def2-SVP level of theory) and was found to correlate well with the resonances observed for 5-2 at -60 °C in THF-d8 (Figure 5.2.4). The central carbon was observed at 133.4 ppm and the two flanking carbons at 93.3 ppm, while the corresponding calculated resonances are 133.9 and 90.9 ppm, respectively. Compound 5-2 decomposes slowly at -60 °C in THF-d8 solution and very rapidly at ambient temperature, forming a complex mixture of products.

5.2.3 Main Group Complexes of Tetraphenylcarbodicycloprenylidene

The formulation of 5-2 and its nucleophilic nature was confirmed by its capture with B(C6F5)3, which yields the η1 adduct 5-3 in 47% yield (Scheme 5.2.3). Room temperature 1H NMR analysis of 5-3 reveals very broad signals assignable to two inequivalent phenyl moieties, which sharpen upon cooling to -40 °C. The room temperature 19F NMR spectrum reveals only broad uninformative resonances. However, upon cooling to -40 °C, 19F NMR signals sharpen to reveal restricted rotation about the B-C_CDC bond and additional restricted rotation in two of the three C6F5 rings, giving rise to 3 sets of ortho and meta C-F resonances integrating to 2 fluorines each, and two para resonances integrating to 2 and 1 fluorine atom, respectively (Figure 5.2.5). A very broad signal centred at 89.3 ppm is observed in the 13C{1H} NMR spectrum at -40 °C, which is assigned to the central carbon atom. The two equivalent flanking carbon atoms give a sharper resonance at 154.2 ppm. Crystals of 5-3 suitable for X-ray diffraction were grown from Et2O at -45 °C (Figure 5.2.6). In the solid state, the planes of the two three-membered rings are canted with respect to one another by 28.7(2)°. The central
C\textsubscript{CDC}-B distance is 1.643(3) Å, and the distances to the flanking carbon atoms are 1.389(3) Å and 1.392(3) Å. Compound \textbf{5-3} is stable at room temperature toward both air and moisture, and can be heated to 110 °C in toluene-d\textsubscript{8} solution without decomposition. At this high temperature, a single C\textsubscript{6}F\textsubscript{6} environment is observed, as well as a single phenyl environment, implying fast rotation about the B-C\textsubscript{CDC} bond as well as the flanking cyclopropenylidene groups (see section 5.2.4 for further discussion).

\begin{Scheme}
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\includegraphics[width=\textwidth]{scheme523}
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\end{Scheme}

\textbf{Scheme 5.2.3.} Synthesis of tetraphenylcarbodicyclopropenylidene main group adducts \textbf{5-3} and \textbf{5-4}.

\begin{Figure}
\begin{center}
\includegraphics[width=\textwidth]{fig525}
\end{center}
\end{Figure}

\textbf{Figure 5.2.5.} \textsuperscript{19}F NMR (THF-d\textsubscript{8}) spectrum of \textbf{5-3} collected at -40 °C.
The analogous, but much more fragile, GaCl₃ complex 5-4 can be accessed by addition of a GaCl₃ solution in Et₂O to freshly generated 5-2 at -45 °C (Scheme 5.2.3), and crystals suitable for X-ray diffraction were grown from CH₂Cl₂/Et₂O solution (Figure 5.2.7). In the solid state, the cant of the two three-membered rings with respect to one another is 27.1(3)°. The central C-Ga distance is 1.960(3) Å, and the distances of the central carbon atom to the flanking carbon atoms are 1.387(4) Å and 1.394(4) Å. Very broad resonances for 5-4 are observed in the room temperature ¹H NMR spectrum, which appears to show a single phenyl environment. Cooling to -80 °C in THF-d₈ was necessary to achieve decoalescence and sharpening of the two inequivalent phenyl environments anticipated from the solid state structure. Compound 5-4 gives a ⁷¹Ga NMR
signal at 251.3 ppm at -80 °C in THF-d$_8$, similar to resonances observed for NHC-GaCl$_3$ adducts.$^{51}$ Compound 5-4 decomposes if exposed to air.

![Figure 5.2.7](image).

**Figure 5.2.7.** Molecular structure of 5-4 with thermal ellipsoids drawn at 50% probability. Hydrogen atoms are removed for clarity. Colours: C, grey; Ga, yellow; Cl, green.

Recently, Gandon and coworkers reported a ‘gallium scale’ whereby the degree of pyramidalization of GaCl$_3$ in a series of adducts L·GaCl$_3$ was shown to correlate with the Tolman electronic parameter (TEP) of the ligand L, with good correlation across a range of 26 ether, amine, phosphine, NHC, cyclic alkyamino carbene (CAAC), and CDC/carbodiphosphorane derivatives.$^{52}$ Placing 5-2 on the gallium scale, we find that $\Sigma_{\text{ClGaCl}} = 320.74(5)^\circ$, which correlates to a TEP of 2044.5 cm$^{-1}$. This indicates that 5-2 is a stronger donor than both NHCs and CAACs, placing it among the strongest electron donors. However, 5-2 is a weaker donor than other members of the carbone family (TEP typically 2039 – 2027 cm$^{-1}$).
5.2.4 Transition Metal Complexes of Tetraphenylcarbodiacyclopropenylidene

Our initial attempts at synthesis of transition metal complexes of 5-2 involved reactions with AgOTf, [Ir(COD)Cl]₂, and [Rh(COD)Cl]₂. Unfortunately all reactions afforded complex mixtures of products. We rationalized that the relatively unprotected LUMO of 5-2 would render its complexes sensitive to nucleophiles, and therefore may be prone to intermolecular decomposition reactions if the nucleophilicity of the central carbon atom is not sufficiently quenched. Indeed, the addition of one equivalent of PMe₃ to complex 5-3 resulted in immediate decomposition to a broad mixture of products. Therefore, we directed our attention to synthesis of Au complexes of 5-2, due to the high carbophilicity of this noble metal.

Addition of an equimolar amount of AuCl(SMe₂) to a freshly generated solution of 5-2 at -45 °C resulted in the immediate precipitation of a yellow solid (Scheme 5.2.4). However, it became apparent that this product is extremely fragile and decomposes rapidly in the solid state at room temperature, changing colour to dark green in a matter of minutes. Broad resonances are observed in the room temperature ¹H NMR spectrum in THF-d₈, similar to those observed for the GaCl₃ adduct 5-4. While variable temperature ¹H NMR experiments on rapidly worked up product identified resonances consistent with an η¹ coordination complex of 5-2, the presence of other unidentified species was also apparent. However, it was found that if excess Et₂O was added to a freshly prepared solution of this precipitate in CH₂Cl₂, yellow X-ray quality crystals rapidly formed within minutes. Remarkably, the crystal structure obtained featured whole molecule substitutional disorder, with the major component (91%) being the AuCl₂ salt of 5-1, and the minor component (9%) being the intended AuCl adduct 5-5. The major component salt most likely arises from decomposition of 5-5 in the presence of CH₂Cl₂. The atomic positions of the organic fragment are shared between the two disordered components (Figure 5.2.8).
Scheme 5.2.4. Reaction of *in situ* generated 5-2 with AuCl(SMe₂)

Figure 5.2.8. Molecular structure of 5-5 disordered with 5-1 (AuCl₂ salt). The minor component 5-5 is highlighted and the major component is faded. Colours: C, grey; H, turquoise; Au, gold; Cl, green.

In the solid state, the Au-C bond length of 5-5 is 1.967(7) Å, slightly shorter than the average ClAu-NHC bond length of 1.98 Å. Although 5-5 proved too fragile to be isolated, the molecular structure obtained provided encouragement that further refinement of the steric and electronic properties of the Au centre would lead to isolable complexes of 5-2.

We next turned our attention to cationic Au complexes, as the more strongly Lewis acidic metal centre should offer even greater electronic stability to
coordinated 5-2. Additionally, bulky NHCs were chosen as ancillary ligands to afford some steric protection of the reactive carbon centre. To our delight, combination of an Et₂O solution of (NHC)AuOTf (NHC = IDipp, IAd) and a freshly generated solution of 5-2 at -45 °C results in the formation of isolable complexes 5-6 and 5-7, respectively (Scheme 5.2.5).

![Scheme 5.2.5. Synthesis of Au complexes 5-6 & 5-7.](image)

The molecular structure of 5-7 was determined by single crystal X-ray diffraction (Figure 5.2.9), and confirmed the η¹ coordination of the carbodicycloprenylidene to the Au centre, as is predicted for members of the carbone family.¹⁶ This is in contrast to conventional allenes in which the resting state is typically η² coordination to Au.¹⁶,⁵⁵ Two molecules of 5-7 are present in an asymmetric unit, which have somewhat different metrical parameters. The Au-C_CDC bond lengths are 2.071(6) Å and 2.047(6) Å, while the corresponding Au-C_CNC bond lengths are 2.073(6) Å and 2.042(7) Å, respectively. We attribute this variation to packing effects within the crystal. The angles of the flanking cyclopropenylidene groups with respect to one another are quite similar at 24.2(8)° and 24.3(7)°, respectively.
Figure 5.2.9. Molecular structure of the cation of 5-7 with thermal ellipsoids drawn at 50% probability. Hydrogen atoms are removed for clarity. Colours: C, grey; Au, gold; N, blue.

The room temperature $^{13}\text{C}_{\text{[}^{1}\text{H}] }$ NMR spectrum of 5-6 reveals a sharp resonance at 98.0 ppm, which is assigned to the central carbodicarbene carbon atom, and an additional resonance for the flanking carbons is observed at 155.8 ppm. Interestingly, a single set of sharp phenyl resonances is observed for Au bound carbodicyclopentadienyldiene in the $^{1}\text{H}$ NMR spectrum at room temperature in THF-$d_8$ (Figure 5.2.10). Upon cooling, these signals gradually broaden and finally decoalesce to give two very broad but inequivalent phenyl environments at
-80 °C, supporting the $\eta^1$ binding mode. Similar $^1$H and $^{13}$C\(\{^1\}H\) NMR resonances are also observed for 5-7.

![Variable temperature $^1$H NMR spectra](image)

**Figure 5.2.10.** Variable temperature $^1$H NMR (THF-d$_8$) spectrum of 5-6. Blue = ortho, Green = meta, red = para. X = C$_6$H$_6$.

5.2.5 Fluxionality in Tetraphenylcarbodicyclopropenylidene Complexes

It is interesting that compounds 5-3 – 5-7 all display some degree of fluxionality in their NMR spectra at room temperature. We postulate that this is due to varying degrees of free rotation in the flanking 1,2-diphenylcyclopropenylidene moieties. In support of this assertion, high temperature variable temperature $^1$H NMR spectra were obtained of 5-1 in 1,1,2,2-tetrachloroethane-d$_2$. Above 40 °C, the sharp inequivalent phenyl environments begin to broaden, and coalescence to a single broad phenyl environment is observed at 120 °C, suggesting that slow rotation of the flanking groups is occurring on the NMR timescale (Figure 5.2.11). We postulate that increasing the $\pi$-acceptor ability of the coordination centre
decreases the barrier to rotation in these flanking groups by delocalization of the electrons in the 3c-2e π bond to the coordination centre (Scheme 5.2.6), thereby resulting in fast rotation and the equivalent phenyl resonances, as is observed in complexes 5-4, 5-6 and 5-7 at room temperature. This result suggests the ability of 5-2 to act as a four electron donor to unsaturated centres, as has been observed with other members of the CDC family (see sections 3.2.2, 3.2.7).

Scheme 5.2.6. Resonance structures of complexes of compound 5.2.

Figure 5.2.11. High temperature ¹H NMR spectra of 5-1 in 1,1,2,2-tetrachloroethane-d₂
Interestingly, 5-1 can be protonated at the central carbon by excess HOTf to form the methylene bridged dicycloprenium salt 5-8 (Scheme 5.2.7), confirming the double basicity of the central carbon atom in 5-2. As expected, a single sharp phenyl environment is observed for 5-8 in CDCl₃ solution, indicating fast rotation of the flanking cycloprenium groups. The central methylene resonance is observed at 5.95 ppm in the ¹H NMR spectrum.

Scheme 5.2.7. Protonation of 5-1

5.2.6 Tetraaminocarbodicycloprenylidene

We next turned our attention to the synthesis of the corresponding tetra-amino carbodicycloprenylidene derivative, as the introduction of the amino substituents is predicted to raise the energy of the LUMO, increasing the stability of both the free ligand and its complexes. Analogous methodology was applied to the isolation of the first cyclopropenylidene by Bertrand and coworkers.³⁷ This substitution should also make the carbodicycloprenylidene more electron releasing, suggesting that such a system may be an effective spectator ligand in catalytic processes.
Scheme 5.2.8. Synthesis of 5-9
The synthesis of a potential precursor to the tetraaminocarbodicycloprenylidene, methylenebis(1,2-diisopropylaminocyclopropenium) bis(perchlorate) was reported by Yoshida in 1982, however, no experimental details or spectroscopic characterization of the product was provided, offering only a reaction scheme suggesting that this product may be obtained by the reaction of 1,2-bis(diisopropylamino)triafulvene with a 1,2-bis(diisopropylamino)-3-methoxycyclopropenium salt. To our delight, we have found that this reaction does indeed proceed cleanly, affording upon acidic workup methylenebis(1,2-diisopropylaminocyclopropenium) bis(tetrafluoroborate) 5-9 (Scheme 5.2.8). The additional π-basicity of the tetraaminocarbodicycloprenylidene is indicated by the fact that the doubly protonated salt is isolated from THF solution, in contrast to the monoprotonated salt 5-1 isolated from Et₂O. A molecular structure of 5-9 was obtained which confirmed the formulation as the methylene bridged dicyclopropenium salt (Figure 5.2.12).

Figure 5.2.12. Molecular structure of the dication of 5-9 with thermal ellipsoids drawn at 50% probability. Hydrogen atoms (except at the central methylene bridge) are removed for clarity. The cyclopropenium rings are related by a twofold rotational axis and are also disordered over two positions. The disordered atoms were refined anisotropically where possible. One position is shown for clarity. Colours: C, grey; H, turquoise; N, blue.
Unfortunately, combination of 5-9 with bases such as KHMDS, LiHMDS and LDA has thus far not afforded the corresponding tetraaminocarbodicyclopropenylidene. However, this project remains an active area of research at the time of writing of this thesis.

5.3 Summary and Conclusion

In summary, we have reported the first example of a carbodicyclopropenylidene, which is also the first example of a CDC based entirely on carbon. Tetraphenylcarbodicyclopropenylidene 5-2 has been observed to form stable η¹ complexes with both main group Lewis acids and transition metals. A precursor to the corresponding tetraamino derivative, which may have applications in transition metal catalysis, has been isolated and is currently under investigation.

5.4 Experimental Section

5.4.1 Crystallographic Details

X-ray Data Collection and Reduction. Crystals were coated in Paratone-N oil in the glovebox, mounted on a MiTegen Micromount, and placed under a N₂ stream, thus maintaining a dry, O₂-free environment for each crystal. The data were collected on a Bruker Kappa Apex II diffractometer using a graphite monochromator with Mo Kα (λ = 0.71073 Å) or Cu Kα (λ = 1.54178 Å) radiation. The data were collected at 150(2) K for all crystals. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the empirical multiscan method SADABS. In cases where non-merohedral twinning was detected, the data was indexed with CELLNOW to determine the contributions of the respective crystal domains, and the data were corrected for absorption effects using TWINABS. The heavy atom positions were determined employing the SHELXTL direct methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least squares techniques on F, minimizing the function \( \omega (F_o-F_c)^2 \) where the weight \( \omega \) is defined as \( 4F_o^2/2\sigma(F_o^2) \) and \( F_o \) and \( F_c \) are the
observed and calculated structure factor amplitudes, respectively. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of positional disordering. The final models of twinned structures were obtained by refinement against the twinned data. C-H atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C-H bond length of 0.95 Å. H-atom temperature factors were fixed at 1.20 times the isotropic temperature factor of the C-atom to which they are bonded. The H-atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance.

Table 5.4.1. Crystallographic information

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</table>

#### 5.4.2 Computational Details

Calculations were carried out with the Gaussian 09 package. Geometry optimizations were performed with the M06-2X functional. The Def2-SVP basis set was used for all the atoms. Frequency calculations at the same level of theory were performed to identify the number of imaginary frequencies (zero for local minimum) and provide frontier molecular orbitals (HOMO and LUMO). Isotropic shifts for 2 were computed at the GIAO-B97-2$^{59}$/Def2-TZVP$^{58}$/M06-2X/Def2-SVP level of theory using C$_4$ (96.9 ppm)$^{60}$ of 1,2,4,4-tetraphenyltriafulvene as the standard reference. Natural bond orbital (NBO) analysis was carried out at M06-2X/TZVP$^{61}$/M06-2X/Def2-SVP level.
5.4.3 Experimental Details

**General Remarks**: All air sensitive manipulations were carried out under an atmosphere of dry, O\textsubscript{2}-free N\textsubscript{2} employing a Vacuum Atmospheres glovebox. Solvents were purified with a Grubbs-type column system manufactured by Innovative Technology and dispensed into thick-walled Straus flasks equipped with Teflon-valve stopcocks. Et\textsubscript{2}O was stored over a potassium mirror. CD\textsubscript{2}Cl\textsubscript{2} and CDCl\textsubscript{3} were distilled under reduced pressure from CaH\textsubscript{2} and degassed by successive freeze-pump-thaw cycles. C\textsubscript{6}D\textsubscript{6} and THF-d\textsubscript{8} were distilled from purple sodium benzophenone ketyl. \textsuperscript{1}H, \textsuperscript{11}B, \textsuperscript{13}C{\textsuperscript{1}H}, and \textsuperscript{19}F and \textsuperscript{71}Ga NMR spectra were collected on Bruker Advance III 400 MHz, Agilent DD2 500 MHz, or Agilent DD2 600 MHz spectrometers. Chemical shifts are reported in parts per million are given relative to SiMe\textsubscript{4} and referenced to the residual solvent signal. \textsuperscript{13}C{\textsuperscript{1}H} NMR signals are reported to a precision of 0.01 ppm to avoid reporting duplicates of spatially close signals, but should be understood to be accurate to 0.1 ppm. Combustion analyses were performed in house employing a Perkin-Elmer CHN Analyzer. B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} was purchased from Boulder Scientific and used as received. Chloro[1,3-bis(adamantly)imidazole-2-ylidene]gold(I) (IAdAuCl) was purchased from Strem chemicals and used as received. GaCl\textsubscript{3} was purchased from Strem chemicals and sublimed immediately before use. Trityl tetrafluoroborate and was purchased from Sigma-Aldrich and used as received. \textsuperscript{13}C{\textsuperscript{1}H} trifluoromethanesulfonate (IDippAuOTf) was synthesized according to a literature procedure.\textsuperscript{62}

**bis(1,2-diphenylcyclopropen-3-yl)methane**: This was prepared according to the procedure of Padwa and coworkers,\textsuperscript{63} and was further purified by recrystallization from pentane to yield a colourless crystalline solid. \textsuperscript{1}H NMR (CD\textsubscript{2}Cl\textsubscript{2}): 7.78 (dm, \textsuperscript{3}J\textsubscript{H-H} = 8.2 Hz, 8H, o-Ph), 7.46 (tm, \textsuperscript{3}J\textsubscript{H-H} = 8.2 Hz, 8H, m-Ph), 7.35 (tm, \textsuperscript{3}J\textsubscript{H-H} = 7.5 Hz, 4H, p-Ph), 2.43 (t, \textsuperscript{3}J\textsubscript{H-H} = 5.2 Hz, 2H), 1.98 (t, \textsuperscript{3}J\textsubscript{H-H} = 5.2 Hz, 2H). \textsuperscript{13}C{\textsuperscript{1}H} NMR (CD\textsubscript{2}Cl\textsubscript{2}): 130.67, 130.08, 129.11, 128.62, 119.39, 41.84, 21.05. Anal. Calcd. For C\textsubscript{31}H\textsubscript{24} (396.53): C, 93.90; H, 6.10; N, 0.00 Found: C, 93.46; H, 6.17; N, 0.00.
5-1: Bis(1,2-diphenylcyclopropan-3-yl)methane (202 mg, 0.51 mmol) and trityl tetrafluoroborate (420 mg, 1.27 mmol) were combined in CH\(_2\)Cl\(_2\) (6 mL) and refluxed for 4 h. After this period, Et\(_2\)O (15 mL) was added to the reaction mixture which was stirred for 1 h, resulting in the precipitation of a yellow solid. The solid was washed with Et\(_2\)O until the washes were colourless. The solid was resuspended in Et\(_2\)O (10 mL) and was stirred at room temperature overnight to decompose any unreacted trityl. The supernatant was then decanted, and the yellow solid obtained was washed with THF (1 x 3 mL) and Et\(_2\)O (2 x 5 mL), and dried under high vacuum (192 mg, 78%). Crystals suitable for X-ray diffraction were grown from CH\(_2\)Cl\(_2\)/Et\(_2\)O.

\(^1\)H NMR (CD\(_2\)Cl\(_2\)): 8.22 (dm, \(^3\)J\(_{H-H}\) = 7.7 Hz, 4H, o-Ph), 8.05 (dm, \(^3\)J\(_{H-H}\) = 7.7 Hz, 4H, o-Ph), 7.86 (tm, \(^3\)J\(_{H-H}\) = 7.6 Hz, 2H, p-Ph), 7.79 (tm, \(^3\)J\(_{H-H}\) = 7.3 Hz, 4H, m-Ph), 7.71 (tm, \(^3\)J\(_{H-H}\) = 7.6 Hz, 2H, p-Ph), 7.50 (tm, \(^3\)J\(_{H-H}\) = 7.9 Hz, 4H, m-Ph), 6.53 (s, 1H, CH).

\(^13\)C{\(^1\)H} NMR (CD\(_2\)Cl\(_2\)): 147.84 (C(CH)C), 144.76 (cyclopropene C=C), 143.08 (cyclopropene C=C), 136.20 (p-Ph), 135.53 (p-Ph), 130.59 (m-Ph), 130.24 (m-Ph), 122.21 (ipso-Ph), 121.88 (ipso-Ph), 68.49 (C(CH)C).

\(^19\)F NMR (CD\(_2\)Cl\(_2\)): -153.2 (s, BF\(_4\)).

\(^{11}\)B NMR (CD\(_2\)Cl\(_2\)): -1.0 (s, BF\(_4\)).

Anal. Calcd. For C\(_{31}\)H\(_{21}\)BF\(_4\) (480.31): C, 77.52; H, 4.41; N, 0.00. Found: C, 77.10; H, 4.11; N, 0.00.

Generation of 5-2: Compound 5-1 (2.0 mg, 4.2 μmol) and KHMDS (1.0 mg, 5.0 μmol) were combined in a J-Young NMR tube. The tube was evacuated, frozen in liquid N\(_2\), and THF-d\(_8\) (0.4 mL) was condensed in the tube. The frozen tube was allowed to thaw to -78 °C in a dry ice/acetone bath, forming a bright red mixture. The tube was quickly inserted into an Agilent DD2 500 MHz spectrometer precooled to -60 °C, and \(^1\)H, \(^13\)C{\(^1\)H}, HSQC and DEPTQ-135 NMR spectra were acquired at this temperature. Care must be taken to not allow the tube to warm up during transfer, as 5-2 decomposes very rapidly at ambient temperature. \(^1\)H NMR (THF-d\(_8\), -60 °C): 7.95 (d, \(^3\)J\(_{H-H}\) = 7.7 Hz, 8H, o-Ph), 7.57 (t, \(^3\)J\(_{H-H}\) = 7.7 Hz, 8H, m-Ph), 7.50 (t, \(^3\)J\(_{H-H}\) = 7.6 Hz, 4H, p-Ph). \(^13\)C{\(^1\)H} NMR (THF-d\(_8\), -60 °C): 133.44 (C=C=C), 130.93 (o-Ph), 130.79 (p-Ph), 130.46 (cyclopropene C=C),
129.77 (m-Ph), 126.76 (ipso Ph), 93.34 (C=C=C). Compound 5-2 was not isolated and was generated in situ for all other syntheses.

5-3: Compound 5-1 (23 mg, 47.9 μmol) was suspended in Et₂O (3 mL) and cooled to -45 °C. KHMDS (10 mg, 50.1 μmol) was added at this temperature, resulting in the immediate formation of a bright red solution, which was stirred for two minutes. A solution of B(C₆F₅)₃ (25 mg, 48.8 μmol) in Et₂O (2 mL) was then added rapidly to the reaction mixture, resulting in a colour change to orange, and was allowed to warm to ambient temperature over a period of 30 minutes. The solvent was removed under high vacuum, and the residue was washed with pentane until the washings were colourless. The yellow residue was extracted with Et₂O (2 x 5 mL), filtered of any insoluble material, and concentrated to 1 mL. Pentane was added to precipitate the product as a yellow-green solid which was collected and dried under high vacuum (20 mg, 47%). Crystals suitable for X-ray diffraction were grown from slow evaporation of an Et₂O solution. ¹H NMR (THF-d₈, -40 °C): 7.78 (dm, ³J₃H-H = 7.1 Hz, 4H, o-Ph), 7.73 (dm, ³J₃H-H = 7.1 Hz, 4H, o-Ph), 7.68 (tm, ³J₃H-H = 7.5 Hz, 2H, p-Ph), 7.54 (t, ³J₃H-H = 7.8 Hz, 4H, m-Ph), 7.34 (tm, ³J₃H-H = 7.4 Hz, 2H, p-Ph), 7.23 (t, ³J₃H-H = 7.8 Hz, 4H, m-Ph). ¹³C{¹H} NMR (THF-d₈, -40 °C): 154.22 (C=C=C), 150.79 (br, C₆F₅), 151.0 – 147.6 (br m, C₆F₅), 150.50 (cyclopropene C=C), 146.42 (cyclopropene C=C), 140.6 – 135.6 (br m, C₆F₅), 134.43 (p-Ph), 133.97 (p-Ph), 132.82 (o-Ph), 131.48 (o-Ph), 129.81 (p-Ph), 129.59 (p-Ph), 123.92 (ipso-Ph), 127.7 – 124.5 (br m, C₆F₅), 123.76 (ipso-Ph).

89.3 (br, C=C=C) ¹⁹F NMR (THF-d₈, -40 °C): -129.4 (br, 2F, o-C₆F₅), -129.9 (br, 2F, o-C₆F₅), -131.9 (br, 2F, o-C₆F₅), -160.7 (t, ³J₃F-F = 22 Hz, 2F, p-C₆F₅), -161.9 (t, ³J₃F-F = 21 Hz, 1F, p-C₆F₅), -164.7 (br t, ³J₃F-F = 19 Hz, 2F, m-C₆F₅), -165.2 (br t, ³J₃F-F = 20 Hz, 2F, m-C₆F₅), -165.5 (br t, ³J₃F-F = 20 Hz, 2F, m-C₆F₅). ¹¹B NMR (THF-d₈, -40 °C): -14.0 (s, B(C₆F₅)₃). Anal. Calcd for C₄₉H₂₀BF₁₅ (904.49): C, 65.07; H, 2.23; N, 0.00. Found: C, 65.19; H, 2.21; N, 0.00.

5-4: Compound 5-1 (22 mg, 45.8 μmol) was suspended in Et₂O (5 mL) and cooled to -45 °C. KHMDS (9.5 mg, 47.6 μmol) was added at this temperature,
resulting in the immediate formation of a bright red solution, which was stirred at -45 °C for two minutes. A solution of freshly sublimed GaCl₃ (8 mg, 45.4 μmol) in Et₂O (3 mL) was then added to the reaction mixture, resulting in the immediate precipitation of a yellow-green solid. The solvent was removed under vacuum, and the residue was washed with pentane (3 x 5 mL) until the washes were colourless. The residue was extracted into CH₂Cl₂ (5 mL), filtered of any insoluble material, and concentrated to 1 mL. Et₂O (15 mL) was added to precipitate the product, resulting in a mixture of 5-4 along with a minor impurity of the chloride salt of 5-1 (approx. 15 mol%). The supernatant was decanted and the insolubles were washed with Et₂O (2 x 3 mL) and dried under high vacuum (20 mg, 77%).

Blocky yellow-green crystals of 5-4 suitable for X-ray diffraction were grown from a CH₂Cl₂ solution layered with Et₂O, although the recrystallization resulted in a significant decrease in product purity by the formation of further 5-1 chloride salt. Mechanically separated crystals of pure 5-4 (<0.5 mg) were determined by ¹H NMR spectroscopy to correspond to the major component of the crude product.

Compound 5-4 is stable in the solid state at -45 °C under N₂, but decomposes in either THF or CH₂Cl₂ solution. ¹H NMR (THF-d₈, -80 °C): 8.64 (d, ³J_H-H = 7.5 Hz, 4H, o-Ph), 8.02 (d, ³J_H-H = 7.5 Hz, 4H, o-Ph), 7.84 (t, ³J_H-H = 7.4 Hz, 2H, p-Ph), 7.77 (t, ³J_H-H = 7.5 Hz, 4H, m-Ph), 7.43 (t, ³J_H-H = 7.4 Hz, 2H, p-Ph), 7.27 (t, ³J_H-H = 7.5 Hz, 4H, m-Ph). ¹³C{¹H} NMR (THF-d₈, -80 °C): 153.61 (C=C=C=C), 150.59 (cyclopropene C=C), 146.21 (cyclopropene C=C), 135.27 (p-Ph), 134.85 (o-Ph), 134.18 (p-Ph), 133.29 (o-Ph), 129.88 (m-Ph), 129.50 (m-Ph), 123.26 (ispo-Ph), 123.21 (ispo-Ph). ⁷¹Ga NMR (THF-d₈, -80 °C): 251.3. Elemental analysis was not obtained due to the extreme fragility and generally uncooperative nature of this compound.

5-6: Compound 5-1 (22 mg, 45.8 μmol) was suspended in Et₂O (5 mL) and cooled to -45 °C. KHMDS (10 mg, 50.1 μmol) was added at this temperature, resulting in the immediate formation of a bright red solution, which was stirred at -45 °C for two minutes. A precooled solution of IDippAuOTf (34 mg, 46.2 μmol) in Et₂O (3 mL) was then added to the reaction mixture at this temperature, resulting
in the immediate precipitation of a pale solid. The solid was collected and washed with Et$_2$O until the washings were colourless. The bright yellow solid obtained was extracted with CH$_2$Cl$_2$ and filtered of any insoluble material through a glass frit. The solution was concentrated to 1 mL and pentane (15 mL) was added to precipitate the product as a yellow-green solid, which was collected and dried under high vacuum (29 mg, 56%). $^1$H NMR (THF-d$_8$): 8.02 (d, $^3$J$_{H-H} = 7.6$ Hz, 8H, o-Ph), 7.72 (s, 2H, NCH), 7.54 (t, $^3$J$_{H-H} = 7.6$ Hz, 4H, p-Ph), 7.44 (t, $^3$J$_{H-H} = 7.6$ Hz, 10H, m-Ph + buried m-Dipp resonance), 7.32 (d, $^3$J$_{H-H} = 7.8$ Hz, 4H, p-Dipp), 3.00 (septet, $^3$J$_{H-H} = 6.8$ Hz, 4H, CH(CH$_3$)$_2$), 1.24 (d, $^3$J$_{H-H} = 6.8$ Hz, 12H, CH(CH$_3$)$_2$), 1.22 (d, $^3$J$_{H-H} = 6.8$ Hz, 12H, CH(CH$_3$)$_2$). $^{13}$C{$_^1$H} NMR (THF-d$_8$): 191.77 (NCN), 155.75 (C=C=C), 147.67 (cyclopropene C=C), 147.27 (ipso-AriPr), 135.97 (ipso-Dipp), 134.25 (p-Ph), 133.37 (o-Ph), 130.99 (p-Dipp), 130.02 (m-Ph), 126.16 (NCH), 124.81 (m-Dipp), 123.75 (ipso-Ph), 98.04 (C=C=C), 29.48 (CH(CH$_3$)$_2$), 24.64 (CH(CH$_3$)$_2$), 24.59 (CH(CH$_3$)$_2$). $^{19}$F NMR (THF-d$_8$): -78.9 (OTf).

**IAdAuOTf:** IAdAuCl (71 mg, 124.8 μmol) was stirred with AgOTf (32 mg, 124.5 μmol) in CH$_2$Cl$_2$ (3 mL) for 2 h in darkness. After this time, the mixture was filtered through celite, and the colourless solution obtained was concentrated to 1 mL, and pentane was added to precipitate the product as a white solid, which was collected and dried under high vacuum (76 mg, 89%). Solutions containing IAdAuOTf should be protected from light. $^1$H NMR (CDCl$_3$): 7.14 (s, 2H, NCH), 2.53 (d, $^3$J$_{H-H} = 3.0$ Hz, 12H, NCCH$_2$), 2.32 – 2.28 (br m, 6H, CH$_2$Ad), 1.82 – 1.75 (br m, 12H, CHCH$_2$CH). $^{13}$C{$_^1$H} NMR (CDCl$_3$): 150.98 (NCN), 116.40 (NCH), 60.00 (NC$_2$Ad), 44.46, 35.84, 30.07. $^{19}$F NMR (CDCl$_3$): -76.6 (OTf). Anal Calcd. for C$_{24}$H$_{32}$AuF$_3$N$_2$O$_3$S (682.55): C, 42.23; H, 4.73; N, 4.10. Found: C, 42.71; H, 4.40; N, 3.86.

**5-7:** This compound was synthesized in an analogous manner to **5-6** (yellow solid, 26 mg, 58% yield). A minor impurity of the triflate salt of **5-1** (approx. 10 mol%) is present. Crystals suitable for X-ray diffraction were grown from CH$_2$Cl$_2$/cyclohexane solution, although the recrystallization resulted in a decrease
in product purity by the formation of further ligand salt. $^1$H NMR (CDCl$_3$): 8.27 – 8.08 (br, 8H, o-Ph), 7.60 (br t, $^3$J$_{H,H} = 7.0$ Hz, 4H, p-Ph), 7.48 (br t, $^3$J$_{H,H} = 7.8$ Hz, 8H, m-Ph), 7.29 (s, 2H, NCH), 2.64 (d, $^3$J$_{H,H} = 2.8$ Hz, 12H, NCCH$_2$), 2.02 – 1.97 (br m, 6H, CH$_{Ad}$), 1.60 – 1.57 (br m, 12H, CHC$_2$H) $^{13}$C{$^1$H} NMR (CDCl$_3$): 184.54 (NCN), 155.03 (C=C=C), 146.75 (br, cyclopropene C=C), 134.21 (p-Ph), 132.62 (o-Ph), 129.64 (m-Ph), 122.82 (ipso-Ph), 116.34 (NCH), 92.69 (C=C=C), 59.22 (NC$_{Ad}$), 44.73 (NC$_2$H$_2$). Anal Calcd. for C$_{55}$H$_{52}$AuF$_3$N$_2$O$_3$S (1075.05): C, 61.45; H, 4.88; N, 2.61. Found: C, 62.44; H, 4.22; N, 2.36.

Generation of 5-8: A sample of 5-1 (5 mg, 10.4 μmol) was dissolved in CDCl$_3$ (0.5 mL). A few drops of HOTf were added and the mixture was shaken briefly, becoming colourless. The organic phase was separated and analyzed by $^1$H, $^{19}$F and $^{13}$C{$^1$H} NMR spectroscopy at ambient temperature. $^1$H NMR (CDCl$_3$): 8.28 (dm, $^3$J$_{H,H} = 7.2$ Hz, 8H, o-Ph), 8.05 (tm, $^3$J$_{H,H} = 7.5$ Hz, 4H, p-Ph), 7.77 (tm, $^3$J$_{H,H} = 7.5$ Hz, 8H, m-Ph), 5.95 (s, 2H, CH$_2$). $^{13}$C{$^1$H} NMR (CDCl$_3$): 161.13 (CPh), 155.85 (CCH$_2$C), 140.86 (p-Ph), 136.56 (o-Ph), 131.00 (m-Ph), 118.54 (q, $^1$J$_{C,F} = 318$ Hz, OTf), 117.92 (ipso-Ph), 27.04 (CH$_2$). $^{19}$F NMR (CDCl$_3$): -76.4 (OTf).

5-9: 1,2-Bis(diisopropylamino)triafulvene$^{56}$ (98 mg, 0.39 mmol) and 1,2- bis(diisopropylamino)-3-methoxycyclopropenium tetrafluoroborate$^{64}$ (138 mg, 0.39 mmol) were combined in anhydrous THF (3 mL) at -40 °C. The mixture was allowed to warm to room temperature and was stirred for 1 h. After this time, the reaction was removed from inert atmosphere and 48% HBF$_4$ in H$_2$O (50 μL, 0.38 mmol) was added, causing the formation of an oily precipitate. The mixture was stirred for a subsequent hour, during which time the precipitate solidified. The supernatant was decanted, and the solid washed with THF until the washes were colourless (4 x 10 mL), followed by Et$_2$O (3 x 10 mL) and dried under high vacuum. White solid (137 mg, 54%) Crystals suitable for X-ray diffraction were grown from CH$_2$Cl$_2$/THF/pentane. $^1$H NMR (CDCl$_3$): 4.40 (s, 2H, CCH$_2$C), 4.11 (septet, $^3$J$_{H,H} = 7.0$ Hz, 4H, NCH(CH$_3$)$_2$), 3.85 (septet, $^3$J$_{H,H} = 7.0$ Hz, 4H,
NCH(CH$_3$)$_2$, 1.39 (d, $^3$J$_{H-H} = 6.9$ Hz, 24H, NCH(CH$_3$)$_2$), 1.35 (d, $^3$J$_{H-H} = 7.0$ Hz, 4H, NCH(CH$_3$)$_2$). $^{13}$C{$_1^1$H} NMR (CDCl$_3$): 134.13, 102.70, 54.30 (NCH(CH$_3$)$_2$), 51.30 (NCH(CH$_3$)$_2$), 22.15 (CH$_2$), 22.02 (NCH(CH$_3$)$_2$), 21.31 (NCH(CH$_3$)$_2$). $^{11}$B NMR (CDCl$_3$): -1.2 (BF$_4$). Anal. Calcd. For C$_{31}$H$_{58}$B$_2$F$_8$N$_4$ (660.44): C, 56.38; H, 8.85; N, 8.48. Found: C, 56.23; H, 8.77; N, 8.29.

5.5 References


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Chapter 6. Conclusions and Future Work

In summary, this thesis has presented results from research on the coordination chemistry of a range of strong donor carbene and carbone type ligands. Anionic imidazol-4-ylidenes were found to be fragile ligands of moderate donor strength, which rearrange in the presence of coordinative unsaturation by a unique proton transfer reaction, and also decompose upon the introduction of hydride into the coordination sphere of the metal. Such ligands will likely not be useful as spectator ligands in catalysis.

A cyclic bent allene was found to be an effective spectator ligand for the Ru catalyzed hydrogenation of olefins, achieving TON comparable to or better than the highly active Crabtree catalyst in the hydrogenation of mono-, di- and tri-substituted olefins. Chemoselective hydrogenations proceed rapidly at exceptionally low loadings, and functional group directed diastereoselective hydrogenations have also been achieved. Chiral variations of the CBA can be readily constructed, however, the precursor salt is difficult to deprotonate, and the free chiral CBA has only been successfully metalated in two cases. This methodology has not so far been applied to Ru based hydrogenation catalysis. What is lacking here is a reliable method of transmetalation of the CBA to another metal centre. Direct metalation of the symmetrical CBA is also challenging; of the ten Ru precursors reacted with the free CBA, only one (RuHCl(CO)(PPh₃)₃) produced an isolable metalated product. Unlike NHCs, it was found Ag-CBA complexes are ineffective for transmetalation. Perhaps a 1st row metal, such as Cu or Ni, may be a more appropriate reagent for CBA ligand transfer due to their more labile metal-ligand bonds.

Cyclic bent allenes and carbodiphosphoranes were also shown to yield highly sensitive and fragile 3-coordinate complexes of Fe. The incorporation of such ligands into chelated systems is likely necessary to improve their stability if they are to be investigated for any catalytic reactions.

The first example of a carbodicyclopropenylidene was synthesized, and its first coordination complexes were prepared. While this derivative, tetraphenylcarbodicyclopropenylidene, is highly sensitive and fleeting in free
form, we predict that the tetraamino analogue should be more stable, due to the stabilization of the LUMO of the carbodicyclopropenylidene by the donor amino groups, and also should also be more electron donating. This ligand is of great interest as a potential spectator ligand in catalysis. Current efforts are focused on the synthesis and exploration of the coordination chemistry of this species.