Ir and Rh Complexes of Under-explored N-Heterocyclic Carbenes:

Synthesis, Mechanism, Dynamics, and Catalysis

by

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Abstract

In this dissertation, my aim is to study different type of under-explored N-Heterocyclic Carbenes (NHC) complexes of Ir and Rh. These complexes have been synthesized, and the reaction mechanism, solution dynamics, and catalytic activity studies are presented in this dissertation.

In Chapter 2 shows that phosphine-tethered imidazolium ions can undergo C-H oxidative addition when treated with [Ir(COD)Cl]_2 to give abnormal iridium(III) NHC hydrides. The effects of the length of the linker, the kinetic studies of C-H activation and catalytic application of these complexes are systematically studied.

Chapter 3 describes the synthesis of iridium and rhodium complexes stabilized by 2-methyleneimidazoline ligands via highly selective intramolecular activation of 2-methyl C-H vs C4/5-H bonds of the imidazolium moieties with the chelation assistance of phosphine ligands. The selectivity of C(sp^3)-H vs C(sp^2)-H activation, the conversion of methyleneimidazoline to abnormal complex and the electronic properties of ligands are also presented.

Chapter 4 shows that the preparation of rhodium and iridium complexes of a new type of abnormal NHCs derived from imidazol[1,2-a]pyridiniums via silver transmetalation. The donating and π-back donation abilities of these new NHC ligands are systematically studied by VT NMR and CO stretching frequency.

Chapter 5 shows that a series of iridium(III) hydride complexes of chelating pyridine-based N-heterocyclic carbenes (py-NHCs) and remote N-heterocyclic carbenes (remote py-NHCs) could be synthesized as from the C-H oxidative addition reactions of
pyridine-tethered pyridinium halides and [Ir(COD)₂⁺]. X-ray crystal studies, catalytic application in transfer hydrogenation of ketone and enones and Computational studies of the donor capacity of those ligands are also described in this chapter.

In chapter 6, we discuss rather rare Ir(I)-induced tautomerization of a pyridine moiety in 2,3-bipyridyls to a carbene. The experimental data indicate that the H-bondings play crucial roles in not only stabilizing the NH tautomers but also accelerating the hydrogen migration process.
Acknowledgement

It is really an arduous work for me to summarize all the work I have done in the past two years and finish this Ph.D. thesis. It is my friends, mentors and families who have been standing behind me, supporting me. I have never worked alone. Taking this opportunity, I would like to express my thanks to those who have helped me in my experiment and life, to those who have made my study in Nanyang Technological University an indelible experience.

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<td>NHC</td>
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</tr>
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<td>$O$</td>
<td>Ortho</td>
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<tr>
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<td>Py</td>
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</tr>
<tr>
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<tr>
<td>R</td>
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<tr>
<td>Abbreviation</td>
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<td>--------------</td>
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<td></td>
</tr>
<tr>
<td>RT</td>
<td>room temperature</td>
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</tr>
<tr>
<td>S</td>
<td>second, singlet</td>
<td></td>
</tr>
<tr>
<td>Sept</td>
<td>Septet</td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>Triplet</td>
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</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
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</tr>
<tr>
<td>TMS</td>
<td>Trimethylsilane</td>
<td></td>
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<tr>
<td>$\gamma_{1/2}$</td>
<td>half-peak-width</td>
<td></td>
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<tr>
<td>X</td>
<td>halogen, anionic two electron donors</td>
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</table>
Chapter 1. Introduction

1.1 Thesis Prospectus

Different types of under-explored N-Heterocyclic Carbenes (NHC) complexes of Ir and Rh have been synthesized, and the reaction mechanism, solution dynamics, and catalytic activity studies are presented in this dissertation.

Chapter 2 shows that phosphine-tethered imidazolium ions can undergo C-H oxidative addition of the backbone C4/5-H bonds when treated with [Ir(COD)Cl]2 to give iridium(III) abnormal NHC hydrides. The effects of the length of the linker between the imidazolium and the phosphine units are systematically studied. These C-H activation products can further undergo base-promoted H-Cl reductive elimination to afford the corresponding Ir(I) abnormal NHC complexes.

Chapter 3 describes the synthesis of iridium and rhodium complexes stabilized by 2-methyleneimidazoline ligands via highly selective intramolecular activation of 2-methyl C-H vs C4/5-H bonds of the imidazolium moieties with the chelation assistance of phosphine ligands. The selectivity of aliphatic C(sp3)-H vs aromatic C(sp2)-H activation could be adjusted by the steric bulk of the OR ligand. Experimental results also confirmed that a 7-membered iridium C(sp3)-H activation product is the kinetic product while the 6-membered iridium abnormal carbene product, resulting from the activation of a C(sp2)-H bond, is the thermodynamic product.

Chapter 4 shows that the preparation of rhodium and iridium complexes of a new type of abnormal NHCs derived from imidazol[1,2-α]pyridiniums via silver transmetalation. The donating abilities of these new NHC ligands have been accessed by
Chapter 1

analyzing the average CO stretching frequencies of their corresponding iridium dicarbonyl complexes. Both VT NMR studies and CO stretching frequency values support significant \( \pi \)-back donation to an abnormal NHC derived from imidazol[1,2-\( a \)]quinoline.

Chapter 5 shows that a series of iridium(III) hydride complexes of chelating pyridine-based N-heterocyclic carbenes (py-NHCs) and remote N-heterocyclic carbenes (remote py-NHCs) could be synthesized as stable products from the C-H oxidative addition reactions of pyridine-tethered pyridinium halides and \([\text{Ir}(\text{COD})_2]^+\). X-ray crystal structures of representative iridium py-NHC and remote py-NHC complexes were determined and in all cases mutual \( cis \) orientations of the halide and hydride ligands were observed in the solid state. Iridium(III) py-NHC hydride complexes have shown high catalytic activity in transfer hydrogenation of ketone and enones. Computational studies of the donor capacity of those ligands indicate that py-NHCs are more donating than imidazole-derived NHCs.

In chapter 6, we discuss rather rare Ir(I)-induced tautomerization of a pyridine moiety in 2,3-bipyridyls to a carbene. The NH carbene tautomer is both stabilized by the chelation effect and by intramolecular hydrogen bonding. The experimental data indicate that the H-bondings play crucial roles in not only stabilizing the NH tautomers but also accelerating the hydrogen migration process.

1.2 N-Heterocyclic Carbenes (NHC)

In the past decade, major advances have focused on the development of electron-rich ligands of late transition metal complexes for various challenges in catalysis, in particular in C-C bond formation.\(^1\) The role of these ligands likely lies in their donating character to
stabilize the Lewis acidic nature of transition metals. In addition, the labilizing ability of these ligands tends to facilitate the rate-limiting steps. Among them, neutral carbon ligands today compete with the numerous types of phosphorus and nitrogen ligands.²

For a long time, as neutral carbon species, carbenes with a divalent carbon atom bearing six valence electrons were considered to be too reactive to be isolated. Metal carbenes have been either classified as Fischer or Schrock carbenes, depending on the oxidation state of the metal.³ Since the introduction of N-heterocyclic carbene complexes, this classification needs to be extended because of the very different electronic character of these ligands.

N-heterocyclic carbenes (NHCs), singlet carbenes which are incorporated in a nitrogen-containing heterocycle, were first investigated by Wanzlick in the early 1960s.⁴ Since the report of the extraordinary stability, isolation and storability of imidazole-based free carbene by Arduengo et al in 1991,⁵ N-heterocyclic carbenes have become powerful C-based ligands to stabilize transition metals in organometallic chemistry and in catalysis.

(eq 1.1)

\[
\begin{align*}
\text{Cl}^- & \quad \text{NaH, DMSO (cata)} \\
\text{MeOH} & \quad \rightarrow \\
\text{H}_2 + \text{NaCl}
\end{align*}
\]

In many cases, metal NHC system provided extraordinary high catalytic activity, often superior to that of ubiquitous phosphines analogous in homogeneous reaction.⁶ The high activities of NHC complexes have been attributed to the strong metal-carbene bonds⁷ and strong σ-donating ability of carbene.⁷ NHC complexes have been key for the
development of a number of applications in catalysis.

As a type of electron-rich carbon-centered neutral donors, NHCs on various platforms and with different substitutes have been reported to demonstrate their tunability in terms of electronic and steric effects. They are not limited to sterically hindered unsaturated Arduengo-type imidazolylidenes (Figure 1.1, A), also 1,2,4-triazolin-5-ylidenes (B), saturated imidazolidin-2-ylidenes (C), tetrahydropyrimid-2-ylidenes (D), acyclic structures (E), systems with larger ring sizes (F), constrained geometry (G) or containing other heteroatom in the cycle (H, I). Pioneering work by Bertrand and others evidenced that singlet carbenes may be isolated also with less pronounced heteroatom stabilization (J, K and L). Reviews of the different synthetic routes from different precursors can be found in the literature.
Synthetic Methods for NHC Complexes.

Unlike phosphines, the coordination of NHCs to metal centers requires the activation or deprotonation of a precursor, which makes NHC-based complexes relatively less accessible than the analogous phosphine compounds. Several activation strategies have been used to prepare NHC-metal complexes: 1) generation of a free carbene by deprotonation of the corresponding imidazolium precursor using a strong base (for example, NaH, KO'Bu, "BuLi) followed by addition to the metal fragment;\textsuperscript{16} 2) transmetalation from a silver–NHC complex prepared from the reaction of an imidazolium precursor and Ag₂O or Ag₂CO₃;\textsuperscript{17} 3) Direct metallation in the reaction of a precursor and basic metal sources such as Pd(OAc)₂\textsuperscript{18}, Pt(acac)₂\textsuperscript{19} or Cp*Ni(acac)\textsuperscript{20}; 4) oxidative addition by activation of the C-X (X=Me, I, H) bond of an imidazolium cation;\textsuperscript{21-22} 5) insertion of a metal into the C=C bond of bis(imidazolidin-2-ylidene)-containing olefins\textsuperscript{23} (Lappert method). (Scheme 1.1)

\begin{center}
\textbf{Scheme 1.1} Pathways for synthesis of NHC metal complexes\textsuperscript{6d}
\end{center}
1.3 Abnormal N-Heterocyclic Carbenes

In general, the NHC complexes can be synthesized by metalation of imidazolium ligands at the C2 carbon due to the high acidity of C2-H. Recent reports have indicated that the metalation at C4 can result in the formation of another binding mode of such carbenes.\textsuperscript{24} This bonding mode provides access to a new type of NHC ligands, in which no canonical resonance form can be drawn without introducing additional charge, and therefore, it was named abnormal NHCs.(Scheme 1.2) Abnormal NHCs could offer useful variants in terms of electronic and steric effects. Crabtree and co-workers have shown that NHCs in this mode are more donating than the most donating neutral ligands such as \(\text{P}^\text{Bu}_3\) and the normal NHCs.\textsuperscript{25} It has been confirmed that abnormal NHC complexes are more active in catalyzing C-C bond coupling and hydrogenation reactions than a normal analogue.\textsuperscript{26}

![Scheme 1.2 Normal and abnormal NHC complexes](image)

Similar to other carbenes that lack extensive heteroatom stabilization, such as pyridylidenes, free C4 carbenes display lower stability than their crystallographically characterized C2 counterparts.\textsuperscript{3} Energy decomposition analysis predicts that the C2 carbene (M) is about 19.1 kcal/mol more stable than C4 carbene (N).\textsuperscript{27} (Scheme 1.2)
1.3.1 Reactivity of CH on NHC Backbone

By the computational studies, the pKₐ values of C2-H and C4-H protons of imidazolium are 24.9 and 33.0, respectively. Although less acidic than C2, the chlorination of C4/5 position in C2 imidazolidene can be achieved under mild conditions using CCl₄ in THF (eq 1.2). The protons (C4 and C5) in C2 imidazolidene also could undergo rapid H/D exchange in DMSO-d₆, D₂O, or CD₃OD.Indeed, the lability of the C4-H bond in C2 imidazolidene could be used for the formation of C4-bound abnormal NHC metal complexes, such as copper, iron and Ru (eq 1.3). The increasing number of metal complexes obtained by this route indicates a potential utility of this method. However, only little the mechanistic details for this procedure have been uncovered. In some case, steric factors derived from the bulky substituent (R) play important roles in the formation of abnormal NHC complexes.

1.3.2 Synthesis and Structures of Abnormal NHC Complexes

In the last few years, owing to their unique structures and properties, various abnormal NHC complexes have received increasing attentions and the synthetic methods have also been developed.
1.3.2.1 Direct metallation via C-H Activation

C-H activation is direct method for formation of normal and abnormal NHC complexes and the chemical selectivity for C2-H or C4-H is an important issue. Although the common metalation of the imidazolium salts takes place through the C2 atom due to the higher acidity of its H atom, the abnormal NHC complexes resulting from metalation at C4 could also obtained with facilitation by chelate and steric effects, in some particular cases via C-H activation.

Crabtree and co-workers have investigated the reaction of the iridium polyhydride precursor IrH5(PPh3)2 and pyridine-tethered imidazolium salts, resulting in metallation at the C4 position to form abnormal NHC complexes.33 (Scheme 1.3) Variations in the imidazolium precursors, in particular modification of the nitrogen substituent R and the counteranion X− revealed a delicate distribution between C2 and C4 metallation (Table 1.1).

![Scheme 1.3]

**Table 1.1** C4 vs. C2–bound Ir complex as a function of counteranion X− and substituent R

<table>
<thead>
<tr>
<th>R</th>
<th>X</th>
<th>Abnormal : Normal</th>
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<td>9 : 91</td>
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Sterically demanding substituents at nitrogen (R = ‘Pr) give rise to predominantly C4 metallation due to spatial interference between the substituent R and the metal-bound phosphine PPh₃. In addition, different pathways have been suggested for the activation of C2-H and the C4-H bonds. It has been proposed that the C2-H bond is cleaved heterolytically, while C4-H bond activation has been calculated to proceed via an oxidative addition pathway.³³b Heterolytic bond cleavage will be favored with small and coordinating anions, such as bromide that can engage in hydrogen bonding to assist the polarization scission. By contrast, oxidative addition will be preferred with non-coordinating and apolar anions, such as BF₄⁻ and SbF₆⁻. In these cases, these pathways are critically dependent on the nature of the counteranion X⁻ of the imidazolium salt.

Esteruelas and Oliván have also described the formation of abnormal Os NHC complexes in the reaction of the pyridine-tethered imidazolium salts and OsH₆(PPr₃)₂.³⁴

In 2004, Nolan and coworker revealed that the metallation of IMes·HCl (N,N-bis(2,4,6- trimethylphenyl) imidazolium chloride) with palladium (II) acetate yielded a monomeric Pd complex supported by normal and abnormal NHC ligands (eq 1.4).²⁶ It appears that the formation of a mono normal NHC–Pd complex is followed by insertion into the C4–H bond of a second imidazolium salt. The bulky N substituent (mesityl) may dominate the formation of abnormal NHC due to steric bulkness. It should be noted that this palladium abnormal NHC complex is more active in catalyzing Suzuki and Heck reactions than a normal analogue.²⁶
1.3.2.2 Protection strategy

Possibly due to the low acidity of the C4-H, the abnormal binding mode of NHCs is rare, and the synthesis of abnormal NHCs remains a challenge. In general, protection of the C2 position by an alkyl or aryl group is required, a methodology first developed by Crabtree and co-workers,25 and has been extended for the preparation of different abnormal NHC including mono and dicarbene complexes.

Transmetallation

Silver carbene complexes have been shown to be useful carbene transfer agents for C2-bound NHC systems, and a transmetallation protocol has also been devised for the introduction of iridium(I) at the C4 position.25,35,36 The tetrasubstituted imidazolium salt with phenyl group at C2 has been metallated with Ag2O, followed by in situ transmetallation to [Ir(COD)Cl]2, thus affording the stable iridium carbene complex25 (eq 1.5).

Other abnormal NHC systems, such as imidazol[1,2-\(\alpha\)]pyridine35, imidazo[1,5-\(\alpha\)]pyridine,36 could also afford abnormal NHC complexes following by this method.
\textit{C-H Activation}

Recently, Albrecht and co-workers have studied the diimidazolium salt systems with methyl group at C2 positions. Metallation of diimidazolium salts with Pd(OAc)$_2$ or with a suitable rhodium precursor proceeded to afford abnormal NHC Pd and Rh complexes, respectively\textsuperscript{37,38} (Scheme 1.4). These results illustrate the potential of this C4-H bond activation methodology for preparing a broad range of transition metal complexes containing C4-bound carbene ligands.

![Scheme 1.4](image)

However, when a bisimidazolium salt with a methylene linker was metallated with [IrCp*Cl$_2$]$_2$ in the presence of NaOAc, both C-H bonds of the 2-methyl group ($sp^3$-H) and the C4 ($sp^2$-H) could also be activated to give a carbodicarbene-abnormal NHC Ir complex\textsuperscript{39}. Moving from a methylene linker to an ethylene one, C($sp^3$)-H bond activation would be suppressed, and at least three products could be obtained, which may be resulted from the increase of the flexibility and the distance between the two donor moieties\textsuperscript{39} (Scheme 1.5).
1.3.2.3 Oxidative addition of C-X bond

C-halide bond activation by Pd(0) is a useful strategy for the preparation of Pd complexes, which could also be used for synthesis the abnormal NHC complexes when a halide is located at C4 position of imidazolium.

A bidentate system containing 4-iodoimidazole has recently been used for preparation of abnormal NHC palladium complexes by oxidative addition in the presence of Pd (0). Variable-temperature analyses indicated that the C4-bonding mode is thermo-stable up to 100 °C.\textsuperscript{22} (Scheme 1.6)
1.4 NHCs Tautomerization

N-H tautomer of pyridine, an N-heterocyclic carbene (NHC), first proposed 70 years ago,\textsuperscript{40} was generated in the gas phase by mass spectrometry.\textsuperscript{41} Theoretical calculations have shown that the N-H tautomer lies 45-50 and 28.5 kcal/mol higher than the C-H tautomer for pyridine and imidazole in energy, respectively (Scheme 1.7).\textsuperscript{41} In many cases, transition metals have remarkable ability to mediate organic moieties, which allows reactions that are otherwise thermodynamically and kinetically unfavorable. Despite the possible stabilization of carbene tautomer by transition metals, experimental examples of metal-mediated pyridine or imidazole tautomerization have not been reported until very recently.\textsuperscript{42}

\begin{center}
\begin{tikzpicture}
  \node (a) at (0,0) {\chemfig{\text{H} / / / / / / / / / / \text{N}}};
  \node (b) at (1,0) {\chemfig{\text{N} / / / / / / / / / / \text{H}}};
  \node (c) at (2,0) {\chemfig{\text{H} / / / / / / / / / / \text{N}}};
  \node (d) at (3,0) {\chemfig{\text{N} / / / / / / / / / / \text{H}}};
  \draw[->, >=latex] (a) -- (b) node[midway, above] {1,2-shift};
  \draw[->, >=latex] (b) -- (c) node[midway, above] {1,2-shift};
  \draw[->, >=latex] (c) -- (d) node[midway, above] {1,2-shift};
  \draw[->, >=latex] (d) -- (a) node[midway, above] {1,2-shift};
  \node (e) at (1.5,-1) {45-50 kcal/mol};
  \node (f) at (2.5,-1) {28.5 kcal/mol};
  \node (g) at (2.75,-2) {R = Me};
\end{tikzpicture}
\end{center}

\textbf{Scheme 1.7}

1.4.1 Monodentate System

\textit{Tautomerization of Pyridine}

Poveda, Carmona and coworkers reported the reaction of 2-substituted pyridines (R = Me, Ph) and [TpMe\textsubscript{2}IrPh\textsubscript{3}(N\textsubscript{2})] (TpMe\textsubscript{2} = hydrotris(3,5-dimethylpyrazolyl)borate)\textsuperscript{43} (Scheme 1.8). In wet benzene, this reaction yields the tautomerization complexes when 2-phenylpyridine is employed. In the case of 2-picoline, the N-bound complex could also
be isolated, which can tautomerize to the C-bound complex at 90 °C. These results suggested that steric effects and the H-bonding play important roles in the procedure of tautomerization. The tautomerization process of 2,2′-bipyridine and 1,10-phenanthroline were also achieved when induced by the appropriate Ir resources.44.

At the same time, Esteruelas and coworkers treated OsCl₂H₂(P’Pr₃)₂ or RuCl₂H₂(P’Pr₃)₂ with quinoline and 8-methylquinoline in toluene to obtain the Os and Ru NH tautomer complexes45 (Scheme 1.9). DFT calculations on a model system indicated that a weak hydrogen bond between Cl and NH plays an important role in stabilizing the carbene tautomer.45a

**Scheme 1.8**

![Scheme 1.8](image)

**Scheme 1.9**

**Tautomerization of imidazole**

Based on computational studies, Crabtree and Eisenstein have predicted C-bound
imidazoles are to be thermodynamically more stable than the conventional N-bound forms for several second- and third-row transition metals. Later, several experimental evidences have supported this proposal.

Li and coworkers described the synthesis of a rare Ir-NHC complex with a hydrogen wing tip via C-N bond cleavage. The C-bound to N-bound tautomerization of this carbene can’t be achieved in this neutral 18-electron Ir(III) complex. Chloride abstraction in MeCN afforded an NHC-acetimidamide complex, where the C-bound to N-bound tautomerization of this carbene was observed in CDCl₃ at 110 °C as decomposition product (Scheme 1.10).

Recent work has also shown that Ru C-bound imidazole tautomer could be synthesized by C-N activation using a free NHC ligand and Ru(PPh₃)₃(CO)HCl. The transformation of the resultant C-bound Ru complex to N-bound complex, needs a free NHC ligand, which is consistent with a base-catalyzed process. (Scheme 1.11)

Mechanism and Applications

Bergman and Ellman have presented the proposed mechanism of C-H activation of
3-methyl-3,4-dihydroquinazoline by (PCy$_3$)$_2$RhCl$_4$ (Scheme 1.12). An N-bound complex was identified along the path to the Rh \textit{N}-heterocyclic carbene product (C-bound complex) in this reaction. Experimental and computational studies suggest that the rate-limiting step is oxidative addition of the C-H bond to the metal center. A directed intramolecular hydrogen migration pathway proceeding \textit{via} Rh-H intermediates was proposed in the mechanism.$^{49}$

Based on this mechanism, the scope of heterocycle \textit{ortho}-alkylation has been dramatically expanded to pyridines and quinolines, which contain only one nitrogen$^{50}$ (eq 1.6). The reactions are conducted at a high concentration (0.8 M) with 1 mol\% Rh loadings. Substitution \textit{ortho} to the heterocycle ring nitrogen is required for efficient alkylation and is consistent with the intermediacy of a C-bound NH tautomer intermediate.

1.4.2 Bidentate System

Since C-H activation is the rate-limiting step in the tautomerization procedure,$^{49}$ bidentate systems could be considered to achieve the process of tautomerization, where a
C-H bond could be activated assisted by the chelation effect.

Treatment of [RuCp*Cl]₄ with N-(2-pyridyl)benzimidazole led to tautomerization of the imidazole, giving the C,N-chelating N-H tautomer complex. In the presence of silver nitrite, the NH tautomer could convert to a nitrosyl-imidazolyl complex, which undergoes reversible protonation to afford the NHC complex.⁵¹ (Scheme 1.13).

Furthermore, the NH tautomer complex also catalyzes the dehydrative condensation of N-(2-pyridyl)benzimidazole and allyl alcohol, leading to the formation of trans- and cis-2-(1-propenyl)-N-(2-pyridyl)benzimidazole.⁵¹ (eq 1.7)

Recent work on the tautomerization of phosphine-functionalized imidazole and [IrCp*Cl₂]₂ revealed that NH-bearing NHC complex could be used as bifunctional ambident reactants due to their unique structure in organometallic chemistry. The NH group of NHC complex could be deprotonated to give a neutral product, from which loss of chloride ion in the presence of silver salts activates the H–H bond of dihydrogen or the C–H bond of acetylene, forming an Ir(III) N-heterocyclic carbene (NHC) complex⁵² (Scheme 1.14). These results highlight new transformations made possible in an NHC complex by the presence of an NH group, as well as reactivity of a conjugate base at the
free heterocyclic nitrogen.

Scheme 1.14

1.5 Other carbon-centered carbenes

1.5.1 Pyridine-based NHC

Abnormal imidazolium NHC provides a binding mode in which the carbene carbon is stabilized by only one nitrogen atom. Pyridinium NHCs derived from the deprotonation of pyridiniums at the 2-position have analogous bond mode. Previous experimental and theory studies have revealed that pyridine-based NHCs (py-NHCs) are generally stronger \( \sigma \)-donors and \( \pi \)-acceptors than the more common imidazole-2-ylidenes.\(^{53}\) More recently, remote N-heterocyclic carbenes derived from pyidine\(^{54}\), quinoline\(^{55}\) or pyrazoline\(^{56}\) where the heteroatom is distal to the carbene carbon (Scheme 1.15), have also received increasing attentions owing to their unique structures and properties.

Scheme 1.15

Raubenheimer \textit{et al} have reported various py-NHC and remote py-NHC derived from
different pyridinium precursors via C-halogen oxidative addition reactions using low valent transition metals.\textsuperscript{54,55} Bercaw and coworkers also prepared a series of py-NHC complexes of Pt\textsuperscript{57a}, Pd\textsuperscript{57b} and Ni\textsuperscript{57b} via intramolecular C-H activation using pyridine tethered pyridinium as precursors. (Scheme 1.16)

\begin{center}
\textbf{Scheme 1.16}
\end{center}

\subsection*{1.5.2 NHC-Phosphonium Ylide Ligands}

As neutral spectator carbon-centered ligands, phosphonium ylides have been represented recently and the catalytic properties of these saturated \textit{sp\textsuperscript{3}-C} ligands have been more illustrated.\textsuperscript{58} Recently, the coordinating properties of the NHC and phosphonium ylide ligand types have been investigated through C,C-chelating ligands containing NHC and phosphonium ylide moieties.\textsuperscript{59} (Scheme 1.17)

\begin{center}
\textbf{Scheme 1.17}
\end{center}

A comparisons of IR spectra of Rh(CO)\textsubscript{2}L type complexes indicated that the bis-NHC ligand is less donating than the hybrid NHC-phosphonium ylide ligand type, which demonstrated that a phosphonium ylide ligand is a stronger donor than a typical NHC ligand.\textsuperscript{59}
1.5.3 Carbodicarbenes

Previous research have reported synthesis and structural characterization of carbodiphosphoranes, in which two donor ligands PR₃ coordinate to a carbon(0) atom (Figure 1.2). Alternatively, a heterocumulene R₃P=C=PR₃ resonance structure and the description as a carbenoid species are possible.⁶⁰

Substitution of the phosphine substituents at the carbon atom of carbodiphosphoranes by NHCs leads to compounds with a carbon(0) atom that is formally stabilized by two NHC-C bonds, named carbodicarbenes (Figure 1.2). Theoretical studies proposed that carbodicarbenes should be experimentally accessible and should have interesting properties.⁶¹

![Figure 1.2](image-url)

Bertrand et al. selected benzimidazolin-2-ylidene as donor group for bent allenes and synthesized a bent acyclic allene (a carbodicarbene) after deprotonation by KHMDS.⁶² The X-ray structure analysis shows that the C-C-C angle is 134.8°, which is in good agreement with the calculation values (125.8°).⁶¹ (Scheme 1.18) The carbonyl stretching vibrations in [RhCl(CO)₂L] complexes demonstrate that the carbodicarbene is a stronger σ donor and weaker π acceptor than N-heterocyclic or acyclic diaminocarbenes.
2-methyleneimidazoline, an electron-rich olefin containing strongly polarized double bonds, is another type carbene-centered carbene, which could be synthesized by deprotonation of 2-methylimidazolium salts by strong bases. Kuhn et al. reported for the first time that 2-methyleneimidazoline can act as an ylidic olefin towards transition metals.\textsuperscript{53} Fürstner et al. isolated 1,3-dimethyl-2-methyleneimidazoline which could react with [Au(PPh\textsubscript{3})Cl] and Rh(CO)\textsubscript{2}Cl to yield gold and rhodium complexes, respectively.\textsuperscript{64} (Scheme 1.19). The carbodicarbene in Rh complex acts as a very strong σ donor with a donor strength comparable to the cyclic carbodiphosphoranes.

Base treatment of di(2-methylimidazolium salts) with [IrCp\textsuperscript{*}Cl\textsubscript{2}]\textsubscript{2} could also afford 2-methyleneimidazoline complexes.\textsuperscript{39} (Scheme 1.5)
1.6 Conclusion

The distinctive $\sigma$-donating character of carbon-centered ligands are undoubtedly relevant to their increasingly important roles in homogeneous catalysis and major advances have been focused on the development of electron-rich ligands of late transition metal complexes. Although the normal N-heterocyclic carbenes have been extensively studied, examples of abnormal NHC, tautomerization, pyridine-NHC and carbodicarbene are still rare due to synthetic challenges. The exploration of these rare bonding complexes will provide us with opportunities to understand the process of conversion in organometallic chemistry and develop new type strong ligands for late transition metal complexes for organic synthesis.
1.7 References


(39) Viciano, M.; Feliz, M.; Corberán, R.; Mata, J. A. Clot, E.; Peris, E. *Organometallics*
2007, 26, 5304.


(42) For a review, see Kunz, D. *Angew. Chem.; Int. Ed.* 2007, 46, 3405.


Chapter 2. Iridium Abnormal N-Heterocyclic Carbene Hydrides via Highly Selective C-H Activation

2.1 Introduction

N-Heterocyclic carbenes (NHCs) have become increasingly powerful ligands in organometallic chemistry and catalysis ever since the isolation of free NHCs by Arduengo and co-workers.\(^1\) In many cases metal NHC complexes are highly robust and active in homogeneous catalysis.\(^2\)–\(^4\) Several general methods have been utilized for the preparation of transition metal NHC complexes.\(^5\) These methods include metalation of free NHCs,\(^6\) transmetalation from silver carbene complexes,\(^7\) insertion of a metal into the C=C bond of an electron-rich olefin such as a bis(imidazolidin-2-ylidene),\(^8\) metalation of carbenes generated in situ by the deportation of carbene precursors using weak bases,\(^9\) and oxidative addition of C-X (X = H, halogen, and C) bonds of imidazoliums.\(^10\),\(^11\)

\[
\begin{align*}
\text{R} & \quad \text{base} \\
\text{N} & \quad \text{N} \\
\text{4} & \quad \text{4} \\
\text{5} & \quad \text{5} \\
\text{C(4) or C(5)} & \quad \text{C(2)} \\
\text{NHC complexes} & \quad \text{NHC complexes}
\end{align*}
\]

Despite the large number of NHC complexes reported, it is still necessary to prepare NHCs with tunable electronic and steric properties. In this regard, abnormal NHCs could offer useful variants in terms of electronic and steric effects. It has been recently shown that under certain conditions metalation can take place at the C(4) or C(5) position of an imidazolium rather than at the normal C(2) position (eq 2.1).\(^12\)–\(^16\) The zwitterion in this binding mode can be treated as an “abnormal” NHC. The rarity of this binding mode of NHCs is possibly due to the low acidity of the C(4/5)-H. So far most of the abnormal NHCs are part of chelating systems if the active C(2) positions are left unblocked. Crabtree and co-workers have shown that NHCs in this mode are more donating than the most donating neutral ligands such as P^3Bu\(_3\) and the normal NHCs.\(^14\) Nolan has reported that a palladium abnormal NHC complex is more active in catalyzing Suzuki and Heck reactions than a normal analogue.\(^15\)
This work will report the synthesis of a series of stable iridium hydrides with abnormal NHCs via highly selective cyclometalation of imidazoliums without any necessity to block the C(2) positions.

2.2 Results and Discussion

It has been recently reported that NHC-directed C-H activation of imidazoliums can take place to afford biscarbene hydride complexes.\textsuperscript{11a,b} We reason that phosphine-directed C-H activation of imidazoliums should also readily occur at low valence metal center such as an Ir(I). To the best of our knowledge, there is no report on well-characterized phosphine-directed C-H oxidative addition of imidazoliums, although many chelating phosphine-NHC complexes have been recently reported.\textsuperscript{9d,17–19}

2.2.1 Synthesis of ligand precursors

The phosphine-tethered imidazolium ligands were synthesized based on Scheme 2.1. Compound 1 with a methylene linker between the imidazolium and the phosphorus was synthesized following a reported procedure.\textsuperscript{17a} Alkylation of 1-\textit{iso}-propylimidazole by (chloromethyl)diphenylphosphine oxide followed by reduction of the P=O bond gave imidazolium chloride 1-Cl in 50 % overall yield. Exchange of the chloride in 1 by using an excess amount of KPF\textsubscript{6} in acetone or acetonitrile readily afforded complex 1-PF\textsubscript{6}. Compounds 2 and 10 with an ethylene linker were prepared following the modification of known procedures using neat dichloroethane under reflux instead of dibromoethane for the monoalkylation of imidazoles.\textsuperscript{9d,17b,18a} This alkylation method proved more selective and took a short reaction time compared to that using CH\textsubscript{2}Br-CH\textsubscript{2}Br, which has to be performed at room temperature for a prolonged reaction time. Phosphination of these alkylation products gave compounds 2-Cl and 10-Cl, which can be subsequently transferred to their PF\textsubscript{6} salts 2-PF\textsubscript{6} and 10-PF\textsubscript{6} by anion exchange with overall yields ranging from 75% to 87%. Analogously, carbene precursor 3 with a propylene linker was synthesized in 88% yield without the isolation of the chloride salt after the phosphination.\textsuperscript{9d}
Scheme 2.1. Synthesis of phosphine-tethered imidazoliums

1-oxide

1-Cl

1-PF₆

2a-(Cl): R₁ = Me, R₂ = H
2b-(Cl): R₁ = iPr, R₂ = H
2c-(Cl): R₁ = R₂ = Me

2a-(PF₆): R₁ = Me, R₂ = H
2b-(PF₆): R₁ = iPr, R₂ = H
2c-(PF₆): R₁ = R₂ = Me

10-Cl

10

3

reflux
2.2.2 Methylene Linker System

2.2.2.1 Metalation and Structures

Having these phosphine-tethered imidazoliums in hand, we then used them to react with Ir (I) complexes. Indeed, stirring a CD$_2$Cl$_2$ solution of 1-(PF$_6$) and 0.5 equiv of [Ir(COD)Cl]$_2$ instantaneously gave Ir(I) phosphine 4 (Scheme 2.2), which decayed cleanly to give iridium(III) hydride 5 (99% NMR yield and 92% isolated yield). Complex 5 can also be synthesized with a similar yield by reacting ligand 1-(Cl) with [Ir(COD)$_2$]PF$_6$. In the $^1$H NMR spectrum (CD$_2$Cl$_2$) of 5, the hydride resonates at $\delta$ -15.81 (d, $^2J_{HP} = 7.5$ Hz) and this small coupling constant here suggests the cis orientation of the hydride and the phosphine. A low-field signal at $\delta$ 8.57 was also observed in the $^1$H NMR spectrum and was ascribed to the C(2)-H of the imidazole ring. In the $^{13}$C-$^1$H NMR spectrum, the Ir-C(4/5) resonates at $\delta$ 135.4 (d, $^2J_{CP} = 5.7$ Hz), comparable to those reported for abnormal NHCs.$^{12-14}$

Scheme 2.2 Synthesis of iridium abnormal complexes 5 and 6

X-ray crystallography confirmed the identity of complex 5 (Figure 2.1 and Table 2.1, 2.2). The hydride is trans to the chloride but cis to the phosphine ligand. The carbene adopts the non-classical binding mode with a Ir-C$_{carbene}$ distance of 2.049(4) Å, comparable to other related systems.$^{13,14}$ The phosphine-tethered imidazolium ligand has a bite angle of 80.9(8) ° and is significantly deviated from 90 ° due to the restraint of a five-membered iridacycle.
Figure 2.1. Molecular structure (ORTEP drawing) of the cation part of complex 5 shown with 50% thermal ellipsoids.

Table 2.1 Selected bond lengths and angles for complexes 5 and 8a-(PF₆)

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<th></th>
<th>5</th>
<th>8a-(PF₆)</th>
</tr>
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<tbody>
<tr>
<td>Ir(1)-C9 (Å)</td>
<td>2.049(4)</td>
<td>2.065(6)</td>
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<tr>
<td>Ir(1)-P(1) (Å)</td>
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<td>2.5076(14)</td>
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<tr>
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<tr>
<td>N(2)-C(9)-Ir(1) (deg)</td>
<td>117.9(3)</td>
<td>126.7(4)</td>
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### Table 2.2 Crystallographic Data for complexes 5 and 8a-(PF₆)

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</table>
Chapter 2

The acidity of complex 5 can be demonstrated by base-promoted reductive elimination of HCl using Cs₂CO₃ in acetone or MeCN (Scheme 2.2). Thus complex 6 was isolated (92%) and was spectroscopically characterized. In the ^1H NMR spectrum (CD₃CN), the C(2)-H resonates at δ 8.51 and the Ir-C_carbene resonates at δ 130.6 (d, ^2J_{PC} = 11.7 Hz) in the ^13C{^1H} NMR spectrum. Base-promoted trans reductive elimination of HCl from Ir(III) biscarbene complexes has been recently reported. Complex 6 can be converted back to 5 when treated with 1 equiv of ethereal HCl in acetone.

2.2.2.2 Kinetic Studies

The clean conversion of 4 to 5 allows kinetic studies of this C-H activation process. The decay of 4 in CDCl₃ follows first order kinetics, consistent with the intramolecularity of this C-H activation process. The rate constants were measured by ^1H NMR spectroscopy at 297.1 K (k = 0.0179 min⁻¹), 302.3 K (k = 0.0306 min⁻¹), 307.6 K (k = 0.0508 min⁻¹), and 312.9 K (k = 0.0847 min⁻¹) (Figure 2.2). The Eyring plot from these data gave activation parameters Δ_H^≠ = 17.4 kcal/mol and Δ_S^≠ = -16 eu (Figure 2.3). The large negative Δ_S^≠ value here indicates a highly ordered transition state, as would be expected in this C-H oxidative addition.

Figure 2.2 The Rate Constants of Decay of 4 on Different Temperature a

![Figure 2.2 Rate Constants of Decay of 4](image)

a The slope of this line is k

Figure 2.3 The Eyring Plot for Activation Parameters of Decay of 4 a
2.2.3 Ethylene Linker Systems

2.2.3.1 Metalation and Structures

Ligands 2a-c-(PF₆ or Cl) with ethylene linker behave analogously to 1-(PF₆) in the reactions with [Ir(COD)Cl]₂ (Scheme 2.3). Complexes 7a-c were also observed as intermediates, leading to the C-H activation products 8a-c. Unlike the analogous complex 4, no complete decay of 7a-c could be observed. Instead, equilibration between complexes 7a-c and 8a-c was reached with oxidative addition products (8a-c) favored in all cases. The $K_{eq}$ is smaller in CD₃CN than in CD₂Cl₂. The mixtures of 7a-c and 8a-c were spectroscopically characterized.

**Scheme 2.3** Synthesis of iridium abnormal complexes 8 and 9
Chapter 2

Complex 8a-(PF$_6$) was further characterized by X-ray crystallography (Figure 2.4, Table 2.1, 2.2). The structure around the iridium can best be described as a distorted octahedron. The Ir(1)-C(9) distance is 2.065(6) Å and is slightly longer than that in 5. The most remarkable difference is probably the bite angle of the phosphine-carbene ligand, which is 92.2(4)$^\circ$ and is considerably larger than that in 5, as can be accommodated by a larger metallacycle. The six-membered iridacycle adopts a boat conformation.

**Figure 2.4** Molecular structure (ORTEP drawing) of the cation part of complex 8a-(PF$_6$) shown with 50% thermal ellipsoids.
2.2.3.2 The Ir(I)-Ir(III) Equilibrium

The effects of temperatures on this equilibrium were studied in CD₃CN, and the van’t Hoff plots of the equilibration systems for 7a-(Cl), 7a-(PF₆), and 7b-(PF₆) gave thermodynamic parameters ΔH° -5.36, -6.96, and -7.15 kcal/mol and ΔS° -13.3, -17.7, and -18.5 cal/(mol · K), respectively (Table 2.3 and Figure 2.5). These data indicate that the steric size of the N-alkyl group has no significant effect on the thermodynamics, while the nature of the counterion does. The large negative value of the ΔS° is consistent with more ordered structures of the products.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>8a-(PF₆)/7a-(PF₆) Kₑq</th>
<th>lnKₑq</th>
<th>8b-(PF₆)/7b-(PF₆) Kₑq</th>
<th>lnKₑq</th>
<th>8a-(Cl)/8b-(Cl) Kₑq</th>
<th>lnKₑq</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.0</td>
<td>15.75</td>
<td>2.757</td>
<td>10.85</td>
<td>2.384</td>
<td></td>
<td></td>
</tr>
<tr>
<td>308.0</td>
<td>10.85</td>
<td>2.384</td>
<td>8.26</td>
<td>2.112</td>
<td></td>
<td></td>
</tr>
<tr>
<td>318.0</td>
<td>7.64</td>
<td>2.034</td>
<td>5.93</td>
<td>1.7814</td>
<td></td>
<td></td>
</tr>
<tr>
<td>323.0</td>
<td>6.11</td>
<td>1.81</td>
<td>5.317</td>
<td>1.671</td>
<td></td>
<td></td>
</tr>
<tr>
<td>328.0</td>
<td>5.20</td>
<td>1.649</td>
<td>4.711</td>
<td>1.55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>330.0</td>
<td>4.63</td>
<td>1.533</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>338.0</td>
<td>3.97</td>
<td>1.378</td>
<td>3.781</td>
<td>1.33</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 2.5 The van’t Hoff Plot of Equilibrium between 7 and 8.

\[ Y = 3498.8X - 8.865 \]  
\[ Y = 3600.4X - 9.3198 \]  
\[ Y = 2699.5X - 6.677 \]

\[ R^2 = 0.9984 \]  
\[ R^2 = 0.9954 \]  
\[ R^2 = 0.9972 \]

\[ a \] The slope of these lines are -ΔH°/R and the intercept is ΔS°/R.
2.2.3.3 NMR Studies of interactions of the anion with proton

Crabtree and co-workers reported that under certain conditions counterions could switch the selectivity of C(2)-H versus C(4/5)-H activation of imidazoliums.\textsuperscript{13} Here C-H activation consistently occurred at the C(4/5) position regardless of the anions (Cl\textsuperscript{-}, PF\textsubscript{6}\textsuperscript{-}, or SbF\textsubscript{6}\textsuperscript{-}). The \textsuperscript{19}F-\textsuperscript{1}H HOESY spectra of both complexes 5 (Figure 2.6) and 8a-(PF\textsubscript{6}) in CD\textsubscript{2}Cl\textsubscript{2} were obtained, and they showed the correlation between the PF\textsubscript{6}\textsuperscript{-} anion and the imidazole C(2)-H, suggesting an ion-paring interaction between these two moieties in solutions.

\textbf{Figure 2.6.} \textsuperscript{19}F,\textsuperscript{1}H-HOESY NMR Spectra (\textsuperscript{19}F, 282 MHz, 298 K, CD\textsubscript{2}Cl\textsubscript{2}) of Complex 5

2.2.3.4 Attempt for C\textsubscript{2}-H Activation

To make the imidazolium C(2)-H activation more favorable, ligand 10 with blocked C(4/5) positions was synthesized and was allowed to react with [Ir(COD)Cl\textsubscript{2}] (Scheme 2.4). Formation of Ir(I) complex 11 was clean and instantaneous, but no cyclometalation product was observed (39 °C, 5 h), nor was there any decomposition. This clearly indicates that our phosphine-tethered imidazoliums system prefers to undergo C(4/5)-H activation. While detailed reasons behind this selectivity remain unclear, the activation of the C(2)-H bond here would be more sterically unfavorable.\textsuperscript{13}
Scheme 2.4

Analogous to complex 5, deprotonation of complex 8a-(PF₆) using Cs₂CO₃ occurred in MeCN to afford 9 (91%) (Scheme 2.3). Field et al. recently reported the synthesis of a related Ir(I) complex with a chelating phosphine-normal NHC ligand via the deprotonation of a phosphine-imidazolium by an internal base (Scheme 2.3). We synthesized complex 12 by directly following this method (Scheme 2.5), where the internal base tert-butoxide reacts preferably with the more acidic C(2)-H. As a comparison, an oxidative addition-base treatment sequence complementarily afforded abnormal NHC complexes 8a-c.

Scheme 2.5 Synthesis of a Related Ir(I) Normal NHC Complex

2.2.4 Propylene Linker System

Ligand 3 (Scheme 2.1) with a propylene linker was allowed to react with [Ir(COD)Cl]₂ (0.5 equiv) in CD₂Cl₂, but no C-H activation occurred and only phosphine coordination was observed together with partial decomposition (39 °C, 5 h). The failure of C-H activation may be due to thermodynamic and/or kinetic reasons, and the ligand is too flexible for the phosphine to exert any chelation assistance (Scheme 2.6).
2.2.5 Catalysis Results

Iridium biscarbene dihalides have been demonstrated as robust catalysts for the ketone transfer hydrogenation,\(^\text{19}\) and Ir(III) monohydrates was also proposed as the active species, a structure related to complexes 5 and 8a-c. We reason that they should also be active in this catalysis. Transfer hydrogenation between acetophenone and \(\text{PrOH}\) proceeded smoothly in the presence of 0.1 mol% of complexes 8a-b-(PF\(_6\)) and 10 mol% NaOH (eq 2.2). Comparisons between complexes 8a-b-(PF\(_6\)), 9, and 12 are displayed in Table 2.5, which shows that complexes 8a-b-(PF\(_6\)) all have similar activity (Table 2.4, entries 1-3). This fact also indicates that complexes 8a-b-(PF\(_6\)) may play their roles through the Ir(I) non-classical NHC complexes in the catalytic cycle since removal of HCl by a strong base is instantaneous and quantitative. Complex 12, however, showed rather low catalytic activity under the same conditions with only 28% yield (entry 4). This great discrepancy may arise from a combination of electronic and steric effects of the non-classical NHCs.

The catalysis was further extended to 8b-(PF\(_6\)) for the transfer hydrogenation of \(\alpha,\beta\)-unsaturated ketones and aldehydes, where chemoselectivity can be an issue. The results in Table 2.4 show that all the substrates examined are exhaustively hydrogenated. Transfer hydrogenation of \(\alpha,\beta\)-unsaturated aldehydes are not as clean, although a nearly full conversion was achieved. Using a weaker base such as Cs\(_2\)CO\(_3\) helped to improve the yield, but only a maximum 68% NMR yield was obtained for cinnamaldehyde. It is obviously possible that the transfer hydrogenation of enones could occur on the C=C bond.

\[
\begin{align*}
\text{Ph}_2\text{P} & \quad \text{BPh}_4^- \\
\text{N} & \quad \text{N} \\
\text{P} & \quad \text{BPh}_4^- \\
\text{Ph}_2\text{P} & \quad \text{BPh}_4^- \\
\end{align*}
\]
first then on the C=O group. To further test whether the other stepwise sequence is possible, we then examined an allylic alcohol. trans-PhCH=CHC(OH)Me can be cleanly hydrogenated under the same reaction conditions (entry 6). These results suggest that the transfer hydrogenation can follow either stepwise sequence and this protocol compliments the reduction of such substrates by NaBH₄ or LiAlH₄, where only the carbonyl group is reduced.

\[
\begin{align*}
\text{C=O} & \quad \text{OH} \\
\text{0.1 mol\% Ir cat.} & \quad \text{5 mol\% KOH} \\
\text{\( ^{1}\text{PrOH, reflux} \)} & \quad \text{(2.2)}
\end{align*}
\]

**Table 2.4** Transfer Hydrogenation of Acetophenone and \( \alpha,\beta \)-Unsaturated Ketones and Aldehydes

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrates</th>
<th>Product</th>
<th>Catalyst (mol%)</th>
<th>Time (h)</th>
<th>Yield (%) c</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PhOPhOH</td>
<td>OH</td>
<td>8a-(PF₆) (0.1)</td>
<td>5</td>
<td>92</td>
</tr>
<tr>
<td>2</td>
<td>PhOPhOH</td>
<td>OH</td>
<td>8b-(PF₆) (0.1)</td>
<td>5</td>
<td>95</td>
</tr>
<tr>
<td>3</td>
<td>OH</td>
<td>OH</td>
<td>9 (0.1)</td>
<td>5</td>
<td>94</td>
</tr>
<tr>
<td>4</td>
<td>OH</td>
<td>OH</td>
<td>12 (0.1)</td>
<td>5</td>
<td>28</td>
</tr>
<tr>
<td>5</td>
<td>OH</td>
<td>OH</td>
<td>8b-(PF₆) (0.5)</td>
<td>4</td>
<td>98</td>
</tr>
<tr>
<td>6</td>
<td>OH</td>
<td>OH</td>
<td>8b-(PF₆) (0.5)</td>
<td>4</td>
<td>95</td>
</tr>
<tr>
<td>7 b</td>
<td>OH</td>
<td>OH</td>
<td>8b-(PF₆) (0.5)</td>
<td>6</td>
<td>68</td>
</tr>
<tr>
<td>9</td>
<td>OH</td>
<td>OH</td>
<td>8b-(PF₆) (0.5)</td>
<td>4</td>
<td>96</td>
</tr>
<tr>
<td>10</td>
<td>OH</td>
<td>OH</td>
<td>8b-(PF₆) (0.5)</td>
<td>3</td>
<td>98</td>
</tr>
<tr>
<td>11 b</td>
<td>OH</td>
<td>OH</td>
<td>8b-(PF₆) (0.5)</td>
<td>2</td>
<td>99</td>
</tr>
</tbody>
</table>

a: \(^{1}\text{PrOH, reflux, 10\% KOH}\)
b: \(^{1}\text{PrOH, reflux, 20 mol\% Cs₂CO₃}\)
c: NMR yield with 1,3,5-trimethoxybenzene as an internal standard.
2.3 Conclusions

We have demonstrated the cyclometalation of imidazoliums with proximal phosphines on iridium(I) complexes such as [Ir(COD)Cl]₂ and Ir(COD)₂PF₆ to afford iridium(III) abnormal NHC hydrides. The linker between the imidazolium and the phosphine has a big effect. Moving from a methylene linker to an ethylene one, cyclometalation is less thermodynamically favorable. The first-order kinetics was measured for the C-H activation for a phosphine-imidazolium with a methylene linker. These cyclometalation products can be deprotonated by Cs₂CO₃ to afford the corresponding Ir(I) complexes. Catalytic applications have shown that both Ir(I) and Ir(III) abnormal NHC complexes are highly active for the transfer hydrogenation of ketones and \( \alpha,\beta \)-unsaturated ketones. These abnormal NHC complex showed higher catalytic activity than the normal analogue in the transfer hydrogenation of acetophenone.
2.4 Experimental Section

General Considerations

All manipulations were performed using standard Schlenk techniques or in a nitrogen-filled glove box. All solvents were distilled under N₂ and were stored in a glove-box (Innovative Technology, PureLab). CDCl₃ was degassed and dried by 4Å molecular sieves. CD₂Cl₂, CD₃CN, and DMSO-d₆ were obtained from Cambridge Isotope Laboratories (CIL) in sealed ampules and were used as received. Air-sensitive chemicals were stored and weighted inside the glove box.

NMR spectra were recorded on Bruker DPX 300 MHz, Bruker AMX 400 MHz or Bruker 500 MHz spectrometers. All spectra were obtained at 298K unless otherwise specified. Temperatures (≥ 290 K) of NMR samples for kinetic and thermodynamic studies were calibrated by using 80% ethylene glycol in DMSO-d₆. The chemical shifts are given as δ values, referenced to tetramethylsilane for ¹H and ¹³C NMR spectroscopy and to 85% H₃PO₄ for ³¹P NMR spectroscopy. Elemental analyses were performed in the Division of Chemistry and Biological Chemistry, Nanyang Technological University. As imidazolium chlorides are highly hygroscopic, their PF₆⁻ salt derivatives were analyzed. HRMS spectra were obtained in ESI or EI mode on a Finnigan MAT95XP GC/HRMS spectrometer (Thermo Electron Corp.). X-ray crystallographic data was collected on a Bruker X8 APEX diffractometer.

**Compound 1-oxide:** Ph₂P(O)CH₂Cl (1 g, 4.0 mmol) and 1-isopropyl-imidazole (450 mg, 4.1 mmol) were charged into a vial, which was sealed and heated at 130 °C for 2 days. The residue was dissolved in dichloromethane (1 mL), followed by addition of diethyl ether (10 ml) to afford a brown solid. The pure 1-oxide could be obtained by successive washing with diethyl ether. Yield: 78 % (1.13 g, 3.1 mmol). ¹H NMR (400 MHz, CDCl₃); δ 10.66 (s, 1H, imidazole H2), 8.11-8.15 (m, 4H, PPh₂), 7.80 (s, 1H, imidazole H4/5), 7.53-7.57 (m, 6H, PPh₂), 7.09 (s, 1H, imidazole H4/5), 5.87 (d, ²J_PH = 5.1 Hz, 2H, N-CH₂), 4.45 (heptet, ³J = 5.4 Hz, 1H, CH of ³Pr), 1.42 (d, ³J = 5.6 Hz, 6H, 2CH₃). ³¹P {¹H} NMR
(161 MHz, CDCl₃): δ 27.73. ¹³C NMR (100 MHz, CDCl₃): δ 136.0 (s, imidazole C2), 133.1 (s, PPh₂), 131.4 (d, JₚC = 10.0 Hz, PPh₂), 129.2 (d, JₚC = 12.4 Hz, PPh₂), 127.6 (d, JₚC = 103 Hz, ipso-PPh₂), 123.7 (s, imidazole C4/5), 119.2 (s, imidazole C4/5), 53.5 (s, CH of 'Pr), 49.1 (d, JₚC = 33.7 Hz, CH₂), 22.9 (s, 2CH₃). HRMS (m/z, ESI⁺): 325.1475; Calcd for [C₁₉H₂₂OPN₂]+: 325.1464.

**Compound 1-Cl:** A mixture of 1-oxide (1.8 g, 5.0 mmol) and chlorobenzene (30 ml) was placed into a glass pressure tube. Trichlorosilane (4 ml, 28.8 mmol) was added to the suspension at room temperature. The mixture was sealed, heated to 120 °C for 3 hour, and cooled to room temperature. After addition of dichloromethane (50 ml), any excess amount of trichlorosilane was quenched by careful addition of degassed aq NaOH solution (10%) at 0 °C. The organic layer was separated by syringe and the aqueous phase was washed with dichloromethane. The organic layers were combined and dried (Na₂SO₄). All volatiles were removed under vacuum and the residue was washed with diethyl ether to give 1-(Cl) as a white hydroscopic solid in 51% yield (880 mg, 2.54 mmol). ¹H NMR (300 MHz, CDCl₃): δ 10.71 (s, 1H, imidazole H2), 7.52-7.58 (m, 4H, PPh₂), 7.38-7.39 (m, 6H, PPh₂), 7.32 (m, 1H, imidazole H4/5), 7.06 (m, 1H, imidazole H4/5), 5.25 (d, 2JₙH = 5.64 Hz, 2H, N-C₇H₅-P), 4.65 (heptet, 1H, J = 6.7 Hz, CH of 'Pr), 1.46 (d, J = 6.7 Hz, 6H, 2CH₃). ³¹P {¹H} NMR (121 MHz, CDCl₃): δ -11.46 (s). No satisfactory microanalysis was obtained for 1-(Cl) due to its hydroscopicity. Instead, satisfactory microanalysis was obtained for the PF₆⁻ salt [1-(PF₆)]⁻.

**Compound 1-(PF₆):** Compound 1-(Cl) (300 mg, 0.868 mmol) was dissolved in acetone (10 mL), to which was added KPF₆ (1.0 g, 5.4 mmol). The mixture was stirred for 12 h followed by removal of all the solvent under reduced pressure. To this residue was added CH₂Cl₂ (15 mL) and all the insolubles were removed by filtration. Removal of all the CH₂Cl₂ gave a white solid and was dried under vacuum to give analytically pure 1-(PF₆). Yield: 98% (387 mg, 0.85 mmol). ¹H NMR (400 MHz, CDCl₃) of 1-(PF₆): δ 8.92 (s, 1H, imidazole H2), 7.80-7.82 (m, 2H, imidazole H4 and H5), 7.45-7.55 (m, 10H, PPh₂), 5.13 (m, 2H, N-CH₂-P), 4.54 (m, 1H, CH of 'Pr), 1.34 (d, 6H, 2CH₃). ³¹P{¹H} NMR (161 MHz, CDCl₃): δ 32.1.
MHz, DMSO-$d_6$): $\delta$ -11.60 (s, PPh$_2$), -144.2 (sept, $J_{PF} = 707$ Hz, PF$_6$). $^{13}$C {$^1$H} NMR (100 MHz, DMSO-$d_6$): $\delta$ 135.0 (s, imidazole C2), 134.0 (d, $J_{PC} = 12.5$ Hz, ipso-PPh$_2$), 133.2 (d, $J_{PC} = 19.3$ Hz, PPh$_2$), 130.5 (d, PPh$_2$), 129.5 (d, $J_{PC} = 6.7$ Hz, PPh$_2$), 123.3 (s, imidazole C4/5), 121.4 (s, imidazole C4/5), 52.8 (s, CH of $^3$Pr ), 47.9 (d, $J_{PC} = 20$ Hz, N-CH$_2$-P), 22.7 (s, CH$_3$). Anal. Calcd for C$_{19}$H$_{22}$F$_6$N$_2$P$_2$ (454.1): C, 50.23; H, 4.88; N, 6.17; Found: C, 50.12; H, 4.62; N, 6.09.

3-(2-chloroethyl)-1-methylimidazolium chloride: 1-methylimidazole (1.0 g, 12.2 mmol) was dissolved in 1,2-dichloroethane (15 ml) and the solution was stirred under reflux for 20 h. 1,2-Dichloroethane was then removed under vacuum and the resulting residue was dissolved in hot acetonitrile (40 mL). Cooling of this solution to -20 °C gave precipitates which were most of the dicationic side product. The precipitates were rapidly removed by filtration while the solution was cold. Removal of acetonitrile of the filtrate gave a colorless viscous liquid which slowly solidified to give a white hygroscopic solid. Yield: 75% (1.65 g, 9.1 mmol). $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 9.31 (s, 1H, imidazole H2), 8.00-8.01 (m, 1H, imidazole H4/5), 7.87-7.88 (m, 1H, imidazole H4/5), 4.61 (t, $^3J = 5.2$ Hz, N-CH$_2$), 4.07 (t, $3J = 5.6$ Hz, Cl-CH$_2$), 3.86 (s, 3H, CH$_3$). $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta$ 137.2 (s, C2), 124.2 (s, C4/5), 122.2 (s, C4/5), 51.4 (s, N-CH$_2$), 43.9 (s, Cl-CH$_2$), 35.8 (s, CH$_3$). HRMS (ESI$^+$): 146.0598. Calcd for [C$_{3}$H$_{10}$Cl$_{5}$N]$^+$ 146.0605.

Compound 2a-(Cl): Potassium diphenylphosphide in THF solution (0.5 M, 10 mL, 5 mmol) was added dropwise to a solution of 3-(2-chloroethyl)-1-methylimidazolium chloride (910 mg, 5 mmol) in DMSO (10 ml). The mixture was stirred at room temperature for 3 hours, followed by removal of DMSO under reduced pressure. Methanol (5 ml) was then added and the mixture was stirred for 20 min followed by removal of all volatiles under vacuum. The residue was then dissolved in dichloromethane (15 mL) and was filtered to remove inorganic salts. All the solvent was then removed under vacuum to afford 2a-Cl as a white solid after washing with diethyl ether (5 × 10 mL). Yield: 92% (1.52 g, 4.6 mmol). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 10.67(s, 1H, imidazole H2), 7.33-7.52 (m, 12H, PPh$_2$ + imidazole CH), 4.39-4.45 (m, 2H, N-CH$_2$), 3.99 (s, 3H, CH$_3$), 2.74-2.79
(m, 2H, P-CH₂). ³¹P{¹H} NMR (121 MHz, CDCl₃): δ -21.33 (s). ¹³C NMR (75 MHz, CDCl₃): δ 137.9 (s, imidazole C2), 136.1 (d, JₚC = 11.6 Hz, ipso-PPh₂), 123.7 (d, JₚC = 19.3 Hz, PPh₂), 129.3 (s, PPh₂), 128.8 (d, JₚC = 7.0 Hz, PPh₂), 123.4 (s, imidazole C4/5), 122.1 (s, imidazole C4/5), 47.6 (d, JₚC = 23.2 Hz, N-CH₃), 36.4 (s, CH₃), 29.1 (d, JₚC = 15.8 Hz, P-CH₂). No satisfactory microanalysis could be obtained for ligand 2a-(Cl) due to its hygroscopic nature. The microanalysis of the PF₆⁻ salt gave satisfactory data [see 2a-(PF₆)].

**Compound 2a-(PF₆):** KPF₆ (900 mg 4.9 mmol) was added to a suspension of 2a-(Cl) (300 mg, 0.9 mmol) in acetone (10 mL) and the mixture was stirred at room temperature for 8 h. Acetone was then removed under vacuum and to this residue was added dichloromethane (15 mL). A clear solution was obtained after filtration. Removal of the solvent followed by addition of diethyl ether gave 2a-(PF₆) as an oil which solidified slowly to give a white solid in 95% yield (377 mg, 0.86). ¹H NMR (400 MHz, DMSO-d₆): δ 9.12 (s, 1H, imidazole H2), 7.77 (d, J = 1.7 Hz, 1H, imidazole H4/5), 5.79 (d, J = 1.7 Hz, 1H, imidazole H4/5), 7.39-7.47 (m, 10H, PPh₂), 4.25-4.33 (m, 2H, N-C₃H₂), 3.78 (s, 3H, C₆H₃), 2.74 (apparent t, J = 7.7 Hz, 2H, P-CH₂). ³¹P{¹H} NMR (121 MHz, DMSO-d₆): δ -21.8 (s, PPh₂), -144.5 (sept, JₚF = 706 Hz, PF₆⁻). ¹³C NMR (100 MHz, CD₃CN): δ 136.8 (d, JₚC = 12 Hz, ipso-PPh₂) 135.8 (s, imidazole C2), 132.6 (d, JₚC = 19.3 Hz, PPh₂), 129.3 (s, PPh₂), 128.8 (d, JₚC = 7.0 Hz, PPh₂), 123.6 (s, imidazole C4/5), 122.3 (s, imidazole C4/5), 47.6 (d, JₚC = 24 Hz, N-CH₃), 35.8 (s, CH₃), 27.9 (d, JₚC = 15.0 Hz, P-CH₂). Anal. Caled for C₁₈H₂₀F₆N₂P₂: C, 49.10; H, 4.58; N, 6.36; Found: C, 49.42; H, 4.78; N, 6.24.

**3-(2-chloroethyl)-1-isopropylimidazolium chloride:** This compound was synthesized by following 3-(2-chloroethyl)-1-methylimidazolium chloride, staring from 1-isopropyl-imidazole (1 g, 9.1 mmol) and 1,2-dichloroethane (15 ml) and a sticky oil was obtained. Yield: 89% (1.69 g, 8.1 mmol). ¹H NMR (300 MHz, DMSO-d₆): δ 9.73 (s, 1H, imidazole H2), 8.04 (m, 1H, imidazole H4/5), 7.98 (m, 1H, imidazole H4/5), 4.66-4.75 (sept, 3J = 6.7 Hz, 1H), 4.59 (t, 3J = 5.7 Hz, N-CH₂), 4.14 (t, 3J = 5.5 Hz, ClCH₂), 1.49 (d, 3J = 6.7 Hz, 6H, 2CH₃). ¹³C{¹H} NMR (75 MHz, DMSO-d₆): δ 136.2, 123.2, 121.2, 52.8,
Compound 2b-(PF₆): This compound was synthesized as a white solid by following 2a-(PF₆), starting from 3-(2-chloroethyl)-1-isopropylimidazolium chloride (600 mg, 2.87 mmol). Yield (after phosphination and anion exchange): 72% (967 mg, 2.07 mmol). 

\[ \text{H NMR (400 MHz, DMSO-}d_6): \delta \text{ 9.24 (s, 1H, H2), 7.79-7.82 (m, 2H, H4 and H5), 7.38-7.45(m, 10H, PPh}_2, 4.53(\text{sept, } J = 6.6 \text{ Hz, 1H, CH of } ^3\text{Pr}), 4.25-4.31 (m, 2H, N-CH}_2, 2.76 (\text{apparent t, } J = 7.6 \text{ Hz, 2H, P-CH}_2), 1.42 (d, J = 6.8 \text{ Hz, 6H, 2CH}_3). \]

\[ \text{³P}{\text{¹H}} \text{ NMR (161 MHz, DMSO-}d_6): \delta \text{ -21.96 (s, PPh}_2, -144.4 (\text{sept, } J_{PF} = 707 \text{ Hz, PF}_6).} \]

\[ \text{¹C NMR (100 MHz, DMSO-}d_6): \delta \text{ 137.2 (d, } J_{PC} = 12.2 \text{ Hz, ipso-PPh}_2, 135.2 (s, C2), 132.9 (d, } J_{PC} = 19.2 \text{ Hz, o-PPh}_2, 129.6 (s, } p\text{-PPh}_2, 129.2 (d, } J_{PC} = 6.8 \text{ Hz, m-PPh}_2, 123.0 (s, C4/5), 120.9 (s, C4/5), 52.68 (s, CH of } ^3\text{Pr), 47.3 (d, } J_{PC} = 27 \text{ Hz, N-CH}_2, 36.4 (s, CH}_3, 27.6 (d, } J_{PC} = 14 \text{ Hz, P-CH}_2), 22.72 (s, CH}_3 of } ^3\text{Pr).} \]


3-(2-chloroethyl)-1,2-dimethylimidazolium chloride: 1,2-Dimethylimidazole (1.0 g, 10.4 mmol) was dissolved in 1, 2-dichloroethane (15 ml) and the mixture was stirred under reflux for 24 h. All the 1,2-dichloroethane was then removed under vacuum and the residue was washed with diethyl ether (3 ×10 mL) to give 3-(2-chloroethyl)-1,2-dimethylimidazolium chloride as a white solid in 91% yield (1.84 g, 9.43 mmol). 

\[ \text{H NMR (300 MHz, DMSO-}d6): \delta \text{ 7.90 (s, 1H, imidazole H4/5), 7.85 (s, 1H, imidazole H4/5), 4.60 (t, } J = 4.0 \text{ Hz, N-CH}_2, 4.08 (t, } J = 4.0 \text{ Hz, Cl-CH}_2, 3.83 (s, 3H, CH}_3, 2.67 (s, 3H, CH}_3). \]

\[ \text{¹C NMR (75 MHz, DMSO-}d_6): \delta \text{ 145.6, 123.0, 121.8, 49.2, 43.7, 35.3, 10.1. HRMS (ESI⁺): 159.0674, Calcd for } [\text{C}_7\text{H}_{12}^\text{35ClN}_2]^+ \text{ 159.0684.} \]

Compound 2c-(Cl): 2c-(Cl) was prepared by following a directly analogous method for the synthesis of 2a-(Cl) starting from 3-(2-chloroethyl)-1,2-dimethylimidazolium chloride (500 mg, 2.56 mmol) and KPPh₂. Yield: 81% (white solid, 714 mg, 2.07 mmol). 

\[ \text{H NMR (300 MHz, CDCl}_3): \delta \text{ 7.92 (s, 1H, imidazole H4/5), 7.71 (s, 1H, imidazole C4/5), 7.34-7.38 (m, 10H, PPh}_2, 4.33-4.41 (m, 2H, N-CH}_2, 3.88 (s, 3H, CH}_3), 2.66 (\text{apparent t,} \]
$J = 7.0$ Hz, 2H, $P-CH_2$), 2.58 (s, 3H, $CH_3$). $^{31}$P $\{^1$H$\}$ NMR (121 MHz, CDCl$_3$): $\delta$ -21.79 (s).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 143.42 (s, imidazole C2), 136.0 (d, $J_{PC} = 11.6$ Hz, ipso-$PPh_2$), 123.6 (d, $J_{PC} = 21.7$ Hz, $PPh_2$), 129.4 (s, $PPh_2$), 123.2 (s, imidazole C4/5), 121.3 (s, imidazole C4/5), 46.3 (d, $J_{PC} = 21$ Hz, N-$CH_2$), 35.7 (s, $CH_3$), 29.1 (d, $J_{PC} = 16.5$ Hz, P-$CH_2$), 10. 51 (d, $J_{PC} = 3$ Hz, $CH_3$). No satisfactory microanalysis could be obtained for ligand 2c-(Cl) due to its hygroscopicity.

**Compound 2c-(PF$_6$):** 2c-(PF$_6$) was obtained as a white solid by anion exchange of 2c-(Cl) (300 mg, 0.87 mmol) using an excess amount of KPF$_6$ (800 mg, 4.3 mmol) in acetone. Yield: 92% (363 mg, 0.8 mmol). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.25-7.40 (m, 10H, $PPh_2$), 7.07 (s, 1H), 7.02 (s, 1H), 4.11 (m, 2H, $PCH_2$), 3.58 (s, 3H, N-$CH_3$), 2.55 (apparent t, $J = 7.3$ Hz, 2H, $PCH_2$), 2.33 (s, $CH_3$). $^{31}$P{$^1$H} NMR (121 MHz, CDCl$_3$): $\delta$ -21.77 (s), -144.6 (sept, $J_{PF} = 704$ Hz, PF$_6^-$). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 143.7 (s, imidazole C2), 136.0 (d, $J_{PC} = 11.4$ Hz, ipso-$PPh_2$), 132.6 (d, $J_{PC} = 21.8$ Hz, $PPh_2$), 129.4 (s, $PPh_2$), 123.2 (d, $J_{PC} = 7.0$ Hz, $PPh_2$), 123.2 (s, imidazole C4/5), 121.3 (s, imidazole C4/5), 46.3 (d, $J_{PC} = 15.8$ Hz, P-$CH_2$), 9.3 (s, $CH_3$). Anal. Calcd for C$_{19}H_{22}F_6N_2P_2$ (FW 468.1): C, 50.23; H, 4.88; N, 6.17; Found: C, 50.10; H, 5.08; N, 6.12.

3-(3-chloropropyl)-1-methylimidazolium chloride: This compound was synthesized by a method directly analogous to the synthesis of 3-(2-chloroethyl)-1-methylimidazolium chloride, starting from 1-methyl-imidazole (1g, 12.2 mmol). Yield: 67% (white solid, 1.6 g, 8.17 mmol). $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 11.0 (s, 1H, imidazole H2), 7.40 (s, 1H, imidazole H4/5), 7.33 (m, 1H, imidazole H4/5), 4.60 (t, $J = 6.93$ Hz, 2H, N-$CH_2$), 4.10 (s, $CH_3$), 3.64 (t, $J = 5.9$ Hz, Cl-$CH_2$), 2.51 (quintet, $J = 6.1$ Hz, $CH_2-CH_2-CH_2$). $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta$ 137.4 (s, imidazole C2), 124.1 (s, C4/5), 122.8 (s, C4/5), 46.8 (s, N-$CH_2$), 42.2 (s, Cl-$CH_2$), 36.2 (s, N-$CH_3$), 32.5 (s, C-$CH_2$). HRMS (ESI$^+$): 159.0653; Calcd for [C$_{10}$H$_{22}$F$_6$N$_2$P$_2$]: 159.0684.

**Compound 3:** Potassium diphenylphosphide in THF solution (0.5 M, 10 mL, 5 mmol) was added dropwise to a solution of 3-(3-chloropropyl)-1-methylimidazolium chloride.
(980 mg, 5 mmol) in DMSO (10 ml). The mixture was stirred at room temperature for 3 hours, followed by removal of DMSO under reduced pressure. A solution of sodium tetr phenylborate (1.71 g, 5.0 mmol) in methanol (15 mL) was added, and a white precipitate formed. The reaction mixture was stirred for 30 min, and approximately 25% of the solvent was removed under vacuum. The precipitate was collected by filtration, washed with deoxygenated water (2×10 mL), methanol (4×15 mL), and diethyl ether (3×15 mL) and dried under vacuum. Compound 3 was obtained as a white solid. Yield: 71% (2.23 g, 3.55 mmol). 1H NMR (300 MHz, CDCl3): δ 7.49 (br, 8H, BPh₄), 7.33-7.39 (m, 10H, PPh₂), 6.88-6.92 (m, 8H, BPh₄), 6.69-6.72 (m, 4H, para-BPh₄), 5.78 (s, 1H, imidazole H4), 5.65 (s, 1H, imidazole, H5), 4.28 (s, 1H, imidazole H2), 3.13 (apparent t, d = 7.6 Hz, 2H, N-C₃H₂), 2.70 (s, 3H, CH₃), 1.79 (apparent t, d = 7.8 Hz, 2H, P-C₃H₂), 1.39-1.46 (m, 2H, C-C₃H₂-C). 31P {1H} NMR (121 MHz, CDCl₃): δ -16.9 (s). 13C NMR (75 MHz, CDCl₃): 164.1 (q, JBC = 48.4 Hz, ipso-BPh₄), 137.3 (d, JPC = 12.1 Hz, ipso-PPh₂), 135.7 (s, BPh₄), 135.1 (s, imidazole C2), 132.6 (d, JPC = 18.7 Hz, o- or m-PPh₂), 129.2 (s, PPh₂), 128.7 (d, JPC = 6.9 Hz, o or m-PPh₂), 126.0 (s, m-BPh₄), 122.4 (s, imidazole C4/5), 122.0 (s, p-BPh₄), 120.3 (s, imidazole C4/5), 49.7 (d, JPC = 13.6 Hz, N-CH₂), 35.6 (s, CH₃), 26.6 (d, JPC = 18.8 Hz, P-CH₂), 24.5 (d, JPC = 13.3 Hz, C-CH₂-C). Anal. Calcd for C₄₃H₄₂BN₂P (FW 628.6): C, 82.16; H, 6.73; N, 4.46; Found: C, 81.93; H, 6.56; N, 6.68.

3-(2-chloroethyl)-1-isopropyl-4,5-dimethyl-imidazolium chloride: This imidazolium salt was synthesized by a method directly analogous to that for 3-(2-chloroethyl)-1,2-dimethylimidazolium chloride, starting from 1-isopropyl-4,5-dimethyl-1H-imidazole (300 mg, 2.17 mmol). Yield: 76% (gray solid, 392 mg, 1.65 mmol). 1H NMR (300 MHz, CDCl₃): δ 10.84 (s, 1H, imidazole H2), 4.72 (t, J = 5.04 Hz, 2H, N-CH₂), 4.41 (heptet, J = 6.6, 1H, CH of ³Pr), 4.14 (t, J = 5.04 Hz, Cl-CH₂), 2.29 (s, 3H, CH₃), 2.27 (s, 3H, CH₃), 1.63 (d, J = 6.6 Hz, 6H, 2CH₃). 13C NMR (75 MHz, CDCl₃): δ 135.6 (s, imidazole C2), 127.3 (s, C4/5), 125.2 (s, C4/5), 50.8 (s, CH of ³Pr), 48.2 (s, N-CH₂), 43.8 (s, Cl-CH₂), 22.8 (s, CH₃ of ³Pr), 8.8 (s, CH₃), 8.7 (s, CH₃). Due to the hygroscopic nature of this chloride salt, no satisfactory microanalysis could be obtained.
Compound 10: Ligand 10 was synthesized as a white solid by directly following the synthesis of compound 2a-(PF₆), starting from 3-(2-chloroethyl)-1-isopropyl-4,5-dimethylimidazolium chloride (200 mg, 0.84 mmol). Yield: 88% (367 mg, 0.74 mmol). ¹H NMR (400 MHz, DMSO-d₆): δ 9.10 (s, 1H, imidazole H₂), 7.39-7.64 (m, 10H, PPh₂), 4.43 (heptet, J = 6.6 Hz, 1H, CH of iPr), 4.21-4.27 (m, 2H, N-C₂H₂), 2.72 (apparent t, J = 7.5 Hz, P-CH₂), 2.16 (s, 6H, 2CH₃), 1.40 (d, J = 6.8 Hz, 6H, 2CH₃). ³¹P {¹H} NMR (161 MHz, DMSO-d₆): δ -21.60 (s, PPh₂), -144.18 (sept, JₚF = 702 Hz, PF₆⁻). ¹³C NMR (100 MHz, DMSO-d₆): δ 137.2 (d, JₚC = 12.3 Hz, ipso-PPh₂), 133.0 (s, PPh₂), 132.8 (s, imidazole C₂), 129.6 (s, PPh₂), 129.15 (d, JₚC = 6.8 Hz, PPh₂), 126.8 (s, imidazole C4/5), 126.3 (s, imidazole C4/5), 49.8 (s, CH of iPr), 44.9 (d, JₚC = 25 Hz, N-CH₂), 27.3 (d, JₚC = 14 Hz, P-CH₂), 22.6 (s, 2CH₃), 8.19 (s, CH₃), 8.16 (s, CH₃). Anal. Calcd for C₂₂H₂₆F₆N₂P₂ (FW 496.2): C, 53.23; H, 5.69; N, 5.64. Found: C, 53.01; H, 5.66; N, 5.53.

General Procedures for the Synthesis of Ir(III) Abnormal NHC Hydride Complexes.

To a stirred solution of [Ir(COD)Cl]₂ (100 mg, 0.149 mmol) in CH₂Cl₂ (2 mL) was added a CH₂Cl₂ solution (3 mL) of a phosphine-imidazolium salt (0.297 mmol). The reaction time was 12 h for the synthesis of complex 5, 2 h for complexes 8a-(Cl), 8a-(PF₆), and 8c-(PF₆), and 5 h for complex 8b-(PF₆), after which time the color of the solution became pale yellow or nearly colorless. The solution was then concentrated to ca. 0.5 mL, and diethyl ether (8 mL) added. Off-white precipitates appeared and were filtered and dried. Analytically pure iridium hydrides were obtained by recrystallization using CH₂Cl₂ and Et₂O.

Complex 5: Complex 5 was synthesized by following the above general procedure using 1a-(PF₆) (130.8 mg, 0.297 mmol) and [Ir(COD)Cl]₂ (100 mg, 0.149 mmol) in CH₂Cl₂. Yields: 92% (pale yellow solid, 212 mg, 0.273 mmol). Intermediate 4 was observed in NMR spectrum in the process reaction. Single crystals suitable for X-ray analysis were obtained by the slow diffusion of ether to a CH₂Cl₂ solution of 5 after one day. For intermediate 4: ³¹P (δ 19.1), ¹H [δ 8.70 (s, imidazole C2-H), 7.20 (d, J = 1.4 Hz, imidazole C4/5-H)]. ¹H NMR (500 MHz, CD₂Cl₂) of 5: δ 8.57 (s, 1H, imidazole C2-H),
7.73–7.75 (m, 2H, PPh₂), 7.49–7.57 (m, 8H, PPh₂), 6.41 (s, 1H, imidazole H4/5), 5.51 (m, 1H, COD), 5.33–5.39 (m, 1H, COD), 4.98–5.01 (m, 2H, N-C\textsubscript{2}H\textsubscript{5}P), 4.40 (sept, \(J = 6.7\) Hz, CH of iPr), 4.17–4.19 (m, 1H, COD), 3.03–3.05 (m, 2H, COD), 2.54–2.63 (m, 4H, COD), 2.29 (m, 1H, COD), 2.06–2.10 (m, 1H, COD), 1.50 (d, \(J = 6.6\) Hz, 3H, C\textsubscript{3}H), -15.81 (d, \(J_{P-H} = 7.5\) Hz, 1H, Ir-H).

\[ \text{31P}^{1\text{H}} \text{NMR (202 MHz, CD}_2\text{Cl}_2): \delta 27.47 \text{ (s, PPh}_2\text{), -144.4 (septet, } J_{P-F} = 709 \text{ Hz, PF}_6\text{).} \]

\[ \text{13C}^{1\text{H}} \text{NMR (125 MHz, CD}_2\text{Cl}_2): \delta 135.4 \text{ (d, } J_{P-C} = 5.7 \text{ Hz, C-Ir), 133.2 \text{ (d, } J_{P-C} = 11.4 \text{ Hz, } o-\text{ or } m-\text{PPh}_2), 132.6 \text{ (s, imidazole C2), 132.2 \text{ (d, } J_{P-C} = 2.58 \text{ Hz, } p-\text{PPh}_2), 131.1 \text{ (d, } J_{P-C} = 11.6 \text{ Hz, ipso-PPPh}_2), 129.5 \text{ (d, } J_{P-C} = 11.0 \text{ Hz, } o-\text{ or } m-\text{PPPh}_2), 128.9 \text{ (d, } J_{P-C} = 11.0 \text{ Hz, } o-\text{ or } m-\text{PPPh}_2), 125.7 \text{ (d, } J_{P-C} = 59.7 \text{ Hz, ipso-PPPh}_2), 119.1 \text{ (s, imidazole C4/5), 95.9 \text{ (d, } J_{P-C} = 15.7 \text{ Hz, CH of COD), 94.3 \text{ (s, CH of COD), 91.7 \text{ (d, } J_{P-C} = 9.7 \text{ Hz, CH of COD), 84.7 \text{ (s, CH of COD), 52.7 \text{ (s, CH of } ^{1}\text{Pr), 49.0 \text{ (d, } J_{P-C} = 48.7 \text{ Hz, N-CH}_2\text{-P), 35.7 \text{ (d, } J_{P-C} = 2.5 \text{ Hz, CH}_2\text{ of COD), 30.1 \text{ (s, CH}_2\text{ of COD), 29.9 \text{ (s, CH}_2\text{ of COD), 27.6 \text{ (d, } J_{P-C} = 2.8 \text{ Hz, CH}_2\text{ of COD), 22.7 \text{ (s, CH}_3\text{ of } ^{1}\text{Pr), 22.5 \text{ (s, CH}_3\text{ of } ^{1}\text{Pr).}}} \]

Anal. Calcd for C\textsubscript{27}H\textsubscript{34}Cl\textsubscript{6}Ir\textsubscript{2}N\textsubscript{2}P\textsubscript{6} (FW 790.1): C, 41.04; H, 4.34; N, 3.55. Found: C, 41.21; H, 4.53; N, 3.48.

**Complex 6.** To a solution of 5 (50 mg, 0.063 mmol) in MeCN (3 mL) was added Cs\textsubscript{2}CO\textsubscript{3} (60 mg, 0.18 mmol), and the mixture was stirred at room temperature for 10 h, during which time the pale yellow solution turned red. A residue was obtained after the removal of MeCN under vacuum, to which was added dichloromethane (5 mL). The inorganic salt was then removed by filtration. Exhaustion of all the dichloromethane gave analytically pure complex 6 as an air-sensitive red solid (45.9 mg, 0.058 mmol, 92%).

\[ \text{1H NMR (300 MHz, CD}_2\text{CN): } \delta 8.51 \text{ (s, 1H, imidazole C-2), 7.51–7.60 (m, 10H, PPh}_2\text{), 6.92 (s, 1H, imidazole H4/5), 4.78 (d, } J_{P-C} = 6.4 \text{ Hz, 2H, N-CH}_2\text{-P), 4.46 (sept, } J = 6.7 \text{ Hz, 1H, CH of } ^{1}\text{Pr), 4.31 (br, 3H, COD), 2.09 (m, 9H, COD), 1.46 (d, } J = 6.6 \text{ Hz, 6H, 2CH}_3\text{).} \]

\[ \text{31P}^{1\text{H}} \text{NMR (121 MHz CD}_2\text{CN): } \delta 40.23 \text{ (s, PPh}_2\text{), -143.9 (sept, } J_{P-F} = 704 \text{ Hz, PF}_6\text{).} \]

\[ \text{13C}^{1\text{H}} \text{NMR (100 MHz, CD}_2\text{CN): } \delta 133.0 \text{ (d, } J_{P-C} = 11.9 \text{ Hz, } o-\text{ or } m-\text{PPPh}_2), 131.3 \text{ (d, } J_{P-C} = 2.1 \text{ Hz, } p-\text{PPPh}_2), 130.9 \text{ (d, } J_{P-C} = 48 \text{ Hz, ipso-PPPh}_2), 130.7 \text{ (s, imidazole C2), 130.6} \]
Complex 8a-(PF₆). A mixture of complexes 7a-(PF₆) [Ir(I), minor] and 8a-(PF₆) [Ir(III), major] was synthesized by following the general procedure for Ir(III) abnormal NHC hydrides. Yields: 87% (pale yellow solid, 200.6 mg, 0.258 mmol). Single crystals of 8a-(PF₆) suitable for X-ray crystallographic studies were obtained by the slow diffusion of ether into a CH₂Cl₂ solution after 2 days. ¹H NMR (300 MHz, CD₂Cl₂) for the major Ir(III) only: δ 8.17 (s, 1H, imidazole C2-H), 7.86–7.91 (m, 2H, PPh₂), 7.42–7.61 (m, 8H, PPh₂), 6.40 (s, 1H, imidazole, H4/5), 5.52 (br, 1H, COD), 4.86–5.02 (m, 2H, N-C₂H₂), 4.66 (br, 1H, COD), 3.93–3.96 (m, 1H, COD), 3.76 (s, 3H, C₃H₃), 3.42–3.55 (m, 2H, COD), 3.00–3.04 (m, 2H, COD), 2.41–2.65 (m, 5H, 2H of P-C₂H₂ and 3H of COD), 1.96–1.99 (m, 2H, COD), -15.30 (d, J_p-c = 8.0 Hz, Ir-H). ³¹P{¹H} NMR (121 MHz, CD₂Cl₂): δ -2.41 [s, major 98.7%, Ir(III)], 13.60 [s, minor 1.3%, Ir(I)]. -143.8 (sept, J_p-F = 709 Hz, PF₆⁻). ¹³C NMR (75 MHz, CD₂Cl₂) for Ir(III) only: δ 135.5 (s, C2), 134.1 (d, J_p-c = 10.6 Hz, o- or m-PPh₂), 132.7 (d, J_p-c = 8.0 Hz, o- or m-PPh₂), 132.5 (d, J_p-c = 2.4 Hz, p-PPh₂), 131.4 (d, J_p-c = 2.4 Hz, p-PPh₂), 129.5 (d, J_p-c = 10.6 Hz, o- or m-PPh₂), 128.7 (d, J_p-c = 58.0 Hz, ipso-PPh₂), 128.4 (d, J_p-c = 57.2 Hz, ipso-PPh₂), 128.1 (d, J_p-c = 14.0 Hz, o- or m-PPh₂), 124.6 (s, imidazole C4/5), 120.6 (d, J_p-c = 9.2 Hz, C-Ir), 98.5 (d, J_p-c = 15.3 Hz, CH of COD), 94.7 (d, J_p-c = 9.4 Hz, CH of COD), 94.4 (s, CH of COD), 84.5 (s, CH of COD), 45.6 (s, N-CH₂), 36.1 (d, J_p-c = 3.4 Hz, CH₁ of COD), 35.1 (s, CH₃), 30.1 (s, CH₂ of COD), 29.8 (d, J_p-c = 2.2 Hz, CH₂ of COD), 27.6 (d, J_p-c = 3.7 Hz, CH₂ of COD), 25.3 (d, J_p-c = 39.3 Hz, P-CH₂). Anal. Calcd for C₃₂H₃₂ClF₆IrN₂P₂ (FW 776.1): C, 40.23; H, 4.16; N, 3.61. Found: C, 40.18; H, 4.21; N, 3.76.

Complex 9. Complex 9 was obtained as a red solid in 91% (43.3 mg, 0.0586 mmol) yield by directly following the synthesis of complex 6, starting from Complex 8a-(PF₆) (50 mg, 0.0644 mmol). ¹H NMR (300 MHz, CD₃CN): δ 8.22 (s, 1H, imidazole C2),
7.49–7.62 (m, 10H, PPh₂), 6.88 (s, 1H, imidazole C4/5), 4.40–4.51 (m, 2H, N-C₂H₂), 3.69 (s, 3H, C₃H₃), 2.65–2.71 (m, 2H, P-C₂H₂), 1.94–2.16 (m, 12H, COD). ³¹P{¹H} NMR (121 MHz, CD₃CN): δ 10.28 (s, PPh₂), -143.9 (sept, J_P-F = 703.6 Hz, PF₆⁻). ¹³C{¹H} NMR (75 MHz, CD₃CN): δ 149.6 (d, J_P-C = 12.2 Hz, C-Ir), 135.3 (s, imidazole C2), 133.2 (d, J_P-C = 10.9 Hz, o- or m-PPh₂), 132.9 (d, J_P-C = 2.4 Hz, p-PPh₂), 128.7 (d, J_P-C = 10.1 Hz, o- or m-PPh₂), 127.5 (s, imidazole C5), 48.8 (d, J_P-C = 2.4 Hz, N-CH₃), 34.5 (s, CH₃), 31.0 (s, CH₂ of COD), 26.1 (d, J_P-C = 34.7 Hz, CH₂-P).

Anal. Calcd for C₂₆H₃₁F₆IrN₂P₂ (FW 739.7): C, 42.22; H, 4.22; N, 3.79. Found: C, 42.13; H, 4.38; N, 3.66.

Complex 8a-(Cl). A mixture of complexes 8a-(Cl) (major) and 7a-(Cl) (minor) was prepared as yellow solid by following the general synthesis of Ir(III) abnormal NHC hydrides. Yield: 81% (160 mg, 0.240 mmol). ¹H NMR (400 MHz, CD₂Cl₂) for the major Ir(III) only: δ 10.00 (s, 1H, C₂), 7.89–7.94 (m, 2H, PPh₂), 7.42–7.61 (m, 8H, PPh₂), 6.38 (s, 1H, imidazole H4/5), 5.50 (br, 1H, COD), 5.01–5.09 (m, 2H, N-C₂H₂), 4.67 (br, 1H, COD), 3.98–4.10 (m, 1H, COD), 3.81 (s, 3H, C₃H₃), 3.72–3.73 (m, 1H, COD), 3.57 (br, 1H of COD), 2.98–3.08 (m, 2H, COD), 2.46–2.68 (m, 5H, 2H of P-C₂H₂ and 3H of COD), 2.01–2.19 (m, 2H, COD), -15.27 (d, J_P-C = 7.8 Hz, Ir-H). ³¹P{¹H} NMR (161 MHz, CD₂Cl₂): δ -2.32 [s, major 92.4%, Ir(III)], 14.60 [s, minor, 7.6%, Ir(I)]. ¹³C{¹H} NMR (100 MHz, CD₂Cl₂) for the major Ir(III) only: δ 137.9 (s, C₂), 134.2 (d, J_P-C = 10.5 Hz, o- or m-PPh₂), 132.8 (d, J_P-C = 7.89 Hz, o-PPh₂), 132.4 (d, J_P-C = 2.1 Hz, p-PPh₂), 131.3 (d, J_P-C = 2.4 Hz, p-PPh₂), 129.3 (d, J_P-C = 10.9 Hz, o- or m-PPh₂), 128.9 (d, J_P-C = 57.9 Hz, ipso-PPh₂), 128.6 (d, J_P-C = 58.5 Hz, ipso-PPh₂), 128.0 (d, J_P-C = 10.4 Hz, o- or m-PPh₂), 123.7 (s, imidazole C4/5), 119.8 (d, J_P-C = 9.2 Hz, C-Ir), 98.2 (d, J_P-C = 15.3 Hz, CH of COD), 94.3 (d, J_P-C = 9.4 Hz, CH of COD), 94.0 (s, CH of COD), 84.1 (s, CH of COD), 45.2 (s, N-CH₃), 36.0 (d, J_P-C = 3.1 Hz, CH₂ of COD), 35.1 (s, CH₃), 30.3 (s, CH₂ of COD), 29.8 (s, CH₂ of COD), 27.7 (d, J_P-C = 3.6 Hz, CH₂ of COD), 25.4 (d, J_P-C = 39.3 Hz, P-CH₂).

Anal. Calcd for C₂₀H₃₁Cl₆IrN₂P₂ (FW 666.6): C, 46.84; H, 4.84; N, 4.20. Found: C, 46.53; H, 4.87; N, 3.92.
Chapter 2

Complex 8b-(PF₆). A mixture of complex 8b-(PF₆) (major) and 7b-(PF₆) (minor) was prepared as yellow solid by following the general synthesis of Ir(III) abnormal NHC hydrides. Yield: 79% (188.7 mg, 0.234 mmol). ¹H NMR (300 MHz, CD₂Cl₂) for the major 8b-(PF₆) only: δ 8.22 (s, 1H, H₂), 7.86–7.92 (m, 2H, PPh₂), 7.39–7.60 (m, 8H, PPh₂), 6.46 (s, 1H, imidazole H₄), 5.51 (br, 1H, COD), 4.91–4.95 (m, 2H, N-CH₂), 4.67 (br, 1H, COD), 4.37 (sept, J = 6.7 Hz, 1H, CH of iPr), 3.94–4.08 (m, 1H, COD), 3.40–3.47 (m, 2H, COD), 3.01–3.05 (m, 2H, COD), 2.41–2.67 (m, 5H, 2H of P-CH₂ and 3H of COD), 2.25 (br, 1H, COD), 1.96–1.99 (m, 1H, COD), 1.47–1.52 (m, 6H, 2C₃H₃ of iPr), -15.29 (d, Jₚ-H = 8.1 Hz, Ir-H). ³¹P {¹H} NMR (121 MHz, CD₂Cl₂): δ -2.44 (s, major 94.7%, Ir(III), PPh₂), 14.71 (s, minor, 5.3% Ir(I), PPh₂), -143.8 (sept, Jₚ-F = 707.6 Hz, PF₆⁻). ¹³C NMR (75 MHz, CD₂Cl₂) for the Ir(III) only: δ 134.1 (d, Jₚ-C = 10.6 Hz, o- or m-PPh₂), 133.2 (s, C₂), 132.6 (d, Jₚ-C = 8.0 Hz, o- or m-PPh₂), 132.4 (d, Jₚ-C = 2.4 Hz, p-PPh₂), 131.4 (d, Jₚ-C = 2.3 Hz, p-PPh₂), 129.4 (d, Jₚ-C = 10.7 Hz, o- or m-PPh₂), 128.9 (d, Jₚ-C = 58.0 Hz, ipso-PPh₂), 128.3 (d, Jₚ-C = 57.8 Hz, ipso-PPh₂), 128.1 (d, Jₚ-C = 10.5 Hz, o-PPh₂), 121.1 (s, imidazole C4/5), 120.3 (d, Jₚ-C = 9.3 Hz, C-Ir), 98.2 (d, Jₚ-C = 15.4 Hz, CH of COD), 94.6 (d, Jₚ-C = 9.0 Hz, CH of COD), 94.5 (s, CH of COD), 84.6 (s, CH of COD), 52.2 (s, CH of iPr), 45.7 (s, N-CH₃), 36.1 (d, Jₚ-C = 3.4 Hz, CH₂ of COD), 30.0 (s, CH₂ of COD), 29.9 (s, CH₂ of COD), 27.5 (d, Jₚ-C = 3.5 Hz, CH₂ of COD), 25.4 (d, Jₚ-C = 39.2 Hz, P-CH₂), 22.7 (s, CH₃), 22.4 (s, CH₃). Anal. Calcd for C₂₈H₃₆ClF₆IrN₂P₂ (FW 804.2): C, 41.82; H, 4.51; N, 3.48. Found: C, 41.41; H, 4.38; N, 3.26.

Complex 8c-(PF₆). A mixture of complexes 8c-(PF₆) (major) and 7c-(PF₆) (minor) was prepared as yellow solid by following the general synthesis of Ir(III) abnormal NHC hydrides. Yield: 89% (209 mg, 0.264 mmol). ¹H NMR (300 MHz, CD₂Cl₂) for the major Ir(III) only: δ 7.61–7.65 (m, 2H, PPh₂), 7.45–7.65 (m, 8H, PPh₂), 6.39 (s, 1H, imidazole H₄/5), 5.58–5.59 (m, 1H, COD), 4.90–5.07 (m, 2H, N-CH₂), 4.66 (br, 1H, COD), 3.48–3.92 (m, 3H, COD), 3.79 (s, 3H, CH₃), 3.05–3.14 (m, 2H, COD), 2.46–2.68 (m, 5H, 2H of P-CH₂ and 3H of COD), 2.57 (s, 3H, CH₃), 1.99–2.04 (m, 2H, COD), -15.34 (d, Jₚ-H = 8.4 Hz, Ir-H). ³¹P {¹H} NMR (121 MHz, CD₂Cl₂): δ -2.34 [s, major 92.2%, Ir(III), PPh₂],
12.29 [s, minor, 7.8%, Ir(I), PPh₂], -143.9 (sept, J\textsubscript{P-F} = 707.6 Hz, PF\textsubscript{6}⁻). \textsuperscript{13}C NMR (75 MHz, CD\textsubscript{2}Cl\textsubscript{2}) for the major Ir(III) only: \(\delta\) 142.2 (s, C2), 134.0 (d, \(J\textsubscript{P-C} = 10.7\) Hz, \(o-\) or \(m-\) PPh₂), 132.6 (d, \(J\textsubscript{P-C} = 8.0\) Hz, \(o-\) or \(m-\) PPh₂), 132.4 (d, \(J\textsubscript{P-C} = 2.2\) Hz, \(p-\) PPh₂), 131.4 (d, \(J\textsubscript{P-C} = 2.4\) Hz, \(p-\) PPh₂), 129.5 (d, \(J\textsubscript{P-C} = 10.7\) Hz, \(o-\) or \(m-\) PPh₂), 128.7 (d, \(J\textsubscript{P-C} = 57.8\) Hz, \(ipso-\) PPh₂), 128.3 (d, \(J\textsubscript{P-C} = 58.0\) Hz, \(ipso-\) PPh₂), 128.1 (d, \(J\textsubscript{P-C} = 10.4\) Hz, \(o-\) or \(m-\) PPh₂), 123.7 (s, imidazole C4/5), 118.2 (d, \(J\textsubscript{P-C} = 9.6\) Hz, C-Ir), 99.1 (d, \(J\textsubscript{P-C} = 15.2\) Hz, CH of COD), 95.7 (d, \(J\textsubscript{P-C} = 9.3\) Hz, CH of COD), 93.9 (s, CH of COD), 84.3 (s, CH of COD), 43.8 (s, N-C\textsubscript{H}₂), 36.3 (d, \(J\textsubscript{P-C} = 2.8\) Hz, CH of COD), 34.5 (s, CH\textsubscript{3}), 29.7 (s, CH\textsubscript{2} of COD), 27.5 (d, \(J\textsubscript{P-C} = 3.5\) Hz CH\textsubscript{2} of COD), 25.5 (d, \(J\textsubscript{P-C} = 39.5\) Hz, P-CH\textsubscript{2}), 9.8 (s, CH\textsubscript{3}). No satisfactory microanalysis of 7c-(PF\textsubscript{6})/8c-(PF\textsubscript{6}) could be obtained. However, the SbF\textsubscript{6}⁻ salt [8c-(SbF\textsubscript{6})], prepared using the ligand 2c-(SbF\textsubscript{6}) and [Ir(COD)Cl]₂, gave satisfactory results. The \textsuperscript{1}H and \textsuperscript{13}C NMR spectra of this 8c-(SbF\textsubscript{6}) are almost identical to those of 8c-(PF\textsubscript{6}). Anal. Calcd for C\textsubscript{27}H\textsubscript{34}ClF\textsubscript{6}IrN\textsubscript{2}PSb: C, 36.81; H, 3.89; N, 3.18. Found: C, 36.45; H, 3.76; N, 3.35.

**Observation of Complex 11.** Compound 10 (13.0 mg, 0.0262 mmol) and [Ir(COD)Cl]₂ (8.8 mg, 0.0131 mmol) were dissolved in CD\textsubscript{2}Cl\textsubscript{2} (0.6 mL), and the solution was loaded into an NMR tube for examination. \textsuperscript{1}H NMR (300 MHz, CD\textsubscript{2}Cl\textsubscript{2}) for complex 11: \(\delta\) 8.59 (s, 1H, C\textsubscript{2}H), 7.57–7.63 (m, 4H, PPh₂), 7.46–7.56 (m, 6H, PPh₂), 5.15–5.17 (m, 2H, COD), 4.80–4.87 (m, 2H, N-CH\textsubscript{2}), 4.33–4.42 (sept, \(J = 6.7\) Hz, 1H, CH of \textsuperscript{1}Pr), 3.03–3.13 (m, 2H, P-C\textsubscript{H}₂), 2.65–2.66 (m, 2H, COD), 2.28 (s, 3H, CH\textsubscript{3}), 2.24 (s, 3H, CH\textsubscript{3}), 1.90–1.95 (m, 2H, COD), 1.59–1.66 (m, 2H of COD), 1.52 (d, \(J = 6.7\) Hz, 6H, 2CH\textsubscript{3}). No hydride was observed even after heating for 5 h at 40 °C. \textsuperscript{31}P{\textsuperscript{1}H} NMR (121 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \(\delta\) 14, 29 (s, PPh₂), -143.8 (sept, \(J\textsubscript{P-F} = 708.0\) Hz, PF\textsubscript{6}⁻). \textsuperscript{13}C NMR (75 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \(\delta\) 133.5 (d, \(J\textsubscript{P-C} = 10.7\) Hz, \(o-\) or \(m-\) PPh₂), 131.3 (s, imidazole C2), 130.9 (d, \(J\textsubscript{P-C} = 2.2\) Hz, \(p-\) PPh₂), 130.4 (d, \(J\textsubscript{P-C} = 49.0\) Hz, \(o-\) PPh₂), 127.4 (s, imidazole C4/5), 126.0 (s, imidazole C4/5), 94.6 (d, \(J\textsubscript{P-C} = 14.0\) Hz, CH of COD), 54.8 (s, CH of \textsuperscript{1}Pr), 50.7 (s, CH of COD), 44.3 (d, \(J\textsubscript{P-C} = 9.5\) Hz, N-CH\textsubscript{2}), 33.2 (d, \(J\textsubscript{P-C} = 3.3\) Hz, CH\textsubscript{2} of COD), 29.4 (d, \(J\textsubscript{P-C} = 28.5\) Hz, P-CH\textsubscript{2}), 29.3 (s, CH\textsubscript{2} of COD), 22.1 (s, 2CH\textsubscript{3}), 8.4 (s, CH\textsubscript{3}), 8.3 (s, CH\textsubscript{3}). No C-H
activation product was observed after this sample of $^{11}$ was heated at 39 °C for 5 h.

**Observation of Complex 13:** Compound $^{3}$ (18.0 mg, 0.0286 mmol) and $[\text{Ir}(\text{COD})\text{Cl}]_{2}$ (9.6 mg, 0.0143 mmol) were dissolved in CD$_2$Cl$_2$ (0.6 mL), and the solution was loaded into a NMR tube for examination. $^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 7.38–7.55 (m, 18H), 6.97–7.02 (m, 8H), 6.87 (s, imidazole H4/5), 6.78–6.83 (m, 4H), 6.63 (s, imidazole H4/5), 5.67 (s, 1H, C2), 5.03 (br, 2H, COD), 3.60–3.64 (t, $J = 6.9$ Hz, N-CH$_2$), 3.24 (s, 3H, CH$_3$), 2.62 (br, 2H, COD), 2.14–2.39 (m, 8H, 2H of P-CH$_2$ and 6H of COD), 1.84–1.87 (m, 2H, COD), 1.52–1.62 (m, 2H, CH$_3$). $^{31}$P$^1$H NMR (121 MHz CD$_2$Cl$_2$): $\delta$ 15.92 (s). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$): $\delta$ 164.1 (q, $J_{B-C} = 48.9$ Hz, ipso-BPh$_4$), 135.7 (s, o-BPh$_4$), 133.5 (d, $J_{P-C} = 6.5$ Hz, o- or m-PPh$_2$), 131.2 (d, $J_{P-C} = 48.4$ Hz, ipso-PPh$_2$), 130.7 (s, imidazole C2), 128.4 (d, $J_{P-C} = 9.7$ Hz, o or m-PPh$_2$), 125.9 (d, $J_{P-C} = 2.67$ Hz, m-BPh$_4$), 122.4 (s, imidazole C4/5), 122.0 (s, p-BPh$_4$), 121.6 (imidazole C4/5), 94.8 (d, $J_{P-C} = 14.1$ Hz, CH of COD), 54.1 (s, CH of COD), 50.1 (d, $J_{P-C} = 14.5$ Hz, N-CH$_2$), 36.0 (s, CH$_3$), 33.2 (d, $J_{P-C} = 3.1$ Hz, CH$_2$ of COD), 29.4 (s, CH$_2$ of COD), 26.4 (s, CH2), 24.4 (d, $J_{P-C} = 31.7$ Hz, P-CH$_2$). No C-H activation product was observed after this sample was heated at 39 °C for 5 h.

**Synthesis of Complex 12.** To a solution of $[\text{Ir}(\text{COD})\text{Cl}]_{2}$ (180 mg, 0.268 mmol) in THF (5 mL) was slowly added tBuOK (0.54 mL, 1 M in THF, 0.54 mmol). The color of the solution turned from red to dark red immediately. The solution was stirred for 2 h followed by addition of a suspension of $^{2a}$-(PF$_6$) (243 mg, 0.535 mmol) in THF. The mixture was stirred at room temperature for another 3 h followed by removal of all volatiles under reduced pressure. CH$_2$Cl$_2$ (5 mL) was added to the residue, and the inorganic salt was removed by filtration. The solution was then concentrated to ca. 0.5 mL under reduced pressure. Addition of diethyl ether (10 mL) afforded red microcrystals (313 mg, 0.423 mmol, 79%). $^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 7.38–7.48 (m, 10H, PPh$_2$), 7.02 (d, $J = 1.9$ Hz, 1H, H4/5), 6.82 (d, $J = 1.8$ Hz, 1H, H4/5), 4.89 (br, 2H, COD), 4.67 (m, 1H, NCH$_2$), 4.59 (m, 1H, NCH$_2$), 4.02 (br, 2H, COD), 3.84 (s, 3H, CH$_3$), 2.69–2.70 (m, 2H, P-CH$_2$), 2.09–2.21 (m, 8H, COD). $^{31}$P$^1$H NMR (161 MHz, CD$_2$Cl$_2$) $\delta$ 17.71 (s, PPh$_2$).
144.4 (sept, $J_{P,F} = 707$ Hz). $^{13}$C{$^1$H} (100 MHz, CD$_2$Cl$_2$) 171.8 (d, $J_{P,C} = 13.9$ Hz, C-Ir), 133.0 (br, ipso-PPh$_2$), 131.3 (s, p-PPh$_2$), 129.0 (d, $J_{P,C} = 10.4$ Hz, m or o-C of PPh$_2$), 123.0 (s, C4/5), 122.2 (s, C4/5), 86.2 (br, CH of COD), 80.1 (s, CH of COD), 49.7 (d, $J_{P,C} = 2.95$ Hz, NCH$_2$), 38.0 (s, CH$_3$), 31.5 (br, CH$_2$ of COD), 25.4 (d, $J_{P,C} = 38.3$ Hz, PCH$_2$). Anal. Calcd for C$_{26}$H$_{31}$F$_6$IrN$_2$P$_2$: C, 42.22; H, 4.22; N, 3.79. Found: C, 42.41; H, 4.41; N, 3.58.

**Kinetic Studies of the Conversion of Complex 4 to 5 (oxidative addition).**

In a typical experiment, ligand 1-(PF$_6$) (13 mg, 0.0286 mmol), [Ir(COD)Cl]$_2$ (9.6 mg, 0.0143 mmol) and an internal standard 1,3,5-trimethoxybenzene (1.0 mg, 0.00595 mmol) was dissolved in CDCl$_3$ (0.6 ml) at -30 °C and the solution was loaded into a stoppered J-Young NMR tube and was analyzed on an NMR spectrometer with a preset temperature. The signals of the imidazole H(2) of 4 (8.70 ppm) and H(2) of 5 (8.80 ppm) and internal standard (6.11 ppm) were used to calculate the conversion of 4 and the formation of 5. The slope of the plot of ln[4] against $t$ give the 1st order rate constant $k$ (Figure 2.2). The Eyring plot [ln($k$/T) against 1/T], gives $\Delta H^\circ$ and $\Delta S^\circ$ based on the Eyring equation ln($k$/T) = -$\Delta H^\circ$/RT + ln($k_0$/h) +$\Delta S^\circ$/R (Figure 2.3).

**The Chemical Equilibrium between Ir(I) and Ir(III) Complexes.**

Complex 8a-(Cl), 8a-(PF$_6$), or 8b-(PF$_6$) (15 mg) was dissolved in CD$_3$CN (0.6 mL) and the solution was loaded into a J-Young NMR tube. The $^{31}$P{$^1$H} spectra were detected at different temperatures. The resonance signals of Ir(I) and Ir(III) were used to calculate the ratio ($K_{eq}$) of [Ir(III)] to [Ir(I)]. The results are showed in Table 2.3. $\Delta H^\circ$ and $\Delta S^\circ$ were obtained by the equation ln$K_{eq}$ = -$\Delta H^\circ$/(RT) +$\Delta S^\circ$/R (Figure 2.5).
2.5 References


Chapter 3. Iridium and Rhodium 2-Methyleneimidazoline Complexes from Highly Selective Activation of C(sp<sup>3</sup>)-H Bonds of Functionalized Imidazoliums

3.1 Introduction

The last decade has witnessed great advances in the investigation and development of highly electron-rich ligands as spectators to stabilize transition metals and these metal complexes help to solve many challenges in organometallic chemistry and catalysis such as C-C coupling reactions. The role of these ligands likely lies in their donating character to stabilize the Lewis acidic nature of transition metals. In addition, the labilizing ability of these ligands tends to facilitate the rate-limiting steps. Consequently neutral carbon-centered ligands have been widely used to offer unique properties to compete with ubiquitous phosphine ligands in organometallic chemistry. N-heterocyclic carbenes (NHCs) are representative of these ligands and NHC complexes have shown superior activity in palladium-catalyzed C-C coupling and ruthenium-catalyzed olefin metathesis reactions.

NHCs on various platforms and with different substituents have been reported to demonstrate their tunability in terms of electronic and steric effects. In this regard, abnormal carbenes (imidazole-based NHC ligands bound through a backbone C4/5 carbon), first discovered by Crabtree and coworkers, constitute a new family of NHCs that are with electronic variants of normal NHCs and have received increasing attention. Abnormal NHCs (A, Figure 3.1), which are essentially zwitterionic ligands, are shown to be more donating than normal C2-bound NHCs. Analogously, metal complexes of ylides (B, Figure 3.1) and 2-methyleneimidazolines (C, Figure 3.1) with a side-on (η<sup>1</sup>) binding mode are all zwitterionic in nature and are structurally related. It has been recently shown that both phosphine ylides and 2-methyleneimidazolines are highly strong σ-donors towards metals.
Despite the simplicity of 2-methyleneimidazoline, there are only very few reports\textsuperscript{15-16} on such complexes and only two synthetic methods have been utilized. In method (a) (Scheme 3.1), 1,2,3-trimethylimidazolium iodide (or pentamethylimidazolium iodide) was deprotonated by a suitable base (KH or BuLi) to give a ylidic 2-methyleneimidazoline, followed by metalation upon addition of transition metals.\textsuperscript{15} In method (b), activation of a methyl C-H bond of a 2-methylimidazolium was mediated by a metal with a basic anionic ligand R (\textit{in situ} metalation), where only one example was reported for transition metals by Peris and coworkers for this method (Scheme 3.1).\textsuperscript{16} One can imagine that selectivity of methyl C($sp^3$)-H vs backbone C4/5-H activation might be problematic if the C4/5 position is left unblocked. Indeed, in Peris’\textprime;s report, low selectivity was observed for the methyl C($sp^3$)-H vs the C4/5-H activation of an imidazolium ring in a chelating system bound to an IrCp* fragment.\textsuperscript{16} No experimental attempts have been made to understand the origin of the selectivity of those C-H bonds; it is thus important to understand not only the thermodynamics of these two products but also the steric and electronic factors underlying the selective metalation of 2-methylimidazoliums.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{scheme31.png}
\caption{Scheme 3.1}
\end{figure}
We now report the synthesis and structures of a series of Ir(I) and Rh(I) 2-methyleneimidazoline complexes. Metalation can be exclusively directed to the 2-methyl group of a phosphine-tethered imidazoliums and the metalation is likely controlled by steric effects. The methyl C-H activation product (the 2-methyleneimidazoline complex) is the kinetic product, while the abnormal carbene complex is the thermodynamic product.

3.2 Results and Discussion

3.2.1 Abnormal and Normal NHC Complexes

In Chapter 2, we have discussed the synthesis of a series of iridium(III) abnormal NHC hydrides via highly selective activation of the C4/5-H bonds of phosphine-tethered imidazoliums, as shown in Scheme 3.2 as an representative example. These abnormal carbene hydrides can undergo base promoted reductive elimination of HCl to afford the corresponding iridium(I) abnormal carbene complexes (Scheme 3.2). As a contrast, the related iridium(I) normal NHC variant could be obtained by following a reported one-pot sequence of base-treatment of [Ir(COD)Cl]2 followed by addition of the phosphine–imidazolium ligand (Scheme 3.3). This method of metalation of imidazolium by rhodium or iridium with an internal alkoxide base was initially developed by Herrmann for the synthesis of monodentate NHC complexes.
3.2.2 H/D Exchange Reaction

We reason that metalation of a phosphine-tethered imidazolium with a 2-methyl group (such as ligand 1a, Scheme 3.4) might be directed to the C4/5 position when it is exposed to 0.5 equiv of [Ir(COD)O\textsubscript{tBu}]\textsubscript{2} that is generated \textit{in situ} from the reaction of [Ir(COD)Cl]\textsubscript{2} and KO\textsubscript{tBu}. This is based the assumption that activation of an aromatic C-H bond is generally lower in barrier than that of an aliphatic one. Furthermore, the resulting C4/5 metalation product, an abnormal carbene complex, has a relatively stable six-membered metalacycle. However, we also noted the rather high acidity (and hence higher reactivity) of the 2-methyl protons of ligand 1a, as evidenced from H/D exchange at this position. Stirring a CD\textsubscript{3}OD solution of 1a at room temperature overnight led to 55% deuteration at the 2-methyl position, while no H/D exchange could be detected by NMR spectroscopy. Therefore, we carried out experiments to weight these two factors and to rationalize the selectivity of these two C-H bonds.

![Chemical Structure of 1a and 2a](eq 3.1)

3.2.3 Metalation and Characterization

3.2.3.1 Synthesis and NMR Spectroscopy

Stirring a solution of 1a and [Ir(COD)O\textsubscript{tBu}]\textsubscript{2} generated in situ afforded red solution, from which only 2a was isolated in 91% yield as an air-sensitive solid and no abnormal complex could be obtained. (Scheme 3.4) Thus the metalation here was exclusively directed to the 2-methyl group. Complex 2a was spectroscopically and crystallographically characterized. In the $^1$H NMR spectrum (acetone-$d_6$) of 2a, the CH\textsubscript{2} protons resonate as a doublet (2H, $^3J_{PH} = 1.8$ Hz) at $\delta$ 2.88 and the imidazolium backbone protons resonate as doublets at $\delta$ 6.81 and 6.38 (d, $^3J_{HH} = 2.1$ Hz), indicating that no metalation took place at the C4/5 position. The fact that the Ir-CH\textsubscript{2} protons are equivalent also indicates that 2a is $C_2$ symmetrical in the solution structure. In the $^{13}$C NMR spectrum,
the CH\textsubscript{2} signal, confirmed by DEPT135, resonates characteristically at δ 13.9 (d, \( ^2J_{P,C} = 5.0 \text{ Hz} \)). Similarly, the rhodium analogue 3a could also be obtained by following the same procedure and it is less sensitive towards air or moisture. (Scheme 3.4) The scope of metatalation by this mode was then extended to ligands 1b-c with yields ranging from 91% to 95% and their characteristic NMR data are shown in Table 3.1. In all cases, no six-membered abnormal carbene products could be detected by NMR spectroscopy. We also noted that only the C-H bond of the 2-methyl group in ligand 1c was activated although metalation can potentially take place on a 4/5-methyl group and this is likely due to the higher acidity of the 2-methyl protons.

![Scheme 3.4](image)

We then further examined the metalation of other imidazoliums (such as 4 and 6) to prepare rhodium 2-methyleneimidazoline complexes with different chelation ring size. Here the synthetic method has to be modified. (Scheme 3.5) Ligand 4 or 6 was treated with [Rh(COD)Cl]\textsubscript{2} to afford the corresponding rhodium(I) phosphine complex in situ. Addition of KO\textsuperscript{t}Bu to this solution at a low temperature led to the selective metatalation of these imidazoliums at the desired 2-methyl position. Characteristic NMR signals of 5 and 7 are displayed in Table 3.1. The most striking spectroscopic difference between 3a and 5 probably lies in their \(^{31}\text{P} \) NMR spectra. The PPh\textsubscript{2} in 5 is significantly more deshielded (δ 74.2) compared with that in 3a (δ 24.5) as a result of ring size contraction and conformational changes of the solution structure. The shape of the -CH\textsubscript{2}PPh\textsubscript{2} resonance
signal in 1H NMR spectroscopy also changes from a well-resolved multiplet in 3a to essentially a poorly resolved singlet in 5, indicating the hardly measurable \( ^2J_{P-H} \) and \( ^3J_{Rh-H} \) values in 5.

\[ \text{Scheme 3.5} \]

| Table 3.1. Characteristic NMR Data of 2-Methyleneimidazoline Complexes (CD$_2$Cl$_2$) |
|---------------------------------|---------|-------|-------|
|                                 | \( ^1H \) | \( ^13C \) | \( ^31P \) |
| M-CH$_2$, imidazole C4-H or C5-H, \( ^3J_{HH} \) | M-CH$_2$ | PPh$_2$ |
| 2a                              | 2.88 (d, 1.8 Hz) | 6.81, 6.38, 2.1 Hz | 13.9 (d, \( J_{PC} = 5.0 \) Hz) | 15.4 (s) |
| 2b                              | 2.96 (d, 1.7 Hz) | 6.97, 6.78, 2.0 Hz | 13.9 (d, \( J_{PC} = 5.0 \) Hz) | 13.2 (s) |
| 3a                              | 2.09 (br) | 6.46, 6.03, 2.0 Hz | 10.0 (dd, \( J_{Rh-C} = 22.0, J_{P-C} = 8.0 \) Hz) | 24.5 (d, 164.9 Hz) |
| 3b                              | 2.13 (br) | 6.64, 6.35, 2.3 Hz | 9.8 (dd, \( J_{Rh-C} = 20.9, J_{P-C} = 8.2 \) Hz) | 21.0 (d, 165.2 Hz) |
| 3c                              | 2.08 (br) | - | 10.9 (dd, \( J_{Rh-C} = 20.7, J_{P-C} = 7.9 \) Hz) | 23.1 (d, 165.7 Hz) |
| 5                               | 1.82 (t, 3.2 Hz) | 6.72, 6.56, 2.2 Hz | 12.7 (dd, \( J_{Rh-C} = 19.2, J_{P-C} = 5.0 \) Hz) | 74.2 (d, 186 Hz) |
| 7                               | 1.65 (t, 4.0 Hz) | - | 8.51 (dd, \( J_{Rh-C} = 23.3, J_{P-C} = 8.2 \) Hz) | 26.0 (d, 159 Hz) |
3.2.3.2 X-ray Analysis

Complexes 2a, 3a, and 5 were further analyzed by X-ray crystallography (Figures 3.2-3.4 and Table 3.3). All these complexes have square planar geometry. The ligated methyleneimidazolines behave very much like “carbon ylides”, as evidenced from the end-on binding mode (Figures 3.1-3.3). Furthermore, the heterocyclic rings show all the structural attributes of imidazolium cations. Complexes 2a and 3a adopt highly folded boat conformation and 2a and 3a bear great similarity in crystallographic parameters and they have nearly identical corresponding bond lengths and angles (Table 3.2). The metal−CH2 distances are 2.145(3) and 2.147(2) Å for 2a and 3a, respectively, which are in agreement with those reported for M−alkyl (M = Ir and Rh) distances.16,19 The C(9)−C(10) bonds are nearly single bonds in character [1.449(4) Å for 2a and 1.4450(3) Å for 3a], consistent with the ylidic character of the methyleneimidazoline ligands.15a

Complex 5 co-crystallized with half equiv of CH2Cl2. Two independent molecules with pseudo-enantiomeric relations and with slightly different bonds lengths and angles were detected in each unit cell and only one is discussed here. The six-membered metalacycle adopts an “open book” conformation. This metalacycle must be fluxional and floppy in the NMR time scale since both Rh−CH2 and N−CH2 protons are equivalent in the solution 1H NMR at room temperature. In contrast, the C(9)−M−P(1) bite angle of 5 [88.97(9)°] is smaller than that in 2a or 3a as a result of a smaller ring size. The Rh−C(9)−C(10) angle in 5 is significantly smaller [113.2(2)°] and the Rh−CH2 carbon is essentially sp3 hybridized.
Figure 3.2. Molecular structure of 2a (cation only) with ellipsoids shown at 50% thermal probability

Figure 3.3. Molecular structure of 3a (cation only) with ellipsoids shown at 50% thermal probability

Figure 3.4. Molecular structure of 5 (cation only) with ellipsoids shown at 50% thermal probability. Two independent molecules co-crystalized in the unit cell and only one is shown here.
Table 3.2. Selected Bond Lengths and Angles for Complexes 2a, 3a, and 5

<table>
<thead>
<tr>
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<th>2a</th>
<th>3a</th>
<th>5·0.5CH₂Cl₂</th>
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<tr>
<td>M–C(9) (Å)</td>
<td>2.145(3)</td>
<td>2.147(2)</td>
<td>2.141(3)</td>
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<td>M–P (Å)</td>
<td>2.2841(6)</td>
<td>2.2816(5)</td>
<td>2.2663(8)</td>
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<tr>
<td>C(9)–C(10) (Å)</td>
<td>1.449(4)</td>
<td>1.450(3)</td>
<td>1.431(4)</td>
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<tr>
<td>C(9)–M–P(1) (deg)</td>
<td>93.47(8)</td>
<td>92.34(6)</td>
<td>88.97(9)</td>
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<tr>
<td>M–C(9)–C(10) (deg)</td>
<td>120.69(19)</td>
<td>121.06(14)</td>
<td>113.2(2)</td>
</tr>
<tr>
<td>N(1)–C(10)–N(2) (deg)</td>
<td>106.1(2)</td>
<td>106.33(17)</td>
<td>106.5(3)</td>
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Table 3.3 Crystallographic Data for Complexes 2a, 3a, and 5·0.5CH2Cl2

<table>
<thead>
<tr>
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<th>2a</th>
<th>3a</th>
<th>5·0.5CH2Cl2</th>
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<tr>
<td>empirical formula</td>
<td>C27H33F6N2P2Rh</td>
<td>C27H33F6N2P2Rh</td>
<td>C34.4H40ClF6 N2 P2Rh</td>
</tr>
<tr>
<td>molecular weight (g mol⁻¹)</td>
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<td>664.40</td>
<td>796.98</td>
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<td>P2₁/c</td>
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<td>a (Å)</td>
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<td>10.3242(4)</td>
<td>19.7387(6)</td>
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<td>b (Å)</td>
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<td>13.7831(6)</td>
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<td>c (Å)</td>
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<td>19.3904(8)</td>
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<td>96.086(2)</td>
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<td>µ (mm⁻¹)</td>
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<td>0.717</td>
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<td>crystal size (mm)</td>
<td>0.26 × 0.15 × 0.14</td>
<td>0.22 × 0.16 × 0.12</td>
<td>0.25 × 0.15 × 0.10</td>
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<td>total, unique no. of rflns</td>
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<td>69771, 13999</td>
<td>198471, 21335</td>
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<td>R int</td>
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<td>0.0439</td>
<td>0.0541</td>
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<td>13999, 0, 344</td>
<td>21335, 1, 839</td>
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<td>R, Rw (all data)</td>
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<td>1.025</td>
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<td>1.132</td>
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<td>min., max. resid dens (eÅ⁻³)</td>
<td>-1.461, 2.212</td>
<td>-1.924, 1.196</td>
<td>-0.556, 0.614</td>
</tr>
</tbody>
</table>
3.2.4 C(sp\(^3\))–H vs C(sp\(^2\))–H Activation

To further understand the factors controlling the selectivity of the C(sp\(^3\))–H vs C(sp\(^2\))–H activation, we examined the effects of anionic ligands (OR) in the rhodium system. [Rh(COD)OR] \(_2\) (R = \(^1\)Bu, Et, Me, and H) was thus either prepared \textit{in situ} by treating [Rh(COD)Cl] \(_2\) with 2 equiv of NaOR or obtained in the analytically pure form (for R = H). Ligand 1a was then allowed to react with all these [Rh(COD)OR] \(_2\) complexes in THF at room temperature. NMR spectroscopic analysis of these products showed that only the C(sp\(^3\))-H activation product (3a) was obtained for R = \(^1\)Bu or Et. However, for R = Me or H, the C(sp\(^3\))-H activation product (8) are in fact the major product and the ratio of 3a to 8 decreased from 1 : 1.2 for R = Me to 1 : 1.9 for R = H (Scheme 3.6). \(^1\)H NMR analysis of the product mixture obtained for R = H also showed that the 3a to 8 ratio is essentially non-time dependent from 30 min to 1 day. Furthermore, heating (35 °C, 1 day) a CD\(_2\)Cl\(_2\) solution of 3a in the presence of 4 equiv of water or MeOH leads to no formation of 8. These data all point to the formation of 3a and 8 via two parallel reactions, instead of the conversion of one to the other. Attempts to isolate complex 8 from the product mixture failed. However, characteristic signals contributed by 8 can be singled out from the \(^1\)H and \(^13\)C NMR spectra (CD\(_2\)Cl\(_2\)) of the mixture. The remaining C4/5-H proton of 8 resonates at \(\delta\) 6.10 (s) and the NCH\(_2\) signal shows up at \(\delta\) 5.08 as a characteristic doublet of multiplets. Two methyl groups with the correct signal integration were also detected with \(\delta\) 2.50 and 3.61. Importantly, the abnormal carbene signal resonate at \(\delta\) 149.9 (dd, \(^2\)\(J_{\text{Rh-C}}\) = 45 Hz, \(^3\)\(J_{\text{P-C}}\) = 6.9 Hz), which is in line with a directly analogous iridium complex. The fact that the ratio of 3a to 8 decreases as the bulk of R group is reduced indicates that the selectivity of C(sp\(^3\))–H vs C(sp\(^2\))–H activation is likely controlled by the steric effects of these OR ligands. The 2-CH\(_3\) group of the imidazolium is sterically more accessible. The conclusion that steric effect of the metal fragment is a key factor controlling the selectivity of the C-H activation agrees with recent theoretical studies reported by Clot, Peris, and coworkers.\(^{16}\) Their studies on the C-H activation of
imidazoliums on Cp*Ir\(_2\) fragment tend to indicate that the C\((sp^3)\)–H vs C\((sp^2)\)–H activation likely have similar activation barriers and activation of one or the other position might be critically influenced by the steric bulk of the metal fragment.\(^{16}\)

**Scheme 3.6**

\[
\text{[Rh(COD)OR]}_2 \xrightarrow{\text{THF, rt, 6h, -HOR}} 3a + 8
\]

\[
\begin{array}{c|c|c}
R & 3a & 8 \\
\hline
\text{^tBu} & 1 & 0 \\
\text{OEt} & 1 & 0 \\
\text{OMe} & 1 & 1.2 \\
\text{H} & 1 & 1.9 \\
\end{array}
\]

It is well known that strong C-H bond often lead to even stronger C–metal bonds.\(^{20}\) However, the thermodynamics of the activation of products resulting from the intramolecular cleavage of aliphatic vs aromatic C-H bonds (cyclometalation) might still be hard to predict, particularly if the regioselectivity issue deals with resulting metalacycle products of the same ring size. For example, Smoliakova and coworkers reported that in the palladation of 2-tert-butyl-4-phenyl-2-oxazoline both methyl C–H activation and phenyl group orthometalation were observed to give a mixture of two 5-membered palladacycles. Computational studies revealed that the methyl C-H activation product is slightly thermodynamically more stable than the other one by 4-20 kJ/mol, depending on the methods used. In evaluating the energetics of 3a and 8 (or their iridium analogous), we reason that both a relatively weaker M-CH\(_2\) bond and a more floppy ring in 3a (or 2a) likely render 3a (or 2a) a thermodynamically less favored product.
3.2.5 Conversion of Methyleneimidazoline to Abnormal NHC Complex

Although essentially no conversion of 3a to 8 could be achieved when a CD$_2$Cl$_2$ solution of 3a was heated in the presence of MeOH or water, we were gratified to find that this type of conversion was successful for the iridium analogue. Heating a CD$_2$Cl$_2$ solution of 2a and MeOH (5 equiv) at 40 °C in a sealed NMR tube slowly but rather cleanly led to abnormal carbene complex 9 and the yield is >95% after two weeks based on $^1$H NMR analysis. (Scheme 3.7) The identity of complex 9 has been confirmed through an independent synthetic method as illustrated in Scheme 3.2 by reacting ligand 1a and [Ir(COD)Cl]$_2$ to give an iridium abnormal hydride complex, followed by base-promoted reductive elimination of HCl. The synthesis and characterization of several direct analogues of 9 have been described in Chapter 1. We propose that 2a undergoes reversible protonolysis by MeOH to give an iridium(I) phosphine methoxide intermediate which is directly analogous to those proposed in scheme 3.7. Owing to the less sterically hindered OMe ligand, activation of the C4/5-H bond of the pendent imidazolium unit is rendered possible, although it could be less kinetically favorable. These results have unambiguously confirmed that 2a is the kinetic product while 9 is the thermodynamic one in the reaction of 1a and [Ir(COD)O'Bu]$_2$.

Scheme 3.7
3.2.6 The Electronic Properties

Rhodium dicarbonyl complex RhCl(CO)$_2$L are often used to assess the electronic properties of a given ligand L. A more donating ligand should result in a lower CO stretching frequency. We attempted the synthesis of complexes 10-11 (or their direct analogues with different N- groups) by bubbling CO through the solutions of their corresponding rhodium COD complexes (3a and 5), but no desired products could be obtained. The electronic effects of these methyleneimidazoline ligands in different chelating platforms were then evaluated and compared with those of normal and abnormal carbene ligands by theoretical methods. The ν$_{CO}$ frequencies of 10-11 were calculated at the DFT level and compared with those of related dicarbonylrhodium(I) complexes containing other P–normal NHC or P–abnormal NHC ligands. For the known complexes, a good agreement between experimental and calculated values is obtained, with a systematic difference of Δ$_{av.}$(calcd-exp) $\approx$ 104–105 cm$^{-1}$, consistent with a recent report.$^{14a}$ The rhodium center of complex 12 is most electron-rich, bearing only one carbonyl ligand and an extra electron-donating phosphine. Neutral dicarbonyl complex 13 is the 2$^{nd}$ most donating and is significantly more electron-rich than isostructural complexes 10 and 11, which possess essentially the same electronic effects. The abnormal carbene in complex 14 is slightly less donating than 2-methyleneimidazolines in 10-13, while the normal NHC ligand in complex 15 is the least donating among all the ligands examined. A general order of donating ability of methyleneimidazole > abnormal carbene > normal carbene can be concluded, consistent with previous reports.$^{15a}$

![Diagram of complexes 10-15]

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<tr>
<th></th>
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<tr>
<td>calcd (cm$^{-1}$)</td>
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<td>2123, 2165</td>
<td>2092</td>
<td>2073, 2143</td>
<td>2130, 2169</td>
<td>2137.5, 2176</td>
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<tr>
<td>av. (calcd)</td>
<td>2144.5</td>
<td>2144</td>
<td>2092</td>
<td>2108</td>
<td>2149.5</td>
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</tr>
<tr>
<td>exp (cm$^{-1}$)</td>
<td></td>
<td>1966, 2040</td>
<td>2003</td>
<td></td>
<td>2023, 2083</td>
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<td>av. (exp)</td>
<td></td>
<td></td>
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- 75 -
3.3 Conclusions

There have been only a few reports on the synthesis and structures of transition metal complexes of 2-methyleneimidazoles. We have successfully synthesized iridium and rhodium COD complexes stabilized by those ligands via highly selective intramolecular activation of 2-methyl C-H vs C4/5-H bonds (if relevant) of the imidazolium moieties with the chelation assistance of phosphine ligands. Metalacycles of 6-, 7-, and 8-membered size in this series were obtained in the reaction of phosphine tethered 2-methylimidazolium ions (1a-c, 4, 6) and [M(COD)(OR)]2 (M = Rh or Ir and R = alkyl or H) and representative complexes have been analyzed by X-ray crystallography. The selectivity of aliphatic C(sp³)-H vs aromatic C(sp²)-H activation could be adjusted by the steric bulk of the OR ligand, which could be regarded as internal bases. A sterically bulkier OR ligand favors the activation of the 2-methyl C-H bond. Experimental results also confirmed that a 7-membered iridium C(sp³)-H activation product is the kinetic product while the 6-membered iridium abnormal carbene product, resulting from the activation of a C(sp2)-H bond, is the thermodynamic product. Theoretical studies at the DFT level have been carried to assess the donating ability of these 2-methyleneimidazole ligands. Theoretical and experimental comparisons of the CO stretching frequencies of their rhodium dicarbonyl complexes with those of related normal and abnormal NHC complexes indicate that the order of donor capacity is 2-methyleneimidazole > abnormal NHC > normal NHC. The strong donating nature of these 2-methyleneimidazole ligands might be a desirable feature of neutral donors in the design of active catalysts. Synthesis of monodentate methyleneimidazole complexes and the catalytic applications of such complexes are under investigation in our laboratory and will be published in due course.
3.4 Experimental Section

General Considerations.

All manipulations were carried out by following the general considerations which has been described in Chapter 2.

Synthesis of Ligands

Compound 1b and 1c were synthesized by following a method analogous to that for 1a which has been described in Chapter 2.

\[
\begin{align*}
\text{N} & \quad \text{N} \\
\text{Ph}_2\text{P} & \quad \text{Cl}^- \\
\text{N} & \quad \text{N} \\
\text{Cl} & \quad \text{Cl}^- \\
\text{N} & \quad \text{N} \\
dichloroethane & \quad \text{Reflux} \\
\text{KPh}_2 & \quad \text{DMSO, RT} \\
\text{Ph}_2\text{P} & \quad \text{DMSO, RT} \\
\text{KPF}_6 & \quad \text{CH}_3\text{CN, RT} \\
1b-\text{Cl} & \quad 1b \\
\end{align*}
\]

3-(2-chloroethyl)-1-isopropyl-2-methylimidazolium chloride 1-isopropyl-2-methyl-imidazole (1.0 g, 8.05 mmol) was dissolved in 1,2-dichloroethane (15 ml), and the mixture was stirred under reflux for 16 h. All the volatiles were removed under vacuum and the residue was washed by diethyl ether to give 3-(2-chloroethyl)-1-isopropyl-2-methyl-imidazolium chloride as a white solid in 85% yield (1.53 g, 6.8 mmol). \(^1\text{H NMR}\) (400 MHz, DMSO-\(d_6\)): \(\delta\) 7.99 (s, 1H, imidazole H4/5), 7.91 (s, 1H, imidazole H4/5), 4.69 (sept, \(J = 6.4\) Hz, 1H, \(CH\) of iPr), 4.55 (t, \(J = 5.0\) Hz, 2H, \(CH_2\)), 4.03(t, \(J = 5.0\) Hz, 2H, \(CH_2\)), 2.67 (s, \(CH_3\)), 1.37 (d, \(J = 6.4\) Hz, 6H, \(2CH_3\)). \(^{13}\text{C NMR}\) (100 MHz, DMSO-\(d_6\)): \(\delta\) 144.4, 122.8, 118.5, 50.6, 49.1, 43.7, 22.4, 10.2. HRMS (ESI\(^+\)): 187.1031; calcd for [C\(_9\)H\(_{16}\)ClN\(_2\)]\(^+\): 187.1002.

Compound 1b-Cl. A solution of KPPH\(_2\) in THF (0.5 M, 4.7 ml, 2.35 mmol) was added dropwise to a DMSO (5 mL) solution of 3-(2-chloroethyl)-1-isopropyl-2-methylimidazolium chloride (500 mg, 2.24 mmol). The mixture was stirred at room temperature for 5 h, followed by removal of DMSO under vacuo (ca 0.01 mmHg). Methanol (5 ml) was then added to quench the reaction and was removed under reduced pressure. The residue was dissolved in dichloromethane and filtered to remove any insoluble. The filtrate was evacuated to dryness to afford 1b-Cl as a
white solid after successive washing with diethyl ether. Yield: 710 mg (1.9 mmol, 85%).

\[ ^1H\text{ NMR (500 MHz, CDCl}_3\]: \(\delta 7.78 (d, J = 2.1\text{ Hz, } 1H, \text{ imidazole H4/5}), 7.35-7.38(\text{m, } 4H, \text{ PPh}_2), 7.34 (d, J = 2.1\text{ Hz, } 1H, \text{ imidazole H4/5}), 7.30-7.32 (\text{m, } 6H, \text{ PPh}_2), 4.63 (\text{sept, } J = 6.6\text{ Hz, } 1H, \text{ CH of } ^3\text{Pr}), 4.45-4.50 (\text{m, } 2H, \text{ N-CH}_2), 2.69 (\text{apparent t, } J = 7.2\text{ Hz, } 2H, \text{ P-CH}_2), 2.68 (\text{s, } 3H, \text{ CH}_3), 1.43 (d, J = 6.7\text{ Hz, } 6H, 2\text{CH}_3). \]

\[ ^{31}\text{P\{^1H\} NMR (121 MHz, CDCl}_3\]: \(\delta -21.74 (s, \text{ PPh}_2). \]

\[ ^{13}\text{C NMR (75 MHz, CDCl}_3\]: \(\delta 142.4 (s, \text{ imidazole C2}), 136.0 \text{ (d, } J_{P-C} = 11.5\text{ Hz, ipso-PhP}_2), 132.6 \text{ (d, } J_{P-C} = 19.3\text{ Hz, PhP}_2), 129.4 \text{ (s, PhP}_2), 128.9 \text{ (d, } J_{P-C} = 7.1\text{ Hz, PhP}_2), 122.7 \text{ (s, C4/5), 117.6 \text{ (s, C4/5), 51.1 (s, CH of } ^3\text{Pr), 46.4 (d, } J_{P-C} = 20.9\text{ Hz, CH}_2), 28.4 \text{ (d, } J_{P-C} = 15.7\text{ Hz, CH}_2), 22.6 \text{ (s, CH}_3 \text{ of } ^3\text{Pr), 10.8 (s, CH}_3). \]

No satisfactory microanalysis could be obtained for this compound (1b-Cl) due to its hygroscopic nature. The microanalysis of the PF\(_6^-\) salt gave satisfactory data (see data for 1b).

**Compound 1b.** KPF\(_6\) (900 mg 4.9 mmol) was added to a solution of 1b-Cl (300 mg, 0.81 mmol) in CH\(_3\)CN (10 mL) and the mixture was stirred at room temperature for 8 h. Acetonitrile was then removed under reduced pressure and to this residue was added dichloromethane (15 mL). A clear solution was obtained after filtration. Removal of the solvent followed by addition of diethyl ether gave 1b as a white solid in 96% yield (373 mg, 0.77 mmol). 

\[ ^1H\text{ NMR (500 MHz, CDCl}_3\]: \(\delta 7.37-7.40 (\text{m, } 4H, \text{ PPh}_2), 7.33-7.35 (\text{m, } 6H, \text{ PPh}_2), 7.15 (d, J = 2.2\text{ Hz, } 1H, \text{ imidazole H4/5}), 7.08 (d, J = 2.2\text{ Hz, } 1H, \text{ imidazole H4/5}), 4.40 (\text{sept, } J = 6.6\text{ Hz, } 1H, \text{ CH of } ^3\text{Pr}), 4.15-4.19 (\text{m, } 2H, \text{ N-CH}_2), 2.57 \text{ (apparent t, } J = 7.6\text{ Hz, } 2H, \text{ P-CH}_2), 2.41 (\text{s, } 3H, \text{ CH}_3), 1.38 (d, J = 6.6\text{ Hz, } 6H, 2\text{CH}_3). \]

\[ ^{31}\text{P\{^1H\} NMR (201 MHz, CDCl}_3\]: \(\delta -22.1 (s, \text{ PPh}_2), -144.6 (\text{sept, } J_{P-F} = 706\text{ Hz, PF}_6). \]

\[ ^{13}\text{C NMR (125 MHz, CDCl}_3\]: \(\delta 142.5 (s, \text{ imidazole C2}), 136.0 (d, J_{P-C} = 11.5\text{ Hz, ipso-PhP}_2), 132.6 (d, J_{P-C} = 19.4\text{ Hz, PhP}_2), 129.5 (s, PhP}_2), 128.9 (d, J_{P-C} = 7.1\text{ Hz, PhP}_2), 121.5 (s, \text{ imidazole C4/5), 117.3 (s, imidazole C4/5), 51.0 (s, CH of } ^3\text{Pr), 46.0 (d, } J_{P-C} = 23\text{ Hz, CH}_2), 28.4 (d, J_{P-C} = 15.6\text{ Hz, CH}_2), 22.1 (s, CH}_3 \text{ of } ^3\text{Pr), 9.4 (s, CH}_3). \]

Anal. Calcd for C\(_{21}\)H\(_{26}\)F\(_6\)N\(_2\)P\(_2\) (482.4): C, 52.29; H, 5.43; N, 5.81; Found C, 52.13; H, 5.51; N, 5.96.
3-(2-chloroethyl)-1,2,4,5-teramethylimidazolium chloride. This imidazolium salt was synthesized by following a method directly analogous to that for 3-(2-chloroethyl)-1-isopropyl-2-methylimidazolium chloride as a white solid in 86% yield.

\[ \text{1H NMR (500 MHz, DMSO-\text{d}_6): } \delta 4.56 (t, J = 5.8 \text{ Hz}, 2H, N-CH}_2, 4.00 (t, J = 5.7 \text{ Hz}, 2H, Cl-CH}_2), 3.66 (s, 3H, CH}_3), 2.68 (s, 3H, CH}_3), 2.29 (s, 3H, CH}_3), 2.24 (s, 3H, CH}_3). \]

\[ \text{13C NMR (125 MHz, DMSO-\text{d}_6): } 144.1, 126.2, 125.4, 46.3, 43.3, 32.7, 10.8, 8.7, 8.5. \]

HRMS (ESI⁺): 187.1028; calcd for \([\text{C}_9\text{H}_{16}\text{ClN}_2]^+\) 187.1002.

Compound 1c-Cl. This compound was synthesized by following a method directly analogous to that for (1b-Cl) as a white solid power in 91% yield.

\[ \text{1H NMR (400 MHz, CDCl}_3): \delta 7.15-7.38 (m, 10H, \text{PPh}_2), 4.20-4.24 (m, 2H, N-CH}_2), 3.61 (s, 3H, N-CH}_3), 2.65 (s, 3H, CH}_3), 2.46 (apparent t, J = 7.2 \text{ Hz}, 2H, P-CH}_2), 2.08 (s, 3H, CH}_3), 2.07 (s, 3H, CH}_3). \]

\[ \text{31P\{1H\} NMR (161 MHz, CDCl}_3): \delta -21.9 (s, \text{PPh}_2), \text{13C NMR (100 MHz, CDCl}_3): 142.6 (s, \text{imidazole C2}), 136.1 (d, J\text{P-C} = 11.5 \text{ Hz}, \text{ipso-PPh}_2), 132.6 (d, J\text{P-C} = 19.2 \text{ Hz}, \text{PPh}_2), 129.5 (s, \text{PPh}_2), 128.8 (d, J\text{P-C} = 7.7 \text{ Hz}, \text{PPh}_2), 126.1 (s, \text{imidazole C4/5}), 124.8 (s, \text{imidazole C4/5}), 43.4 (d, J\text{P-C} = 23.0 \text{ Hz}, \text{N-CH}_2), 32.8 (s, \text{CH}_3), 28.8 (d, J\text{P-C} = 17.3 \text{ Hz}, \text{P-CH}_2), 11.6 (s, \text{CH}_3), 10.1 (s, \text{CH}_3), 8.9 (s, \text{CH}_3). \]

No satisfactory microanalysis could be obtained for ligand 1c-Cl due to its hydroscopicity. The microanalysis of the PF6⁻ salt gave satisfactory data (see 1c).

Compound 1c. This phosphine tethered 2-methylimidazolium salt was synthesized by following a method directly analogous to that for 1b as a white solid power in 95% yield.

\[ \text{1H NMR (300 MHz, CDCl}_3): \delta 7.34-7.43 (m, 10H, \text{CH of PPh}_2), 4.04-4.11 (m, 2H, N-CH}_2), 3.45 (s, 3H, N-CH}_2), 2.47 (apparent t, J = 7.9 \text{ Hz}, 2H, P-CH}_2), 2.39 (s, 3H, CH}_3), 2.08 (s, 3H, CH}_3), 2.07 (s, 3H, CH}_3). \]

\[ \text{31P\{1H\} NMR (121 MHz, CDCl}_3): \delta -22.1 (s, \text{PPh}_2), -144.1 (\text{sept, J}_\text{PF-F} = 708 \text{ Hz}, \text{PF}_6^-). \]

\[ \text{13C NMR (75 MHz, CDCl}_3): 141.9 (s, \text{imidazole C2}), 136.1 (d, J\text{P-C} = 11.2 \text{ Hz}, \text{ipso-PPh}_2), 132.5 (d, J\text{P-C} = 19.3 \text{ Hz}, \text{PPh}_2), 129.5 (s, \text{PPh}_2), 128.8 \]
(d, \( J_{P-C} = 7.1 \) Hz, PPh\(_2\)), 126.2 (s, imidazole C4/5), 124.6 (s, imidazole C4/5), 42.8 (d, \( J_{P-C} = 24.9 \) Hz, N-CH\(_3\)), 31.7 (s, CH\(_3\)), 28.4 (d, \( J_{P-C} = 15.7 \) Hz, P-CH\(_2\)), 10.0 (s, CH\(_3\)), 10.1 (s, CH\(_3\)), 8.4 (s, CH\(_3\)). Anal. Calcd for C\(_{21}\)H\(_{26}\)F\(_6\)N\(_2\)P\(_2\) (482.4): C, 52.29; H, 5.43; N, 5.81; Found C, 52.41; H, 5.48; N, 5.94.

**Compound 4-oxide.** Ph\(_2\)P(O)CH\(_2\)Br (1 g, 3.4 mmol) and 1-mesityl-2-methyl-imidazole (700 mg, 3.5 mmol) were charged into a vial, which was sealed and heated at 130 °C for 3 days. The residue was dissolved in dichloromethane (1 mL), followed by addition of diethyl ether (10 ml) to afford a brown solid. The pure 4-oxide could be obtained by successive washing with diethyl ether. Yiled: 77% (1.3 g, 2.6 mmol). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.22-8.24 (m, 4H, PPh\(_2\)), 8.08 (s, 1H, imidazole H4/5), 7.55-7.59 (m, 6H, PPh\(_2\)), 7.03 (s, 2H, Mesityl), 6.80 (s, 1H, imidazole H4/5), 6.08 (d, \( J_{P-H} = 5.0 \) Hz, 2H, N-CH\(_3\)), 2.56 (s, 3H, CH\(_3\)), 2.36 (s, 3H, CH\(_3\)), 1.91 (s, 6H, 2CH\(_3\)). \(^{31}\)P\(^{1}\)H NMR (161 MHz, CDCl\(_3\)): \( \delta \) 28.1 (s, P(O)Ph\(_2\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 146.3, 141.9, 134.6, 133.2 (d, \( J_{P-C} = 1.9 \)Hz, \( p\)-PPh\(_2\)), 131.7 (d, \( J_{P-C} = 10.5 \)Hz, PPh\(_2\)), 130.1, 129.9, 129.4 (d, \( J_{P-C} = 12.4 \) Hz, PPh\(_2\)), 128.4 (d, \( J_{P-C} = 102.1 \) Hz, \( ipso\)-PPh\(_2\)), 125.0, 120.6, 50.1 (d, \( J_{P-C} = 65.8 \) Hz, N-CH\(_3\)), 21.2, 17.4, 10.9. HRMS (ESI\(^+\)): 415.1929; calcd for [C\(_{26}\)H\(_{28}\)N\(_2\)OP\(^+\)] 415.1939.

**Compound 4.** A mixture of 4-oxide (1.0 g, 2.0 mmol) and chlorobenzene (15 ml) was placed into a glass pressure tube. Trichlorosilane (1.6 ml, 11.5 mmol) was added to the suspension at room temperature. The mixture was then sealed under nitrogen, heated to 120 °C for 3 h, and was cooled to room temperature. After addition of dichloromethane (30 ml), excess trichlorosilane was quenched by careful addition of a degassed aqueous
NaOH solution (10%) at 0 °C. The organic phase was separated and the aqueous phase was extracted with dichloromethane. The dichloromethane layers were combined and dried by Na₂SO₄. Dichloromethane was then removed under vacuum and the residue was washed with diethyl ether to afford a white solid. This white solid was then dissolved in acetonitrile (10 ml), to which was added KPF₆ (2 g, 10.7 mmol). The mixture was stirred at room temperature overnight. Acetonitrile was then removed under vacuo and to this residue was added dichloromethane (15 mL). A clear solution was obtained after filtration. Removal of the solvent followed by addition of diethyl ether gave 4 as a white solid. Yield: 48% (520 mg, 0.96 mmol). ¹H NMR (400 MHz, CDCl₃): δ 7.48-7.52 (m, 4 H, PPh₂), 7.43-7.45 (m, 6 H, PPh₂), 7.27 (d, J = 1.8 Hz, 1 H, imidazole H4/5), 7.03 (s, 2 H, Mesityl), 7.01 (d, J = 1.9 Hz, 1 H, imidazole H4/5), 5.02 (d, J₀/H = 5.9 Hz, 2 H, N-CH₂), 2.36 (s, 3 H), 2.02 (s, 3 H, CH₃), 1.91 (s, 6 H, 2CH₃). ³¹P{¹H} NMR (161 MHz, CDCl₃): δ -14.4 (s, PPh₂), -144.5 (sept, J₀/P = 709 Hz, PF₆). ¹³C NMR (100 MHz, CDCl₃): δ 144.9 (s), 141.6 (s), 134.8 (s), 133.2 (d, J₀/C = 10.8 Hz, ipso-PPh₂), 133.1 (d, J₀/C = 19.4 Hz, PPh₂), 130.5 (s), 130.1 (s), 129.9 (s), 129.3 (J₀/C = 7.1 Hz, PPh₂), 122.9 (J₀/C = 3.6 Hz, imidazole C4/5), 121.4 (s), 49.5 (d, J₀/C = 18.7 Hz, N-CH₂), 21.1 (s), 17.1 (s), 9.85 (s). Anal. Calcd for C₂₆H₂₈F₆N₂P₂ (FW 544.5): C, 57.36; H, 5.18; N, 5.15; Found C, 57.19; H, 5.31; N, 5.47.

**Compound 6-Cl.** (2-(chloromethyl)phenyl)diphenylphosphine (310 mg, 1 mmol) and 1,2,4,5- tetramethyl-imidazole (125 mg, 1 mmol) was dissolved in THF (5 ml), and the mixture was refluxed under nitrogen for 24 hours. THF was removed under vacuum and the residue was washed with diethyl ether to give 6-Cl as a white solid in 74% yield (322 mg, 0.74 mmol). ¹H NMR (300 MHz, CDCl₃): δ 7.30-7.40 (m, 8 H), 7.14-7.19 (m, 4 H), 7.04-7.07 (m, 1 H), 6.91-6.94 (m, 1 H), 5.38 (s, 2 H, CH₂), 3.71 (s, 3 H, N-CH₃), 2.62 (s, 3 H,
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$\text{CH}_3$, 2.12 (s, 3H, $\text{CH}_3$), 2.03 (s, 3H, $\text{CH}_3$). $^{31}\text{P}\{^{1}\text{H}\}$ NMR (121 MHz, CDCl$_3$): $\delta$ -15.5 (s, $\text{PPh}_2$). $^{13}\text{C}$ NMR (75 MHz, CDCl$_3$): $\delta$ 143.6 (s, imidazole C2), 136.6 (d, $J_{\text{P-C}}$ = 23.4 Hz, ipso-$\text{PPh}_2$), 135.3 (d, $J_{\text{P-C}}$ = 16.3 Hz, $\text{PPh}_2$), 134.3 (s), 134.1 (d, $J_{\text{P-C}}$ = 7.8 Hz, $\text{PPh}_2$), 133.8 (d, $J_{\text{P-C}}$ = 19.7 Hz, $\text{PPh}_2$), 130.1 (s), 129.5 (s), 129.1 (s), 128.8 (d, $J_{\text{P-C}}$ = 7.3 Hz, $\text{PPh}_2$), 127.6 (d, $J_{\text{P-C}}$ = 5.3 Hz, $\text{PPh}_2$), 126.2 (s, imidazole C4/5), 125.6 (s, imidazole C4/5), 48.0 (d, $J_{\text{P-C}}$ = 25.5 Hz, $\text{CH}_2$), 33.0(s, N-$\text{CH}_3$), 11.7 (s, $\text{CH}_3$), 9.10 (s, $\text{CH}_3$), 8.92 (s, $\text{CH}_3$). No satisfactory microanalysis could be obtained for ligand 6-Cl due to its hygroscopic nature.

The microanalysis of the PF$_6^-$ salt gave satisfactory data (see 6).

**Compound 6.** This imidazolium salt was synthesized by following method directly analogous to that for 1b, starting from 6-Cl (200 mg, 0.46 mmol) and KPF$_6$ (430 mg, 2.33 mmol) in CH$_3$CN (10 ml), as a white solid power in 94% yield (235.4 mg, 0.43 mmol). $^{1}\text{H}$ NMR (300 MHz, CDCl$_3$): $\delta$ 7.30-7.46 (m, 6H), 7.21-7.25 (m, 6H), 6.91-6.97 (m, 2H), 5.31 (s, 2H, $\text{CH}_2$), 3.54 (s, 3H, N-$\text{CH}_3$), 2.37 (s, 3H, $\text{CH}_3$), 2.14 (s, 3H, $\text{CH}_3$), 2.02 (s, 3H, $\text{CH}_3$). $^{31}\text{P}\{^{1}\text{H}\}$ NMR (161 MHz, CDCl$_3$): $\delta$ -16.2 (s, $\text{PPh}_2$), -144.7(sept, $J_{\text{P-F}}$ = 710 Hz, PF$_6^-$). $^{13}\text{C}$ NMR (100 MHz, CDCl$_3$): $\delta$ 142.8 (s, imidazole C2), 136.3 (d, $J_{\text{P-C}}$ = 23.3 Hz, ipso-$\text{PPh}_2$), 135.1 (d, $J_{\text{P-C}}$ = 16.2 Hz, $\text{PPh}_2$), 134.2 (s), 134.0 (d, $J_{\text{P-C}}$ = 6.2 Hz, $\text{PPh}_2$), 133.8 (d, $J_{\text{P-C}}$ = 19.7 Hz, $\text{PPh}_2$), 130.4 (s), 129.6 (s), 129.1 (s), 128.8 (d, $J_{\text{P-C}}$ = 7.3 Hz, $\text{PPh}_2$), 127.0 (d, $J_{\text{P-C}}$ =5.1 Hz, $\text{PPh}_2$), 126.5 (s, imidazole C4/5), 125.6 (s, imidazole C4/5), 48.0 (d, $J_{\text{P-C}}$ = 25.5 Hz, $\text{CH}_2$), 32.0(s, N-$\text{CH}_3$), 10.4 (s, $\text{CH}_3$), 8.86 (s, $\text{CH}_3$), 8.58 (s, $\text{CH}_3$). Anal. Calcd for C$_{26}$H$_{28}$F$_6$N$_2$P$_2$ (FW 544.5): C, 57.36; H, 5.18; N, 5.15; Found C, 57.29; H, 5.11; N, 5.09.

**Syntheses of Rh and Ir Complexes**

**General procedure for synthesis of complexes 2 and 3.**

To a solution of [M(COD)Cl]$_2$ (M = Rh, Ir, 0.05 mmol) in THF (5 mL) was slowly added KO'Bu (0.11 mL, 1 M in THF, 0.11 mmol). The solution was stirred for 2 h followed by addition of a suspension of phosphine-tethered imidazolium salt (0.1 mmol) in THF. The mixture was stirred at room temperature for another 6 h followed by removal of all volatiles under reduced pressure. CH$_2$Cl$_2$ (5 mL) was added to the residue, and the inorganic salt was
removed by filtration through celite. The solvent was removed and the residue was washed by pentane (5ml × 3) to afford the final products.

**Complex 2a.** Yields: 91% (red solid, 68.5 mg, 0.091 mmol). Single crystals suitable for X-ray analysis were obtained by the slow diffusion of diethyl ether to a CH2Cl2 solution of 2a after 7 days at -20°C. 1H NMR (300 MHz, acetone-d6): δ 7.47-7.55 (m, 10H, PPh2), 6.81 (d, J = 2.2 Hz, 1H, imidazole H4/5), 6.38 (d, J = 2.1 Hz, 1H, imidazole H4/5), 4.83-4.86 (m, 2H, COD), 4.48-4.58 (m, 2H, N-C6H2), 3.62 (s, 3H, N-C6H3), 3.04-3.11 (m, 2H, P-C6H2), 2.88 (d, J = 1.6 Hz, 2H, CH2-Ir), 2.81-2.83 (m, 2H, COD), 2.21-2.31 (m, 2H, COD), 1.95-2.15 (m, 4H, COD). 31P{1H} NMR (121 MHz, acetone-d6): δ 15.4 (s, PPh2), -143.6 (sept, JPF = 703.8 Hz, PF6). 13C NMR (100 MHz, acetone-d6): δ 159.9 (s, imidazole C2), 133.5 (d, JPC = 13.0 Hz, o- or m-PPh2), 130.9 (d, JPC = 2.0 Hz, p-PPh2), 130.3 (d, JPC = 49.3 Hz, ipso-PPh2), 128.4 (d, JPC = 10.0 Hz, CH of COD), 118.7 (s, CH of COD), 113.8 (s, C4/5), 88.9 (d, JPC = 10.0 Hz, CH of COD), 64.1 (s, CH of COD), 49.1 (s, CH of Pr), 42.7 (s, N-C6H2), 31.6 (d, JPC = 2.8 Hz, CH2 of COD), 30.5 (s, CH2 of COD), 21.4 (s, CH3), 19.5 (d, JPC = 29.5 Hz, P-CH2), 13.9 (d,
$J_{P,C} = 4.9$ Hz, Ir-CH$_2$). Anal. Calcd for C$_{20}$H$_{37}$F$_6$IrN$_2$P$_2$ (FW 781.8): C, 44.55; H, 4.77; N, 3.58; Found C, 44.72; H, 4.67; N, 3.68.

**Complex 3a.** Yields: 95% (bright yellow solid, 61 mg, 0.092 mmol). Single crystals suitable for X-ray analysis were obtained by the slow diffusion of diethyl ether to a THF solution of 3a after 2 days at room temperature. $^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 7.40-7.51 (m, 10H, PPh$_2$), 6.46 (d, $J = 2.2$ Hz, 1H, imidazole H4/5), 6.03 (d, $J = 2.0$ Hz, 1H, imidazole H4/5), 5.16-5.18 (m, 2H, COD), 4.26-4.34 (m, 2H, N-CH$_2$), 3.37-3.38 (m, 2H, COD), 3.35 (s, 3H, N-CH$_3$), 2.60-2.67 (m, 2H, P-CH$_2$), 2.43-2.49 (m, 2H, COD), 2.23-2.33 (m, 4H, COD), 2.08-2.09 (m, 2H, Rh-CH$_2$), 2.02-2.04 (m, 1H, COD), 1.83-1.87 (m, 1H, COD). $^{31}$P$^1$H NMR (121 MHz, CD$_2$Cl$_2$): $\delta$ 24.5 (d, $J_{Rh-P} = 164.9$ Hz, PPh$_2$), -143.8 (sept, $J_{P-F} = 708$ Hz, P$_F$$_6$). $^{13}$C NMR (75 MHz, CD$_2$Cl$_2$): $\delta$ 159.2 (s, imidazole C2), 133.1 (d, $J_{P-C} = 11.6$ Hz, o- or m-PPh$_2$), 130.9 (d, $J_{P-C} = 1.9$ Hz, p-PPh$_2$), 130.8 (d, $J_{P-C} = 40.3$ Hz, ipso-PPh$_2$), 128.5 (d, $J_{P-C} = 9.6$ Hz, o- or m-PPh$_2$), 118.2 (s, imidazole C4/5), 116.7 (s, imidazole C4/5), 100.5 (dd, $J_{P-C} = 10.8$ Hz, J$_{Rh-C} = 8.0$ Hz, CH of COD), 80.7 (d, $J_{Rh-C} = 9.2$ Hz, CH of COD), 42.9 (s, N-CH$_2$), 34.0 (s, CH$_3$), 31.5 (d, $J_{P-C} = 2.3$ Hz, CH$_2$ of COD), 30.0 (s, CH$_2$ of COD), 21.1 (d, $J_{P-C} = 21.6$ Hz, P-CH$_2$), 10.0 (dd, $J_{P-C} = 8.0$ Hz, $J_{Rh-C} = 20.2$ Hz, Rh-CH$_2$). Anal. Calcd for C$_{27}$H$_{33}$F$_6$N$_2$P$_2$Rh (FW 664.4): C, 48.81; H, 5.01; N, 4.22; Found 48.69; H, 5.14; N, 4.09.

**Complex 3b.** Yields: 91% (bright yellow solid, 63 mg, 0.091 mmol). $^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 7.40-7.53 (m, 10H, PPh$_2$), 6.64 (d, $J = 2.3$ Hz, 1H, imidazole H4/5), 6.35 (d, $J = 2.3$ Hz, 1H, imidazole H4/5), 5.12 (br, 2H, COD), 4.27-4.34 (m, 2H, N-CH$_2$), 4.21 (septet, $J = 6.7$ Hz, 1H, CH of iPr), 3.40-3.41 (m, 2H, COD), 2.62-2.69 (m, 2H, P-CH$_2$), 2.42-2.50 (m, 2H, COD), 2.26-2.30 (m, 4H, COD), 2.13 (apparent t, $J = 2.6$ Hz, 2H, Rh-CH$_2$), 1.99-2.11 (m, 1H, COD), 1.83-1.86 (m, 1H, COD), 1.38 (d, $J = 6.7$ Hz, 6H, CH$_3$). $^{31}$P$^1$H NMR (121 MHz, CD$_2$Cl$_2$): $\delta$ 21.0 (d, $J_{Rh-P} = 165.2$ Hz, PPh$_2$), -143.8 (sept, $J_{P-F} = 708$ Hz, P$_F$$_6$). $^{13}$C NMR (75 MHz, CD$_2$Cl$_2$): $\delta$ 157.9 (s, imidazole C2), 133.1 (d, $J_{P-C} = 11.6$ Hz, o- or m-PPh$_2$), 131.0 (d, $J_{P-C} = 39.2$ Hz, ipso-PPh$_2$), 130.7 (d, $J_{P-C} = 2.0$ Hz, p-PPh$_2$), 128.7 (d, $J_{P-C} = 9.5$ Hz, o- or m-PPh$_2$), 118.0 (s, imidazole C4/5), 113.2 (s, imidazole C4/5), 99.9 (dd, $J_{P-C} = 10.8$ Hz, $J_{Rh-C} = 8.1$ Hz, CH of COD), 81.1 (d, $J_{Rh-C} = 9.1$ Hz, CH of COD), 49.1 (s, CH of $^3$Pr), 42.7 (s, N-CH$_2$), 31.4 (d, $J_{P-C} = 2.4$ Hz, CH$_2$ of COD), 30.5 (s, CH$_2$ of COD), 21.8 (s, CH$_3$), 20.8 (d, $J_{P-C} = 21.7$ Hz, PPh$_2$).
Hz, P-CH2), 9.8 (dd, J P-C = 8.2 Hz, J Rh-C = 20.9 Hz, Rh-CH2). Anal. Caled for C29H37F6N2P2Rh (FW 692.5): C, 50.30; H, 5.39; N, 4.05; Found C, 50.42; H, 5.28; N, 4.17.

Complex 3c. Yields: 94% (yellow solid, 65.1 mg, 0.094 mmol). 1H NMR (400 MHz, CD2Cl2): δ 7.42-7.48 (m, 10H, PPh2), 5.17 (br, 2H, COD), 4.29-4.36 (m, 2H, N-CH2), 3.35 (br, 2H, COD), 3.19 (s, 3H, CH3), 2.61-2.65 (m, 2H, P-CH2), 2.46-2.49 (m, 2H, COD), 2.24-2.31 (m, 4H, COD), 2.08 (m, 2H, Rh-CH2), 2.03-2.06 (m, 1H, COD), 1.88 (s, 3H, CH3), 1.84-1.87 (m, 1H, COD), 1.57 (s, 3H, CH3). 31P{1H} NMR (161 MHz, CD 2Cl2): δ 23.1 (d, J Rh-P = 165.7 Hz, PPh2), -144.5 (sept, J P-F = 707 Hz, PF6). 13C NMR (100 MHz, CD2Cl2): δ 158.5 (s, imidazole C2), 133.1 (d, J P-C = 11.9 Hz, o- or m-PPh2), 131.0 (d, J P-C = 40.3 Hz, ipso-PPh2), 130.8 (s, p-PPh2), 128.4 (d, J P-C = 9.5 Hz, o- or m-PPh2), 121.2 (s, imidazole C4/5), 120.2 (s, imidazole C4/5), 100.7 (dd, J P-C = 10.7 Hz, J Rh-C = 8.0 Hz, CH of COD), 80.5 (d, J Rh-C = 9.0 Hz, CH of COD), 39.7 (s, N-CH2), 31.5 (br, CH2 of COD), 30.4 (s, CH3), 30.4 (s, CH2 of COD), 20.8 (d, J P-C = 22.0 Hz, P-CH2), 10.9 (dd, J P-C = 7.9 Hz, J Rh-C = 20.7 Hz, Rh-CH2), 7.6 (s, CH3), 7.5 (s, CH3). Anal. Caled for C29H37F6N2P2Rh (FW 692.5): C, 50.30; H, 5.39; N, 4.05; Found C, 50.39; H, 5.48; N, 4.30

General Procedure for Synthesis of complexes 5 and 7.

A mixture of ligand 4 or 6 (0.20 mmol) and [Rh(COD)Cl]2 (0.10 mmol) was dissolved in THF (5 ml) and stirred at room temperature for 30 min. The mixture was then cooled to -78°C, and KOtBu (0.22mL, 1 M in THF, 0.22 mmol) was added by syringe. After stirred at -78°C for 1 hour, the mixture was slowly warmed to room temperature, and stirred for another 2 hours followed by removal of all volatiles under reduced pressure. CH2Cl2 (5 mL) was added to the residue, and the inorganic salt was removed by filtration through celite. The solution was then concentrated and the residue was washed by pentane (5 ml × 2) to afford a yellow solid.

Complex 5. Yield: 93% (bright yellow solid, 140 mg, 0.182 mmol). Single crystals suitable for X-ray analysis were obtained by layering its dichloromethane solution with n-pentane after one day at room temperature. 1H NMR (400 MHz, CD2Cl2): δ 7.43-7.59
(m, 10H, PPh₂), 7.06 (s, 2H, mesityl), 6.73 (d, J = 2.3 Hz, 1H, imidazole H4/5), 6.56 (d, J = 1.8 Hz, 1H, imidazole H4/5), 4.77 (br, 2H, COD), 4.53 (d, J = 1.4 Hz, 2H, N-CH₂), 3.71 (br, 2H, COD), 2.34 (s, 3H, CH₃), 2.01-2.19 (m, 8H, COD), 2.09 (s, 6H, 2CH₃), 3.36 (apparent t, J = 2.7 Hz, 2H, Rh-C₂). ³¹P{¹H} NMR (161 MHz, CD₂Cl₂): δ 74.2 (d, JRh-P = 187.3 Hz, PPh₂), -143.8 (septet, JP-F = 714 Hz, PF₆). ¹³C NMR (100 MHz, CD₂Cl₂): 157.5 (d, JP-C = 5.7 Hz, imidazole C2), 141.0, 135.4, 132.8 (d, JP-C = 12.5 Hz, o- or m-PPh₂), 131.8, 130.9, 129.9 (d, JP-C = 38.3 Hz, ipso-PPh₂), 129.7, 129.5 (d, JP-C = 9.6 Hz, o- or m-PPh₂), 118.7 (s, imidazole C4/5), 118.5 (s, imidazole C4/5), 102.3 (dd, JP-C = 10.5 Hz, JRh-C = 7.8 Hz, CH of COD), 82.4 (d, JRh-C = 8.6 Hz, CH of COD), 49.0 (d, JP-C = 20.1 Hz, N-CH₂), 31.2 (s, CH₂ of COD), 30.1 (s, CH₂ of COD), 20.9 (s, CH₃), 17.8 (s, CH₃), 12.8 (dd, JP-C = 5.3 Hz, JRh-C = 18.7 Hz, Rh-CH₂). Anal. Calcd for C₃₄H₃₉F₆N₂P₂Rh (FW 754.5): C, 54.12; H, 5.21; N, 3.71; Found C, 54.33; H, 5.51; N, 3.69;

**Complex 7.** Complex 7 was synthesized as a yellow solid. It was further washed with cold THF to get the analytically pure product. Yield: 65% (98 mg, 0.130 mmol). ¹H NMR (300 MHz, CD₂Cl₂): δ 7.42-7.58 (m, 12H, PPh₂ and Ar-H), 7.31 (t, J = 8.0 Hz, 1H, Ar-H), 7.20 (t, J = 7.9 Hz, 1H, Ar-H), 6.08 (br, 2H, N-CH₂), 4.69 (br, 2H, COD), 3.77 (br, 2H, COD), 3.26 (s, 3H, N-CH₃), 2.28 (s, 3H, CH₃), 2.00-2.24 (m, 8H, COD), 2.05 (s, 3H, CH₃), 1.65 (apparent t, J = 4.0 Hz, 2H, Rh-CH₂). ³¹P{¹H} NMR (121 MHz, CD₂Cl₂): δ 26.1 (d, JRh-P = 158.4 Hz, PPh₂), -143.9 (septet, JP-F = 708 Hz, PF₆). ¹³C NMR (75 MHz, CD₂Cl₂): δ 157.5 (d, JP-C = 5.7 Hz, imidazole C2), 138.8 (d, JP-C = 15.6 Hz, ipso-PPh₂), 134.7 (s), 139.9 (d, JP-C = 12.1 Hz, o- or m-PPh₂), 132.2 (s), 132.1 (d, JP-C = 2.1 Hz, Ar-PPh₂), 131.6 (s), 131.3 (d, JP-C = 1.7 Hz, p-PPh₂), 129.8 (d, JP-C = 5.6 Hz, Ar-PPh₂), 129.5 (d, JP-C = 20.6 Hz, Ar-PPh₂), 129.4 (d, JP-C = 9.5 Hz, o- or m-PPh₂), 123.1 (s, imidazole C4/5), 122.7 (s, imidazole C4/5), 97.9 (apparent tr, JP-C = JRh-C = 8.9 Hz, CH of COD), 84.1 (d, JRh-C = 8.6 Hz, CH of COD), 48.8 (JP-C = 17.2 Hz, N-CH₂), 31.9 (s, N-CH₃), 31.6 (d, JP-C = 2.1 Hz, CH₂ of COD), 31.1 (s, CH₂ of COD), 9.8 (s, CH₃), 9.2 (s, CH₃), 8.5 (dd, JP-C = 8.2 Hz, JRh-C = 23.3 Hz, Rh-CH₂). Anal. Calcd for C₃₄H₃₉F₆N₂P₂Rh (FW 754.5): C, 54.12; H, 5.21; N, 3.71; Found: C, 54.31; H, 5.29; N, 3.60.
Observation of a Mixture of Complex 3a and 8

To a solution of [Rh(COD)(OH)]$_2$ (50 mg, 0.108 mmol) in THF (2 ml) was added a suspension of ligand 1a (48.9 mg, 0.108 mmol) in THF (3 ml). The mixture was stirred at room temperature for 6 h and a yellow solution was formed. All volatiles were removed under vacuo and the residue was washed by diethyl ether (3 ml × 2) to form the mixture of 3a and 8 as a yellow solid. The ratio of 3a and 8 was determined to be 1:1.9 by $^1$H NMR. A analogous method was used when [Rh(COD)(OMe)]$_2$ or [Rh(COD)(OEt)]$_2$ were allowed to react with ligand 1a. Selected NMR signals: 3a $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ 6.46 (d, $J = 2.1$ Hz, imidazole H4/5), 6.03 (d, $J = 2.1$ Hz, imidazole H4/5), 5.17 (br, COD), 4.26-4.33 (m, N-CH$_2$); 8 $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ 6.55 (s, imidazole H4/5), 5.18 (br, COD), 4.50-4.57 (m, N-CH$_2$). $^{31}$P {$^1$H} NMR (121 MHz CD$_2$Cl$_2$): $\delta$ 26.5 (8, d, $J_{Rh-P} = 121.1$Hz), 23.1 (3a, d, $J_{Rh-P} = 122.7$ Hz), -144.4 (septet, $J_{P-F} = 706$ Hz, PF$_6^-$). $^{13}$C NMR (100 MHz CD$_2$Cl$_2$): $\delta$ 3a 10.1 (dd, $J = 8.8$, 20.6 Hz, Rh-C); 8:150.3 (dd, $J = 13.9$, 40.0 Hz, Rh-C).

The conversion of 2a to 9

Complex 2a (15.0 mg, 0.02 mmol) and methanol alcohol (4 ul, 0.10 mmol) were dissolved in CD$_2$Cl$_2$ (0.6 mL), and the solution was loaded into a stoppered J-Young NMR tube. The NMR tube was heated at 50°C. The reaction was monitored by $^1$H and $^{31}$P {$^1$H} NMR spectroscopy, 94% conversion was observed after 2 weeks. The pure product 9 was obtained by removal of all volatiles, followed by washing with diethyl ether. A red solid. Yield: 91%.

The complex 9 could also be synthesized by following a method described in Chapter 2.

$^1$H NMR (400 MHz CD$_2$Cl$_2$): $\delta$ 7.46-7.52 (m, 10H, PPh$_2$), 6.69 (s, 1H, imidazole H4/5), 4.92 (br, 2H, COD), 4.46-4.55 (m, 2H, N-CH$_2$), 3.64 (s, 3H, CH$_3$), 3.30 (br, 2H, COD), 2.65-2.71 (m, 2H, P-CH$_2$), 2.54 (s, 3H, CH$_3$), 2.04-2.30 (m, 8H of COD). $^{31}$P {$^1$H} NMR (121 MHz, CD$_2$Cl$_2$): $\delta$ 11.21 (s, PPh$_2$), -144.4 (septet, $J_{P-F} = 706$ Hz, PF$_6^-$). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$): $\delta$ 149.6 (d, $J_{P-C} = 12.1$ Hz, Ir-C), 141.7 (s, imidazole C2), 133.2 (d, $J_{P-C} = $...
11.1 Hz, o- or m-PPh₂), 132.7 (d, $J_{P-C} = 50.7$ Hz, ispo-PPh₂), 130.9 (d, $J_{P-C} = 2.3$ Hz, p-PPh₂), 128.7 (d, $J_{P-C} = 10.2$ Hz, o or m-PPh₂), 125.8 (s, imidazole C4/5), 89.5 (d, $J_{P-C} = 12.3$ Hz, CH of COD), 72.9 (s, CH of COD), 47.8 (d, $J_{P-C} = 2.4$Hz, N-CH₂), 34.4 (s, CH₃), 31.6 (d, $J_{P-C} = 2.9$ Hz, CH₂ of COD), 31.1 (d, $J_{P-C} = 1.9$ Hz, CH₂ of COD), 26.8 (d, $J_{P-C} = 34.6$ Hz, CH₂-P), 9.67 (s, CH₃). Anal. Calcd for C₂7H₃₃F₆IrN₂P₂ (FW 753.7): C, 43.03; H, 4.41; N, 3.72; Found C, 43.71; H, 4.23; N, 4.01.

Acknowledgment. Miss Su Yan’s contribution for Chapter 3. The calculation studies for the electronic properties of different ligand in this chapter were performed by Miss Su.
3.5 References


Chapter 3


Chapter 4. Rh and Ir Complexes of Abnormal N-Heterocyclic Carbenes Derived from Imidazol[1,2-a]pyridine

4.1 Introduction

Ever since their isolation in the free state,1 N-heterocyclic carbenes (NHCs) have attracted increasing attentions as ligands in organometallic chemistry and catalysis and they are rapidly challenging the ubiquitous trivalent phosphines.2-3 In many cases NHC complexes show higher catalytic activities and thermal stability partially owing to the strong NHC-metal bonds and the high δ-donating ability of NHC ligands.4-5 Despite the large number of NHC complexes reported using various synthetic methods,6 the synthesis of NHCs with tunable electronic and steric properties remains a challenge. Consequently, acyclic carbenes7 and six to eight membered,9-10 NHCs have been reported on various platforms besides the more common five-membered imidazole or benzimidazole-based NHC systems.

In 2002 Crabtree and co-workers discovered metalation could take place at the C(4/5) position of imidazoliums,11 rather than the more common classical C(2) positions. It was also subsequently shown that NHCs in this mode are more donating than the most donating neutral ligands such as P(3)Bu3 and the classical NHCs.12 The resulting zwitterionic ligands can be treated as “abnormal” or non-classical NHCs (Figure 4.1). Several groups have reported chelating or monodentate NHCs with this binding mode ever since (Figure 4.1).13-18 The relative rarity of this binding mode of NHCs is possibly due to the synthetic challenges since the C(4/5)-H is less acidic than the C(2)-H. So far, most of the non-classical NHCs are part of chelating systems if the active C(2) positions are left unblocked. Applications of these abnormal NHC complexes in catalysis are rather limited. Nolan has shown that a palladium non-classical NHC complex is more active in catalyzing Suzuki reactions than its classic analogue.14
Here we report the synthesis, characterization, solution dynamics, and electronic effects of a new type of abnormal NHC ligands based on imidazol[1,2-\(a\)]pyridine, where metallation can be directed to either the C(2) or C(3) position of this heterocyclic. Abnormal NHCs of this type have great tunability by varying the N-alkyl groups or fusing the pyridine moiety with an aromatic ring.

4.2 Results and Discussion

4.2.1 N-alkylated imidazol[1,2-\(a\)]pyridine

N-Alkylation of imidazol[1,2-\(a\)]pyridines takes place at the 1- position to give imidazol[1,2-\(a\)]pyridiums, structurally analogous to imidazoliums which are commonly used as NHC precursors. Base treatment of an imidazol[1,2-\(a\)]pyridium can in principle lead to
the deprotonation at the H-2 or H-3 position. H-2 should be more acidic since the resulting anion can be further delocalized to the pyidine ring (Figure 4.2), while that obtained from H-3 deprotonation is only localized in the imidazole ring.

![Figure 4.2 Deprotonation at the 2- vs 3-position.](image)

4.2.2 Metalation at 2-position

4.2.2.1 Preparation

Imidazolium halides with blocked C-2 positions have been used as precursors to abnormal NHCs for the synthesis of transition metal complexes via the silver transmetalation.\textsuperscript{12} Therefore, initial attempts were made by reacting 1-benzylimidazo[1,2-\textit{a}]pyridinium chloride with Ag\textsubscript{2}O, and metalation at the more acidic C-2 position was anticipated (eq 4.1). However, only unidentifiable species were obtained. We reasoned that blocking the 3-position with an alkyl group should enhance the regioselectivity of silver carbene formation and it might also offer steric protection against decomposition such as protonolysis.\textsuperscript{12a}

\[
\text{N} \quad \text{N} \quad \text{R}
\]

\[
\text{Cl}^{-} \quad 0.5 \text{Ag}_{2}\text{O} \quad \text{CH}_{2}\text{Cl}_{2} \quad \text{decomposition} \quad (4.1)
\]

Hence 3-methylimidazo[1,2-\textit{a}]pyridine and 1-methyl-imidazo[1,2-\textit{a}]quinoline were synthesized according to literature reports.\textsuperscript{19,20} Alkylation using \textit{para} substituted benzyl chlorides gives imidazo[1,2-\textit{a}]pyridinium ions \textbf{1a-d} and \textbf{4} (eq 4.2, 4.3). Indeed, stirring a mixture of Ag\textsubscript{2}O (0.5 equiv) and \textbf{1a-d} in CH\textsubscript{2}Cl\textsubscript{2} afforded the corresponding silver carbene
chlorides, which were used as transmetalation reagents without isolation (Scheme 4.1). Addition of 0.5 equiv of \([M(COD)Cl]_2\) \((M = \text{Ir or Rh})\) immediately afforded complexes 2a-d and 3a-d with isolated yields ranging from 79\% to 91\%. Analogously, compound 4 was also successfully applied as a carbene precursor leading to iridium abnormal NHC complex 5 (Scheme 4.1). It should be noted that no silver carbene complex could be obtained when 1-allyl-3-methylimidazo[1,2-\(a\)]pyridinium or 1-\(n\)-propyl-3-methylimidazo[1,2-\(a\)]pyridinium chloride was treated with Ag\(_2\)O. The higher acidity of the C(2)-\(H\) in 1a-d might be accountable.

\[
\begin{align*}
1a: R &= H \\
1b: R &= \text{OMe} \\
1c: R &= F \\
1d: R &= \text{CF}_3 \\
2a: R &= H, M = \text{Ir} \\
2b: R &= \text{OMe}, M = \text{Ir} \\
2c: R &= F, M = \text{Ir} \\
2d: R &= \text{CF}_3, M = \text{Ir} \\
3a: R &= H, M = \text{Rh} \\
3b: R &= \text{OMe}, M = \text{Rh} \\
3c: R &= F, M = \text{Rh} \\
3d: R &= \text{CF}_3, M = \text{Rh}
\end{align*}
\]

\textbf{Scheme 4.1}. Synthesis of Ir and Rh Abnormal NHC Complexes via Silver Transmetalation
4.2.2.2 NMR Spectroscopy

All these rhodium and iridium NHC complexes were fully characterized by NMR spectroscopy and complexes 3a and 3d were further analyzed by X-ray crystallography. In the $^1$H NMR spectra, all the methylene protons give AB quartet systems in CDCl$_3$, indicative of C$_1$ symmetry for all the molecules. No line broadening of the CH$_2$ signals was observed when the NMR sample was heated up to 60 °C in CDCl$_3$, which suggests that the rotation along Ir-C$_{carbene}$ carries quite a high barrier.$^{12a}$ However, when measured in CD$_2$Cl$_2$, the appearance of the methylene proton signals of 3a and 3d can be quite different and they are generally closer in chemical shifts. For example, the CH$_2$ protons in 3c are accidentally equivalent at $\delta$ 6.18 (s, 2H) in CD$_2$Cl$_2$, while an AB pattern ($\delta$ 6.40 and 6.10, $^2$J$_{HH}$ = 16 Hz) was observed for them in CDCl$_3$. In the $^{13}$C NMR spectra, the carbene C atoms resonate in a narrow range of $\delta$ 167 to 170, which are slightly more deshielded compared to those in abnormal NHC complexes derived from imidazoliums.$^{12a}$

4.2.2.3 X-ray Crystallography.

Single crystals of 3a and 3d suitable for X-ray crystallographic analysis were obtained by layering their CH$_2$Cl$_2$ solutions with pentane. Crystallographic analysis confirmed the C-2 [labeled as C(9) in Figures 4.3 and 4.4] binding mode in both 3a (Figure 4.3) and 3d (Figure 4.4). The coordination sphere is square planar for both complexes, and the selected bond lengths, bond angles, and torsion angles are shown in Table 4.1. As expected for NHCs, the Rh-C$_{carbene}$ distance is 2.039(2) Å for 3a and 2.021(5) Å for 3d and is consistent with a Rh-C single bond. The most remarkable difference between these two structures probably lies in their torsion angles [N(1)-C(9)-Rh(1)-Cl(1)]. The NHC ring in complex 3d (-81.3° torsion angle) is nearly perpendicular to the coordination plane, while in complex 3a there is significant deviation from this orientation (-70.6° torsion angle).
Figure 4.3. ORTEP diagram of 3a, showing 50% probability ellipsoids.

Figure 4.4. ORTEP diagram of 3d, showing 50% probability ellipsoids.
Table 4.1 Selected bond lengths and angles for complex 3a and 3d.

<table>
<thead>
<tr>
<th></th>
<th>3a</th>
<th>3d</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bond lengths (Å)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rh(1)-C(9)</td>
<td>2.039(2)</td>
<td>2.021(5)</td>
</tr>
<tr>
<td>Rh(1)-C(1)</td>
<td>2.097(2)</td>
<td>2.101(5)</td>
</tr>
<tr>
<td>Rh(1)-C(2)</td>
<td>2.110(2)</td>
<td>2.103(6)</td>
</tr>
<tr>
<td>Rh(1)-C(5)</td>
<td>2.194(2)</td>
<td>2.222(6)</td>
</tr>
<tr>
<td>Rh(1)-C(6)</td>
<td>2.218(2)</td>
<td>2.189(6)</td>
</tr>
<tr>
<td>C(9)-N(1)</td>
<td>1.412(2)</td>
<td>1.422(7)</td>
</tr>
<tr>
<td>C(9)-C(10)</td>
<td>1.380(2)</td>
<td>1.368(8)</td>
</tr>
<tr>
<td>N(2)-C(16)</td>
<td>1.368(2)</td>
<td>1.383(7)</td>
</tr>
<tr>
<td><strong>Bond angles (deg)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(9)-Rh(1)-Cl(1)</td>
<td>89.83(5)</td>
<td>89.72(14)</td>
</tr>
<tr>
<td>N(1)-C(9)-C(10)</td>
<td>104.62(15)</td>
<td>104.3(4)</td>
</tr>
<tr>
<td><strong>Torsion angle (deg)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(1)-C(9)-Rh(1)-Cl(1)</td>
<td>-70.6</td>
<td>-81.3</td>
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</table>
Table 4.2 Crystallographic Data for Complexes 3a, 3d, and 9d

<table>
<thead>
<tr>
<th></th>
<th>3a</th>
<th>3d</th>
<th>9d</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>empirical formula</strong></td>
<td>C$<em>{23}$H$</em>{26}$ClN$_2$Rh</td>
<td>C$<em>{23}$H$</em>{25}$ClF$_3$N$_2$Rh</td>
<td>C$<em>{18}$H$</em>{13}$ClF$_3$IrN$_2$O$_2$</td>
</tr>
<tr>
<td><strong>formula weight</strong></td>
<td>468.82</td>
<td>536.82</td>
<td>573.95</td>
</tr>
<tr>
<td><strong>temperature</strong></td>
<td>173(2) K</td>
<td>223(2)</td>
<td>173(2) K</td>
</tr>
<tr>
<td><strong>crystal system</strong></td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td><strong>space group</strong></td>
<td>P2(1)/c</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>a (Å)</strong></td>
<td>15.6914(6)</td>
<td>11.7872(4)</td>
<td>14.2118(6)</td>
</tr>
<tr>
<td><strong>b (Å)</strong></td>
<td>8.8419(3)</td>
<td>16.2148(6)</td>
<td>8.7062(3)</td>
</tr>
<tr>
<td><strong>c (Å)</strong></td>
<td>14.6448(6)</td>
<td>11.9178(4)</td>
<td>15.8811(6)</td>
</tr>
<tr>
<td><strong>α (deg)</strong></td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td><strong>β (deg)</strong></td>
<td>95.747(2)</td>
<td>102.218(2)</td>
<td>110.789(2)</td>
</tr>
<tr>
<td><strong>γ (deg)</strong></td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td><strong>V (Å$^3$)</strong></td>
<td>2021.63(13)</td>
<td>2226.22(13)</td>
<td>1837.05(12)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td><strong>d$_{calc}$ (g/cm$^3$)</strong></td>
<td>1.540</td>
<td>1.602</td>
<td>2.075</td>
</tr>
<tr>
<td><strong>μ (mm$^{-1}$)</strong></td>
<td>0.987</td>
<td>0.926</td>
<td>7.458</td>
</tr>
<tr>
<td><strong>crystal size (mm)</strong></td>
<td>0.30 x 0.20 x 0.20</td>
<td>0.26 x 0.24 x 0.14</td>
<td>0.14 x 0.12 x 0.10</td>
</tr>
<tr>
<td><strong>total, unique no. of rflns</strong></td>
<td>25614, 6127</td>
<td>23557, 4382</td>
<td>20651, 4816</td>
</tr>
<tr>
<td><strong>R(int)</strong></td>
<td>0.0274</td>
<td>0.0562</td>
<td>0.0334</td>
</tr>
<tr>
<td><strong>data, restraints, parameters</strong></td>
<td>6127, 0, 245</td>
<td>4382, 85, 309</td>
<td>4816, 129, 249</td>
</tr>
<tr>
<td><strong>R, R$_w$ (all data)</strong></td>
<td>0.0261, 0.0338</td>
<td>0.0555, 0.0645</td>
<td>0.0287, 0.0365</td>
</tr>
<tr>
<td><strong>GOF</strong></td>
<td>1.089</td>
<td>1.194</td>
<td>1.044</td>
</tr>
<tr>
<td><strong>peak and hole (eÅ$^{-3}$)</strong></td>
<td>0.577, -0.573</td>
<td>1.354, -0.888</td>
<td>1.651, -1.042</td>
</tr>
</tbody>
</table>
4.2.3 Metalation at the Complementary Position

Although H-3 is less acidic than H-2 in imidazo[1,2-\(\alpha\)]pyridiniums, we reason that blocking the 2- position by a withdrawing group such as a phenyl group should favor the deprotonation of H-3, and the resulting negative charge can be stabilized (Scheme 4.2). Carbene precursor 7 was then synthesized by the N-alkylation of 6 followed by halide exchange using a chloride exchange resin. Indeed, silver transmetalation to iridium was successful, and complex 8 was isolated in 71% yield. Fluxionality in the NMR time scale was observed for 8. In the NMR spectrum (CD\(_2\)Cl\(_2\)) at -20 °C, all the methylene protons in the \(^n\text{Bu}\) group are sharp and diastereotopic, while they are all broad at 25 °C and coalescence of the NCH\(_2\) signals was observed. This clearly shows that the barrier of the Ir-C carbene bond rotation is lower. In the \(^{13}\text{C}\) NMR spectrum of 8, the carbene C atom resonates at \(\delta\) 151.9, and it is more shielded than those in 2a-d. It is worth mentioning that no analogous silver carbene could be obtained when 1-\(n\)-butyl-2-methylimidazo[1,2-\(\alpha\)]pyridinium chloride was treated with Ag\(_2\)O. The acidity of H-3 might play an important role here, although steric differences might also be accountable.

**Scheme 4.2. Metalation at the 3-position of an Imidazo[1,2-\(\alpha\)]pyridinium**
4.2.4 Iridium Dicarbonyl Complexes

4.2.4.1 Preparation

The electronic effects of these new ligands were analyzed for all the iridium complexes. Iridium carbonyl complexes of the generic structure Ir(NHC)(CO)₂Cl were synthesized by bubbling CO (1 atm, 15 min) through solutions of 2a-d, 5, and 8, resulting in the substitution of the COD ligand. The cis geometry proposed in Figure 4.5 is supported by IR spectroscopy, which shows two CO stretching (symmetric and asymmetric) vibrations of similar intensity. In equivalent CO carbon atoms have also been observed by ¹³C NMR spectroscopy.

![Image of iridium complexes](image)

**Figure 4.5** Iridium abnormal NHC carbonyl complexes.

4.2.4.2 X-ray analysis

Single crystals of 9d suitable for X-ray analysis were obtained by layering its CH₂Cl₂ solution with pentane. As shown in Figure 4.6, the two CO ligands are in a cis arrangement. The NHC plane is nearly perpendicular to the iridium coordination plane. The Ir-C carbene distance is 2.075(4) Å and is comparable to those in Ir-NHC complexes. The Ir(1)-C(18) distance [1.899(4) Å] is significantly longer than the Ir(1)-C(17) distance [1.841(6) Å], undoubtedly due to the high trans influence of the NHC ligand. (Table 4.2, 4.3)
Figure 4.6 ORTEP diagram of 9d, showing 50% probability ellipsoids.

Table 4.3 Selected Bond Lengths (Å) and Bond Angles (deg) of 9d

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir(1)-C(1)</td>
<td>2.075(4)</td>
</tr>
<tr>
<td>Ir(1)-C(18)</td>
<td>1.899(4)</td>
</tr>
<tr>
<td>Ir(1)-C(17)</td>
<td>1.841(6)</td>
</tr>
<tr>
<td>Ir(1)-Cl(1)</td>
<td>2.075(4)</td>
</tr>
<tr>
<td>C(1)-C(2)</td>
<td>1.364(5)</td>
</tr>
<tr>
<td>C(1)-N(1)</td>
<td>1.413(5)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond angles (deg)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C(17)-Ir(1)-C(18)</td>
<td>90.3(2)</td>
</tr>
<tr>
<td>C(1)-Ir(1)-Cl(1)</td>
<td>88.53(11)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Torsion angle (deg)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)-C(1)-Ir(1)-Cl(1)</td>
<td>91.72</td>
</tr>
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</table>
4.2.4.3 Solution Dynamics

The methylene protons of complexes 9a-d and 11 all showed broad singlet signals in the $^1$H NMR spectrum at room temperature (CDCl$_3$), indicated that the rotation along the Ir-C$_{\text{carbene}}$ bond is within the NMR time scale. Decoalescence of the CH$_2$ peaks was observed for 9a-d and 11 at temperatures below -10 °C. VT NMR (-50 to -20 °C) and line shape analysis of the CH$_2$ signals of 9a afforded enthalpy of activation $\Delta H^\neq = 14.4$ kcal/mol for the rotation along Ir-carbene bond. (Table 4.4, Figure 4.7)

Table 4.4 VT NMR Measurement of Fluxionality of Complex 9a

<table>
<thead>
<tr>
<th>T (K)</th>
<th>1/T×1000 (1/K)</th>
<th>$\Delta$(w$_{1/2}$) (Hz)$^a$</th>
<th>k (Hz)</th>
<th>ln(k/T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>241.19</td>
<td>4.146</td>
<td>1.17</td>
<td>3.676</td>
<td>-4.187</td>
</tr>
<tr>
<td>245.18</td>
<td>4.0786</td>
<td>2.14</td>
<td>6.723</td>
<td>-3.596</td>
</tr>
<tr>
<td>249.29</td>
<td>4.0114</td>
<td>3.39</td>
<td>10.65</td>
<td>-3.153</td>
</tr>
<tr>
<td>253.35</td>
<td>3.947</td>
<td>5.28</td>
<td>16.59</td>
<td>-2.726</td>
</tr>
</tbody>
</table>

$^a$ w$_0$=3.740Hz (228.8K)

Figure 4.7 The Erying Plot for the Fluxionality of Complex 9a$^a$

$y = -7269.8x + 25.996$

$R^2 = 0.9947$

$^a$ The slope of this line is $\Delta H^\neq /R$, and the intercept is [$\Delta S^\neq /R + \ln(k_b/h)$]
The appearance of methylene protons signals for **10** is, however, significantly different from that of **9a-d** or **11**. Although they are broad \( (W_{1/2} = 12.4 \text{ Hz}) \) at room temperature, these signals are not coalesced and an AB pattern was observed \((\delta 6.27 \text{ and } 5.82, J_{HH} = 15.4 \text{ Hz})\), indicating a higher barrier of rotation along the Ir-C{\text{carbene}} here. Indeed, VT NMR (-10 to 25 °C) line shape analysis of those CH\(_2\) signals of **10** afforded \( \Delta H^\circ = 17.9 \text{ kcal/mol} \) for the rotation along the Ir-C{\text{carbene}} bond. (Table 4.5, Figure 4.8)

### Table 4.5 VT NMR Measurement of Fluxionality of Complex **10**

<table>
<thead>
<tr>
<th>T (K)</th>
<th>1/T×1000 (1/K)(^a)</th>
<th>(\Delta W_{1/2}) (Hz)</th>
<th>k (Hz)</th>
<th>ln(k/T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>277.84</td>
<td>3.599</td>
<td>1.050</td>
<td>3.299</td>
<td>-4.433</td>
</tr>
<tr>
<td>282.33</td>
<td>3.542</td>
<td>1.691</td>
<td>5.312</td>
<td>-3.973</td>
</tr>
<tr>
<td>287.0</td>
<td>3.484</td>
<td>2.896</td>
<td>9.098</td>
<td>-3.451</td>
</tr>
<tr>
<td>291.0</td>
<td>3.436</td>
<td>4.606</td>
<td>14.47</td>
<td>-3.001</td>
</tr>
<tr>
<td>295.0</td>
<td>3.39</td>
<td>7.265</td>
<td>22.82</td>
<td>-2.559</td>
</tr>
</tbody>
</table>

\(^a\) \(w_0 = 2.805 \text{Hz} \) (266K)

### Figure 4.8 The Erying Plot for the Fluxionality of Complex **10\(^a\)**

![Erying Plot](image)

\(^a\) The slope of this line is \(\Delta H^\circ / R\), and the intercept is \([\Delta S^\circ / R + \ln(k_0/h)]\)
The barrier of rotation along Ir-C_{carbene} of complex 10 is clearly higher than that in 9a. It follows that the steric differences between the NHC ligands in 10 and 9a are rather small; therefore, the differences of the barrier of rotation along the Ir-C_{carbene} bond is very likely electronic in origin. The significantly higher barrier of bond rotation in 10 is ascribed to a higher bond order of the Ir-C_{carbene} bond here. With the presence of an extra fused ring, this imidazo[1,2-a]quinoline-derived NHC ligand should be a better π-acceptor and consequently less electron-donating (Figure 4.9). Hence the Ir-C bond in 10 has more double-bond character as a result of the back-donation and carries a higher barrier of rotation. Further evidence to support the less electron-donating nature of the NHC ligand in 10 has been obtained from IR analysis of an iridium biscarbonyl complex (Table 4.5).

As a comparison with normal NHC complexes of transition metals, there have been debates on the significance of π-back-bonding effects in these complexes.\textsuperscript{21a} Herrmann\textsuperscript{4a} reported that π-back-bonding in NHC-transition metal complexes was negligible, and this conclusion was supported by theoretical studies.\textsuperscript{21b} This idea of negligible back-donation is, however, challenged by some recent reports.\textsuperscript{21a,c,d} Heinicke also reported that annulation of normal NHCs could efficiently increase the π-back-bonding interactions as a result of extended NHC π-systems,\textsuperscript{21e,f} a scenario directly analogous to ours in abnormal NHC complexes.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4_9}
\caption{Back-donation to an abnormal NHC derived from imidazo[1,2-a]quinoline.}
\end{figure}
4.2.4.4 Electronic Effects

The infrared carbonyl stretching frequencies of the rhodium and iridium complexes cis-M(CO)₂(L)Cl well documented as a good measure of the donor ability of the L ligand: the more basic the ligand, the lower the observed ν(CO) values. In Table 4.6, the carbonyl frequencies of Ir(CO)₂(NHC)Cl are listed and compared with those of analogous complexes. The average CO stretching frequency \[ ν_{av}(CO) = 1999 \text{ cm}^{-1} \] of 9a is the lowest among all the iridium complexes in this work and is lower than those in all related complexes in the literature. The fact that \[ ν_{av}(CO) \] of 10 (2015 cm\(^{-1}\)) is significantly higher than that of 9a (1999 cm\(^{-1}\)) indicates that the NHC in 10 is less electron-donating, consistent with the afore-mentioned VT NMR data, and the imidazo[1,2-a]quinoline-derived NHC in 10 can be best described as a stronger π-acceptor. Furthermore, the NHC ligand becomes less donating when a OMe, F, or CF\(_3\) group is introduced to the para position of the benzyl group. The difference between the \[ ν_{av}(CO) \] of 9a and that of 9b or 9d is surprisingly large considering that the metal center and the para-substituted aromatic groups are isolated by a methylene group. As a contrast, changing the N-alkyl/aryl group of imidazole-based normal NHC ligands, however, has very limited influence on the electronic effects.\(^{24}\) A plot of the average CO frequency of 9a-d against the inductive substituent constant\(^{23}\) (σ) of the para substituent is shown in Figure 4.10. The good correlation here (\(R^2 = 0.99\)) indicates that electron density on the iridium is inductively and sensitively tuned by the para substituent.

Table 4.6 shows the wide tunability of these new abnormal NHCs. They can be tuned to meet the donating level of abnormal NHCs derived from imidazolium ions (considering the resolution of 4 cm\(^{-1}\) in IR spectroscopy) or the relatively less electron-donating normal NHCs (imidazolin-2-ylidenes).
Table 4.6 Carbonyl Stretching Frequencies for Compounds cis-Ir(L)(CO)₂Cl

<table>
<thead>
<tr>
<th>Ir(L)(CO)₂Cl</th>
<th>ν(CO) (cm⁻¹)</th>
<th>νav(CO) (cm⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2041, 1957</td>
<td>1999</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>2054, 1986</td>
<td>2020</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>2049, 1967</td>
<td>2008</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>2050, 1984</td>
<td>2017</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>2050, 1981</td>
<td>2015</td>
<td>this work</td>
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<td></td>
<td>2046, 1965</td>
<td>2006</td>
<td>this work</td>
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<td></td>
<td>2045, 1961</td>
<td>2003</td>
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</tr>
<tr>
<td></td>
<td>2059, 1974</td>
<td>2017</td>
<td>12c</td>
</tr>
<tr>
<td></td>
<td>2062, 1978</td>
<td>2020</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>2072, 1989</td>
<td>2031</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>2058, 1973</td>
<td>2016</td>
<td>9</td>
</tr>
<tr>
<td>PCy₃</td>
<td>2072, 1984</td>
<td>2028</td>
<td>12c</td>
</tr>
</tbody>
</table>
Figure 4.10. Correlation between the average CO frequency and the inductive effect of the
para substituent in complexes 9a-d.

4.3 Conclusion

Rhodium and iridium complexes of a new type of abnormal NHCs derived from
imidazo[1,2-a]pyridinium ions have been prepared via silver transmetalation and fully
characterized by NMR and IR spectroscopy and X-ray crystallography. Metalation can
take place at the C-2 or the C-3 positions provided that the other position is appropriately
blocked. The electron-donating abilities of these new NHC ligands have been analyzed
from the $\nu_{\text{av}}$(CO) values of their corresponding iridium dicarbonyl complexes, which show
a wide range of tunability. Both VT NMR studies and CO stretching frequency values
support the $\pi$-accepting ability of an NHC ligand derived from imidazo[1,2-a]quinoline.
The wide range of tunability of these abnormal NHCs is a desirable characteristic in many
catalytic applications, and further studies on the catalytic properties of these carbene
complexes are currently in progress.
4.4 Experimental Section

General Consideration:

All manipulations were performed using standard Schlenk techniques except where otherwise noted. All solvents and chemicals were used as received without any further treatment if not noted otherwise. NMR spectra were obtained on a Bruker DPX 300 MHz, AMX400 MHz or 500 MHz spectrometer. All spectra were collected at 298K unless otherwise specified. The temperature for variable temperature NMR was carried out on Bruker DPX300 MHz and calibrated by CIL 4% methanol in methanol-d4. The chemical shift is given as dimensionless $\delta$ values referenced to TMS for $^1$H and $^{13}$C. Elemental analyses were performed in house. HRMS spectra were obtained in EI or ESI mode on a Finnigan MAT95XP GC/HRMS system (Thermo Electron Corp.). X-ray crystallographic analysis was performed on a Bruker X8 APEX diffractometer. IR spectra were measured on a SHIMADZU IRPESTIGE-21 FTIR spectrometer from 4000 to 600 cm$^{-1}$.

General Method for the Synthesis of 1a-d

3-Methylimidazol[1,2-a]pyridine (150 mg, 1.136 mmol) and para substituted benzyl chloride (1.7 mmol) were dissolved in CH$_3$CN (5 ml) and the mixture was stirred under reflux for 12 h. After reaction, the solvent was removed under vacuo. The white solids obtained were washed several times with diethyl ether and used for complex formation without further purification.

**Compound 1a.** Yield 86% (white solid, 252 mg, 0.974 mmol). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.86 (d, $J = 6.8$ Hz, 1H), 8.43 (d, $J = 9.1$ Hz, 1H), 8.33 (s, 1H), 8.06 (t, $J = 7.4$ Hz, 1H), 7.60 (t, $J = 6.8$ Hz, 1H), 7.45-7.47 (m, 2H), 7.33-7.36 (m, 3H), 5.80 (s, 2H, CH$_2$), 2.59 (s, 3H. CH$_3$). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 138.9, 135.6, 133.7, 129.4, 128.9, 128.4, 128.2, 124.1, 122.9, 117.4, 111.6, 50.0, 9.1. HRMS (ESI$^+$): 223.1266 Caled for [C$_{15}$H$_{15}$N$_2$]$^+$: 223.1235.

**Compound 1b.** Yield 91% (white solid, 298 mg, 1.03 mmol). $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ 8.83 (d, $J = 6.8$ Hz, 1H), 8.44 (d, $J = 9.2$ Hz, 1H), 8.26 (s, 1H), 8.07 (t, $J = 8.5$ Hz, 1H), 7.60 (t, $J = 7.0$ Hz, 1H), 7.44 (d, $J = 8.7$ Hz, 1H), 6.95 (d, $J = 8.7$ Hz, 1H),
5.68 (s, 2H, CH₂), 3.74 (s, 3H, OCH₃), 2.58 (s, 3H, CH₃). ¹³C NMR (75 MHz, DMSO-d₆) δ 159.9, 138.8, 133.6, 130.2, 128.1, 127.4, 124.0, 122.7, 117.3, 114.7, 111.6, 55.7, 49.6, 9.0. HRMS (ESI⁺): 253.1349. Calcd for [C₁₆H₁₇N₂O⁺]: 253.1341.

**Compound 1c.** Yield 87% (white solid, 273 mmol, 0.99 mmol). ¹H NMR (300 MHz, DMSO-d₆) δ 8.82 (d, J = 6.8 Hz, 1H), 8.42 (d, J = 9.2 Hz, 1H), 8.26 (d, J = 0.8 Hz, 1H), 8.05 (t, J = 8.2 Hz, 1H), 7.52-7.61 (m, 3H), 7.22 (t, J = 8.8 Hz, 2H), 5.75 (d, J = 0.7 Hz, 2H, CH₂), 2.57 (d, J = 0.7 Hz, 3H, CH₃). ¹⁹F NMR (282 MHz, DMSO-d₆) δ -113.4. ¹³C NMR (75 MHz, DMSO-d₆) δ 162.6 (d, J_F-C = 243.5 Hz), 138.9, 133.8, 131.7 (d, J_F-C = 3.1 Hz), 130.9 (d, J_F-C = 8.4 Hz), 128.1, 124.1, 122.7, 117.4, 116.2 (d, J_F-C = 21.5 Hz), 111.5, 49.3, 9.0. HRMS (ESI⁺): 241.1114. Calcd for [C₁₅H₁₄N₂F⁺]: 241.1141.

**Compound 1d.** Yield 93% (white solid, 345 mg, 1.06 mmol). ¹H NMR (400 MHz, DMSO-d₆) δ 8.87 (d, J = 6.5 Hz, 1H), 8.41 (d, J = 9.2 Hz, 1H), 8.32 (s, 1H), 8.08 (t, J = 7.1 Hz, 1H), 7.77 (d, J = 8.2 Hz, 2H), 7.61-7.70 (m, 3H), 5.92 (s, 2H, CH₂), 2.60 (s, 3H, CH₃). ¹⁹F NMR (282 MHz, DMSO-d₆) δ -61.1 ppm. ¹³C NMR (100 MHz, DMSO-d₆) δ 140.2, 139.2, 133.9, 129.4 (q, J_F-C = 31.7 Hz), 129.1, 128.2, 126.2 (q, J_F-C = 3.7 Hz), 124.5 (q, J_F-C = 270.6 Hz, CF₃), 124.3, 122.9, 117.5, 111.5, 49.4, 9.1. HRMS (ESI⁺): 291.1058 Calcd for [C₁₆H₁₄N₂F³⁺]: 291.1109.

**Synthesis of 4-I:** The mixture of 3-amino quinoline (1.44 g, 10.0 mmol), triethyl orthoformate (1.48 g, 10.0 mmol) and nitroethane (0.71 g, 10.0 mmol) was stirred under reflux for 16 h. The pure product was obtained as yellow solid (0.71 g, 3.1 mmol) after chromatography on silica gel using hexanes/ethyl acetate as eluent. Yield: 31%. ¹H NMR (400 Hz, CDCl₃): δ 10.84 (d, J = 11.0Hz, 1H), 8.50 (d, J = 12.3Hz, 1H), 8.11 (d, J = 8.6 Hz, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.69 (t, J = 7.8 Hz, 1H), 7.45 (t, J = 7.5 Hz, 1H), 7.01 (d, J = 8.7Hz, 1H), 2.26 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 149.1, 147.0, 139.2, 133.6, 130.6, 127.7, 127.6, 126.0, 125.3, 122.9, 112.9, 16.5.

**Synthesis 4-II:** 4-I (400 mg, 1.75 mmol) was dissolved in 40% sulphuric acid solution in methanol (10 ml) and the mixture was stirred under reflux for 6 h. After reaction, the mixture was diluted with ice-water, neutralised by sodium carbonate, and
extracted by dichloromethane. The organic phase was dried by sodium sulfate and solvent was removed under vacuo. The pure product could be obtained by chromatography on silica gel using hexanes/ethyl acetate as eluent with the yield 40% (127 mg, 0.70 mmol).

$^1$H NMR (400 Hz, CDCl$_3$): $\delta$ 8.28 (d, $J$ = 8.6 Hz, 1H), 7.68 (d, $J$ = 8.4 Hz, 1H), 7.13-7.50 (m, 5H), 2.82 (s, 3H).

**Compound 4:** 4 was synthesized through an analogous method of 1 by reacting 4-II (80 mg, 0.439 mmol) and benzyl chloride (80 mg, 0.63 mg). Yield: 90% (white solid, 122 mg, 0.395 mmol). $^1$H NMR (400 Hz, DMSO-$d_6$): $\delta$ 8.73 (d, $J$ = 8.7 Hz, 1H), 8.50 (d, $J$ = 9.6 Hz, 1H), 8.34 (d, $J$ = 9.6 Hz, 1H), 8.28 (br, 2H), 7.99 (t, $J$ = 7.5 Hz, 1H), 7.84 (t, $J$ = 7.5 Hz, 1H), 7.30-7.47 (m, 5H), 5.85 (s, 2H, CH$_2$), 3.05 (s, 3H, CH$_3$). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 139.4, 135.3, 135.2, 133.7, 132.1, 130.7, 129.4, 129.0, 128.3, 128.2, 127.8, 124.9, 123.3, 118.1, 109.7, 50.3, 14.9. HRMS (ESI$^+$): 273.1359 Calcd for [C$_{19}$H$_{17}$N$_2$]: 273.1386.

**Compound 6:** The mixture of 4-methylpyridin-2-amine (1.08 g, 10 mmol), 2-bromoacetophenone (1.99 g, 10 mmol) and sodium bicarbonate (2.1 g, 15 mmol) in ethanol alcohol (25 ml) was stirred for 3 h under reflux. After removing ethanol alcohol under vacuo, dichloromethane was added to the residue and the inorganic salt was removed by filtration. The pure product could be obtained by removing dichloromethane in 91% yield (yellow solid, 1.89 g, 9.1 mmol). $^1$H NMR (400 Hz, CDCl$_3$): $\delta$ 7.96 (t, $J$ = 7.2 Hz, 3H), 7.77 (s, 1H), 7.44 (t, $J$ = 7.4 Hz, 2H), 7.39 (s, 1H), 7.31 (t, $J$ = 7.4 Hz, 1H), 6.59 (d, $J$ = 6.9 Hz, 1H), 3.40 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 146.2, 145.5, 135.6, 134.0, 128.7, 127.8, 125.9, 124.8, 115.9, 115.0, 107.5, 21.4. HRMS (EI): 208.1039 Calcd for [C$_{14}$H$_{12}$N$_2$]: 208.1000.

**Compound 7:** compound 6 (800 mg, 3.85 mmol) and 1-iodobutane (1.06 g, 5.78 mmol) were dissolved in acetonitrile (15 ml) and the mixture was stirred overnight under reflux. After removing acetonitrile, the residue was washed by diethyl ether to give a yellow solid in 96% yield. Iodide to chloride exchange was performed by stirring a mixture of the iodide salt (200 mg, 0.51 mmol) and DOWEX 21K chloride exchange resin
(2 g) in methanol for 10 h. A residue was obtained after the removal of methanol, to which was added CH₂Cl₂ (20 mL). A clear solution was obtained after filtration. Product 7 was obtained as a white solid after the removal of CH₂Cl₂. Yield: 148 mg (97%). ¹H NMR (400 Hz, CDCl₃): δ 9.54 (d, J = 6.4 Hz, 1H), 8.87 (s, 1H), 7.91 (s, 1H), 7.48-7.55 (m, 5H), 7.19 (d, J = 6.2 Hz, 1H), 4.39 (t, J = 7.5 Hz, 2H, N-C₂H₅), 2.63 (s, 3H, Ph-C₃H₃), 1.61-1.68 (m, 2H, CH₂), 1.17-1.23 (m, 2H, CH₂), 0.76 (t, J = 7.3 Hz, 3H, CH₃). ¹³C NMR (100MHz ,CDCl₃) δ 146.9, 139.5, 137.1, 131.0, 129.9, 129.8, 129.4, 125.1, 119.9, 113.5, 109.7, 45.2, 31.4, 22.3, 19.6, 13.5. HRMS (ESI⁺): 265.1732 Calcd for [C₁₈H₂₁N₂]: 265.1705.

**General Procedure for Synthesis of Rhodium and Iridium Complexes 2, 3, 5, and 8.**

Imidazo[1,2-a]pyridinium chloride (0.2 mmol) was dissolved in dry dichloromethane. Several drops of methanol could be added if the solubility is poor. Silver oxide (23.2 mg, 0.1 mmol) was added, and the mixture was stirred at room temperature in the dark for 0.5–1 h. The mixture was then filtered to give a clear solution, to which was added 0.1 mmol of [M(COD)Cl]₂ (M = Ir or Rh); the mixture was stirred for 1 h. The suspension was filtered through Celite to remove AgCl, and the solvent was removed under reduced pressure. The residue was filtered through a short column of Al₂O₃ using dichloromethane to give analytically pure products after the removal of dichloromethane.

**Complex 2a.** Yield: 93% (red solid, 104 mg, 0.186 mmol). ¹H NMR (300 MHz, CD₂Cl₂) δ 7.94 (d, J = 6.7 Hz, 1H), 7.27-7.36 (m, 5H), 7.16-7.19 (m, 2H), 7.05 (t, J = 6.7 Hz, 1H), 6.07 (d, J = 15.8 Hz, 1H, CH₂), 6.00 (d, J = 15.8 Hz, 1H, CH₂), 5.32 (t, J = 1.0 Hz, 2H, COD), 3.07 (m, 1H, COD), 2.71 (s, 3H, CH₃), 2.68-2.71 (m, 1H, COD), 2.10-2.29 (m, 3H, COD), 1.83-1.87 (m, 1H, COD), 1.59-1.65 (m, 3H, COD), 1.38-1.41 (m, 1H, COD). ¹³C NMR (75 MHz, CD₂Cl₂) δ 168.6 (Ir-C), 140.3, 136.6, 128.6, 127.7, 127.3, 125.0, 122.2, 122.1, 114.6, 109.0, 82.0 (CH of COD), 80.9 (CH of COD), 53.6 (Ph-CH₂), 52.9(CH of COD), 50.8 (CH of COD), 33.7 (CH₂ of COD), 33.3(CH of COD), 29.9 (CH₂ of COD), 29.5(CH₂ of COD), 11.0 (CH₃). Anal. Calcd for C₂₃H₂₆ClIrN₂ (FW, 558.1): C, 49.49; H, 4.70; N, 5.02; Found: C, 49.81; H, 4.52; N, 5.09.
Complex 2b. Yield: 87% (red solid, 102 mg, 0.173 mmol). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.88 (d, $J = 6.6$ Hz, 1H), 7.28-7.30 (m, 2H), 7.13-7.22 (m, 2H), 7.04 (t, $J = 6.4$ Hz, 1H), 6.86 (d, $J = 8.6$ Hz, 2H), 6.16 (d, $J = 15.6$ Hz, 1H, CH$_2$), 5.85 (d, $J = 15.6$ Hz, 1H, CH$_2$), 4.50 (br, 2H, COD), 3.78 (s, 3H, OCH$_3$), 3.07-3.11 (m, 1H, COD), 2.72 (br, 4H, CH$_3$ and 1H of COD), 2.17-2.33 (m, 3H, COD), 1.90-1.92 (m, 1H, COD), 1.51-1.69 (m, 3H, COD), 1.42-1.43 (m, 1H, COD). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 169.1 (Ir-C), 159.2, 140.2, 128.6, 128.4, 124.6, 122.2, 121.7, 114.5, 114.2, 109.2, 82.5 (CH of COD), 81.4 (CH of COD), 77.2, 55.3 (CH of COD), 53.4, 53.1, 50.8 (CH of COD), 34.0 (CH$_2$ of COD), 33.4(CH$_2$ of COD), 30.0(CH$_2$ of COD), 29.4(CH$_2$ of COD), 11.3 (CH$_3$). Anal. Calcd for C$_{24}$H$_{28}$ClIrN$_2$O (FW 588.2) C, 49.01; H, 4.80; N, 4.76; Found: C, 49.21; H, 4.70; N, 4.65.

Complex 2c. Yield: 90% (red solid, 104 mg, 0.18 mmol). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.90 (d, $J = 6.7$ Hz, 1H), 7.32-7.35 (m, 2H), 7.20-7.22 (m, 1H), 7.12-7.14 (m, 1H), 7.07 (t, $J = 6.8$ Hz, 1H), 7.01 (d, $J = 8.6$ Hz, 2H), 6.14 (d, $J = 15.8$ Hz, 1H, CH$_2$), 5.92 (d, $J = 15.8$ Hz, 1H, CH$_2$), 4.50 (t, $J = 2.8$ Hz, 2H, COD), 3.07 (t, $J = 7.1$ Hz, 1H, COD), 2.72 (s, 3H, CH$_3$), 2.68 (td, $J = 7.2$, 3.0 Hz, 1H, COD), 2.10-2.34 (m, 3H, COD), 1.81-1.90 (m, 1H, COD), 1.58-1.71 (m, 3H, COD), 1.39-1.45 (m, 1H, COD). $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -114.2. $^{13}$C NMR (100 MHz CDCl$_3$) $\delta$ 169.1 (C-Ir), 162.3(d, $J_{F-C} = 245.2$ Hz, C-F), 140.2, 132.1(d, $J_{F-C} = 3.2$ Hz), 129.1 (d, $J_{F-C} = 8.1$Hz), 124.9, 122.4, 121.9, 115.7 (d, $J_{F-C} = 21.4$ Hz), 114.7, 108.9, 82.8 (CH of COD), 81.8 (CH of COD), 53.2 (CH of COD), 50.0 (CH$_3$), 50.8 (CH of COD), 33.9 (CH$_2$ of COD), 33.4(CH$_2$ of COD), 30.0(CH$_2$ of COD), 29.4(CH$_2$ of COD), 11.3 (CH$_3$) ppm. Anal. Calcd for C$_{23}$H$_{25}$ClIrN$_2$O (FW 586.1) C, 47.95; H, 4.37; N, 4.86; Found: C, 47.59; H, 4.21; N, 4.70.

Complex 2d. Yield: 86% (red solid, 106 mg, 0.17 mmol). $^1$H NMR (300 MHz, CD$_2$Cl$_2$) $\delta$ 7.97 (d, $J = 6.7$ Hz, 1H), 7.60 (d, $J = 8.2$ Hz, 2H), 7.49 (d, $J = 8.1$ Hz, 2H), 7.25-7.31 (m, 1H), 7.10-7.16 (m, 2H), 6.11 (s, 2H, CH$_2$), 4.36 (br, 2H, COD), 3.07 (t, $J = 6.0$ Hz, 1H, COD), 2.72 (s, 3H, CH$_3$), 2.59-2.65 (m, 1H, COD), 2.11-2.30 (m, 3H, COD), 1.82-1.90 (m, 1H, COD), 1.59-1.69 (m, 3H, COD), 1.39-1.41 (m, 1H, COD). $^{19}$F NMR
(282 MHz, CD$_2$Cl$_2$) δ -62.9. $^{13}$C NMR (75 MHz CD$_2$Cl$_2$) δ 168.6 (Ir-C), 140.7, 140.3, 129.7 (q, $J_{F,C} = 32.2$ Hz), 127.7, 125.5 (q, $J_{F,C} = 3.8$ Hz), 125.4, 124.2 (q, $J_{F,C} = 270.4$ Hz, CF$_3$), 122.5, 122.2, 114.8, 108.7, 82.4 (CH of COD), 81.3 (CH of COD), 53.0 (CH of COD), 52.9 (CH$_2$), 50.8 (CH of COD), 33.8 (CH$_2$ of COD), 33.3(CH$_2$ of COD), 29.9(CH$_2$ of COD), 29.4(CH$_2$ of COD), 10.0 (CH$_3$). Anal. Calcd for C$_{24}$H$_{25}$ClF$_3$IrN$_2$ (FW 626.1) C, 46.04; H, 4.02; N, 4.47; Found: C, 46.16; H, 3.92; N, 4.61.

Complex 3a. Yield: 87% (yellow solid, 82 mg, 0.175 mmol). $^1$H NMR (300 MHz, CD$_2$Cl$_2$) δ 7.91 (d, $J = 6.7$ Hz, 1H), 7.31-7.40 (m, 5H), 7.15-7.21 (m, 2H), 7.05 (t, $J = 6.5$ Hz, 1H), 6.30 (d, $J = 16.0$ Hz, 1H, CH$_2$), 6.10 (d, $J = 15.9$ Hz, 1H, CH$_2$), 4.84 (br, 2H, COD), 3.41 (br, 1H, COD), 3.03 (br, 1H, COD), 2.78 (s, 3H, CH$_3$), 2.20-2.49 (m, 3H, COD), 1.83-1.93 (m, 4H, COD), 1.72 (br, 1H, COD). $^{13}$C NMR (75 MHz CD$_2$Cl$_2$) δ 169.3 (d, $J_{Rh-C} = 46.0$ Hz, Rh-C), 140.4, 136.8, 128.7, 127.7, 127.2, 124.8, 121.8, 121.6 (d, $J_{Rh-C} = 2.5$Hz), 114.3, 108.7, 96.9 (d, $J_{Rh-C} = 6.7$ Hz, CH of COD), 96.2 (d, $J_{Rh-C} = 6.6$ Hz, CH of COD), 68.8 (d, $J_{Rh-C} = 14.7$ Hz, CH of COD), 67.0 (d, $J_{Rh-C} = 14.7$ Hz, CH of COD), 54.0 (Ph-CH$_2$), 32.9 (d, $J_{Rh-C} = 14.3$ Hz, CH$_2$ of COD), 28.9(s, CH$_2$ of COD), 11.3 (CH$_3$). Anal. Calcd for C$_{23}$H$_{26}$ClN$_2$Rh (FW 468.8) C, 58.92; H, 5.59; N, 5.98; Found: C, 58.76; H, 5.60; N, 5.89.

Complex 3b. Yield: 87% (yellow solid, 87 mg, 0.174 mmol). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.85 (d, $J = 6.6$ Hz, 1H), 7.26-7.30 (m, 2H), 7.13-7.22 (m, 2H), 7.01 (td, $J = 6.5$, 2.3 Hz, 1H), 6.86 (d, $J = 8.7$ Hz, 2H), 6.41 (d, $J = 15.7$ Hz, 1H, CH$_2$), 5.93 (d, $J = 15.7$ Hz, 1H, CH$_2$), 4.95 (br, 2H, COD), 3.79 (s, 3H, OCH$_3$), 3.41-3.46 (m, 1H, COD), 3.07-3.12 (m, 1H, COD), 2.78 (s, 3H, CH$_3$), 2.26-2.55 (m, 3H, COD), 2.01-2.06 (m, 1H, COD), 1.85-1.92 (m, 4H, COD). $^{13}$C NMR (75 MHz CDCl$_3$): δ 168.9 (d, $J_{Rh-C} = 45.8$ Hz, Rh-C), 158.2, 139.2, 127.6, 127.5, 123.5, 120.6 (d, $J_{Rh-C} = 2.3$ Hz), 120.5, 113.2, 113.1, 107.9, 96.3 (d, $J_{Rh-C} = 6.8$ Hz, CH of COD), 95.6 (d, $J_{Rh-C} = 6.8$ Hz, CH of COD), 67.9 (d, $J_{Rh-C} = 15.0$ Hz, CH of COD), 65.9 (d, $J_{Rh-C} = 14.8$ Hz, CH of COD), 55.3, 54.3 (Ph-CH$_2$), 32.0 (d, $J_{Rh-C} = 17.9$ Hz, CH$_2$ of COD), 28.9(d, $J_{Rh-C} = 13.3$ Hz, CH$_2$ of COD), 10.6 (CH$_3$). Anal. Calcd for C$_{24}$H$_{28}$ClN$_2$ORh (FW 498.9) C, 57.78; H, 5.66; N, 5.62; Found: C, 57.35; H,
Complex 3c. Yield: 91% (yellow solid, 88.6 mg, 0.182 mmol). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.86 (d, $J = 6.7$ Hz, 1H), 7.32-7.36 (m, 2H), 7.17-7.21 (m, 1H), 7.10-7.12 (m, 1H), 7.01-7.06 (m, 3H), 6.40 (d, $J = 15.9$ Hz, 1H, CH$_2$), 5.92 (d, $J = 15.9$ Hz, 1H, CH$_2$), 4.96 (br, 2H, COD), 3.40-3.43 (m, 1H, COD), 3.02-3.05 (m, 1H, COD), 2.79 (s, 3H, CH$_3$), 2.39-2.51 (m, 2H, COD), 2.24-2.27 (m, 1H, COD), 1.85-2.01 (m, 4H, COD), 1.75-1.76 (m, 1H, COD). $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -114.3. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.9 (d, $J_{Rh-C} = 45.9$ Hz, Rh-C), 162.3 (d, $J_{C-F} = 245.0$ Hz, C-F), 140.2, 132.3 (d, $J_{F-C} = 3.1$ Hz, 128.9 (d, $J_{F-C} = 8.0$ Hz), 124.7, 121.8 (d, $J_{Rh-C} = 2.2$ Hz), 121.6, 115.8 (d, $J_{F-C} = 21.4$ Hz), 114.4, 108.7, 97.5 (d, $J_{Rh-C} = 6.9$ Hz, CH of COD), 96.7 (d, $J_{Rh-C} = 6.9$ Hz, CH of COD), 69.0 (d, $J_{Rh-C} = 15.0$ Hz, CH of COD), 67.0 (d, $J_{Rh-C} = 14.9$ Hz, CH of COD), 53.6 (Ph-CH$_2$), 33.0 (d, $J_{Rh-C} = 13.9$ Hz, CH$_2$ of COD), 28.9 (d, $J_{Rh-C} = 11.6$ Hz, CH$_2$ of COD), 11.7 (CH$_3$). Anal. Calcd for C$_{23}$H$_{25}$ClFN$_2$Rh (FW 486.8) C, 56.75; H, 5.18; N, 5.75; Found: C, 56.49; H, 5.24; N, 5.65.

Complex 3d. Yield: 88% (yellow solid, 94 mg, 0.176 mmol). $^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 7.97 (d, $J = 6.6$ Hz, 1H), 7.65 (d, $J = 8.2$ Hz, 2H), 7.54 (d, $J = 8.1$ Hz, 2H), 7.27-7.31 (m, 1H), 7.11-7.18 (m, 2H), 6.39 (d, $J = 16.3$ Hz, 1H, CH$_2$), 6.25 (d, $J = 16.3$ Hz, 1H, CH$_2$), 4.88 (br, 2H, COD), 3.43-3.46 (m, 1H, COD), 2.99-3.03 (m, 1H, COD), 2.74 (s, 3H, CH$_3$), 2.38-2.58 (m, 2H, COD), 2.21-2.28 (m, 1H, COD), 1.86-2.03 (m, 4H, COD), 1.74-1.76 (m, 1H, COD). $^{19}$F NMR (282 MHz, CD$_2$Cl$_2$) $\delta$ -62.8. $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) $\delta$ 169.4 (d, $J_{Rh-C} = 45.8$ Hz, C-Rh), 141.1, 140.3, 129.7 (q, $J_{C-F} = 32.0$ Hz), 127.7, 125.5 (q, $J_{C-F} = 3.6$ Hz), 125.4, 124.8 (q, $J_{C-F} = 272.0$ Hz, CF$_3$), 122.0, 121.9 (d, $J_{Rh-C} = 2.3$ Hz), 114.6, 108.5, 97.2 (d, $J_{Rh-C} = 6.7$ Hz, CH of COD), 96.5 (d, $J_{Rh-C} = 6.7$ Hz, CH of COD), 69.0 (d, $J_{Rh-C} = 14.9$ Hz, CH of COD), 67.1 (d, $J_{Rh-C} = 14.9$ Hz, CH of COD), 53.4 (Ph-CH$_2$), 32.9 (d, $J_{Rh-C} = 14.1$ Hz, CH$_2$ of COD), 28.8(s, CH$_2$ of COD), 11.3 (CH$_3$). Anal. Calcd for C$_{24}$H$_{25}$ClF$_3$N$_2$Rh (FW 536.8) C, 56.75; H, 5.18; N, 5.75; Found: C, 56.49; H, 5.24; N, 5.65.

Complex 5. Yield: 85% (red solid, 103 mg, 0.17 mmol) $^1$H NMR (300 MHz, CD$_2$Cl$_2$)
δ 8.67 (d, J = 8.8 Hz, 1H ), 7.87 (dd, J = 7.9, 1.3Hz, 1H), 7.75 (td, J = 8.8, 1.6 Hz, 1H), 7.52-7.60 (m, 2H), 7.28-7.36 (m, 5H), 7.16 (d, J = 9.4 Hz, 1H ), 6.12 (s, 2H, CH₂), 4.36 (br, 2H, COD), 3.32 (s, 3H, CH₃), 3.09 (td, J = 6.9, 2.5Hz, 1H, COD), 2.572 (td, J = 7.2, 3.1Hz, 1H, COD), 2.06-2.35 (m, 3H, COD), 1.81-1.93 (m, 1H, COD), 1.58-1.68 (m, 3H, COD), 1.34-1.37 (m, 1H, COD). ¹³C NMR (75 MHz, CD₂Cl₂) δ 168.8 (Ir-C), 140.0, 136.9, 133.2, 130.2, 129.7, 129.1, 128.1, 127.6, 127.4, 126.9, 126.3, 125.0, 117.9, 108.8, 81.9 (CH of COD), 81.0 (CH of COD), 54.0 (CH₂), 53.4 (CH of COD), 51.3 (CH of COD), 34.2 (CH₂ of COD), 33.8(CH₂ of COD), 30.3 (CH₂ of COD), 30.3 (CH₂ of COD), 18.2 (CH₃) ppm. Anal. Calcd for C₂₇H₂₈ClIrN₂ (FW 608.2) C, 53.32; H, 4.64; N, 4.61; Found: C, 53.43; H, 4.71; N, 4.65.

**Complex 8.** Yield: 71% (red solid, 85 mg, 0.142 mmol). ¹H NMR (300 MHz, CD₂Cl₂, 253K) δ 9.23 (d, J = 6.9 Hz, 1H), 7.88 (d, J = 6.8 Hz, 2H), 7.45-7.53 (m, 3H), 7.18 (s, 1H), 6.94 (d, J = 6.9 Hz, 1H), 4.31-4.34 (m, 1H, COD), 4.21-4.24 (m, 1H, COD), 4.11-4.16 (m, 2H, N-CH₂), 2.80-2.83 (m, 1H, COD), 2.52 (s, CH₃), 2.31-2.34 (m, 1H, COD), 1.90-2.13 (m, 3H, COD), 1.72-1.77 (m, 2H, CH₂), 1.44-1.50 (m, 4H, COD), 1.27-1.30(m, 2H, CH₂), 1.24-1.27 (m, 1H, COD), 0.86 (t, J = 7.3 Hz, 3H, CH₃CH₃). ¹³C NMR (75 MHz, CD₂Cl₂, 298K) δ 151.9 (Ir-C), 141.7, 141.0, 136.5, 132.9, 131.4, 130.8, 127.9, 116.1, 107.7, 79.7, 44.3, 31.5, 29.9, 21.5, 19.8, 13.2 ppm. Anal. Calcd C₂₇H₃₂ClIrN₂ (FW 600.2) C, 52.03; H, 4.64; N, 4.61; Found: C, 51.90; H, 5.42; N, 4.55.

**General Method for the Synthesis of Bicarbonyl Complexes 9, 10, and 11.** An iridium COD complex (2, 5, or 8, 0.1 mmol) was dissolved in dry dichloromethane (8 ml) to give a solution, through which CO was bubbled for 15 min. The solvent was removed under vacuum, followed by addition of diethyl ether to afford yellow dicarbonyl complexes.

**Complex 9a.** Yield: 46 mg, 95%. ¹H NMR (300 MHz, CD₂Cl₂): δ 8.07 (d, J = 6.8 Hz, 1H), 7.32-7.48 (m, 7H), 7.22 (t, J = 6.8 Hz, 1H), 5.87 (br, 2H, CH₂), 2.66 (s, 3H, CH₃). ¹³C NMR (75 MHz, CD₂Cl₂): δ 183.4 (CO), 169.6 (Ir-C), 160.1 (CO), 140.3, 135.7, 128.8, 128.1, 127.7, 127.2, 126.4, 123.6, 115.3, 109.9, 53.3, 11.2. FTIR (Nujol), νₘₚ = 2041, 1957 cm⁻¹. Anal. Calcd for C₇₁H₇₄ClIrN₂O₂ (FW 506.0) C, 40.35; H, 2.97; N, 5.54; C,
40.19; H, 3.17; N, 5.51; Found C, 40.31; H, 3.04; N, 5.40.

**Complex 9b.** Yield: 51.5 mg, 96%. $^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 8.05 (d, $J = 6.8$ Hz, 1H), 7.42-7.47 (m, 2H), 7.37-7.39 (m, 2H), 7.20-7.21 (m, 1H), 6.85 (d, $J = 6.7$ Hz, 2H), 5.80 (br, 2H, CH$_2$), 3.76 (s, 3H, OCH$_3$), 2.66 (s, 3H, CH$_3$). $^{13}$C NMR (75 MHz, CD$_2$Cl$_2$): $\delta$ 183.4 (CO), 169.6 (Ir-C), 160.1 (CO), 159.6, 139.5, 130.7, 128.7, 127.7, 127.6, 123.5, 115.3, 114.0, 109.9, 55.2, 52.7, 11.2. FTIR (Nujol), $\nu_{CO} = 2048, 1966$ cm$^{-1}$. Anal. Calcd for C$_{18}$H$_{16}$ClIrN$_2$O$_3$ (FW 536.0) C, 40.31; H, 3.04; N, 5.40. Found C, 40.31; H, 3.04; N, 5.40.

**Complex 9c.** Yield: 51 mg, 97%. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.06 (d, $J = 6.7$ Hz, 1H), 7.44-7.46 (m, 1H), 7.34-7.39 (m, 3H), 7.20-7.24 (m, 1H), 7.02 (t, $J = 7.5$ Hz, 2H), 5.74 (br, 2H, CH$_2$), 2.70 (s, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 182.7 (CO), 169.3 (Ir-C), 162.5 (d, $J_{F-C} = 246$ Hz), 160.6 (CO), 140.1, 131.2 (d, $J_{F-C} = 3.0$ Hz), 129.1 (d, $J_{F-C} = 8.1$ Hz), 127.5, 126.5, 123.4, 115.9 (d, $J_{F-C} = 11.5$ Hz), 115.4, 109.9, 52.7, 11.5. FTIR (Nujol), $\nu_{CO} = 2054, 1986$ cm$^{-1}$.

Anal. Calcd for C$_{17}$H$_{13}$ClFIrN$_2$O$_2$ (FW 524.0) C, 39.02; H, 2.53; Found C, 40.26; H, 3.29; N, 5.47. Found C, 39.02; H, 2.66; N, 5.47.

**Complex 9d.** Yield: 53 mg, 93%. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.07 (d, $J = 6.8$ Hz, 1H), 7.59 (d, $J = 8.0$ Hz, 2H), 7.42-7.48 (m, 2H), 7.28-7.31 (m, 3H), 5.97 (br, 2H, CH$_2$), 2.70 (s, CH$_3$). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 183.4 (CO), 169.2 (Ir-C), 160.8 (CO), 159.6, 139.2, 130.5 (q, $J_{F-C} = 32.4$ Hz), 127.8, 127.5, 126.7, 125.9 (q, $J_{F-C} = 3.8$ Hz), 123.8 (q, $J_{F-C} = 270$ Hz), 123.5, 115.6, 109.7, 52.9, 11.5. FTIR (Nujol), $\nu_{CO} = 2050, 1984$ cm$^{-1}$.

Anal. Calcd for C$_{18}$H$_{13}$ClF$_3$IrN$_2$O$_2$ (FW 574.0) C, 37.39; H, 2.50; N, 5.35; Found C, 39.02; H, 2.66; N, 5.21.

**Complex 10.** Yield: 52 mg, 94%. $^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 8.73 (d, $J = 8.8$ Hz, 1H), 7.98 (d, $J = 7.9$ Hz, 1H), 7.86 (t, $J = 8.8$ Hz, 1H), 7.78 (d, $J = 8.9$ Hz, 1H), 7.69 (t, $J = 8.0$ Hz, 1H), 7.34-7.37 (m, 6H), 6.17 (br, 1H, CH$_2$), 5.80 (br, 1H, CH$_2$), 3.27 (s, 3H, CH$_3$). $^{13}$C NMR (75 MHz, CD$_2$Cl$_2$): $\delta$ 183.2 (CO), 169.5 (Ir-C), 158.9 (CO), 139.3, 135.6, 133.2, 130.6, 130.5, 130.0, 128.6, 128.8, 128.1, 127.0, 126.5, 124.6, 117.4, 108.5, 53.5, 18.1. FTIR (Nujol), $\nu_{CO} = 2050, 1981$ cm$^{-1}$. Anal. Calcd for C$_{21}$H$_{16}$ClIrN$_2$O$_2$ (FW 556.0) C, 45.36; H, 2.90; N, 5.04; Found C, 45.45; H, 3.11; N, 4.94.

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Complex 11. Yield: 51.5 mg, 94%. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 9.20 (d, $J = 7.0$ Hz, 1H), 7.64-7.66 (m, 2H), 7.48-7.50 (m, 3H), 7.20 (s, 1H), 6.93 (d, $J = 7.0$ Hz, 1H), 4.10 (t, $J = 7.7$ Hz, 2H, N-CH$_2$), 2.54 (s, 3H, Ph-CH$_3$), 1.60-1.68 (m, 2H, CH$_2$), 0.82 (t, $J$=7.3Hz, 3H, CH$_2$-CH$_3$). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 182.8(CO), 168.8 (Ir-C), 145.4, 143.2, 141.6, 140.9, 133.0, 131.3, 130.0, 129.2, 128.4, 116.7, 107.7, 44.4, 31.5, 21.9, 19.8, 13.4. FTIR (Nujol), $\nu$$_{CO} = 2046, 1965$ cm$^{-1}$. Anal. Calcd for C$_{20}$H$_{20}$ClIrN$_2$O$_2$ (548.1) C, 43.83; H, 3.68; N, 5.11; Found C, 43.54; H, 3.80; N, 4.89.

The Solution Dynamics Research of Ir complex 9a and 10: VT NMR spectra (300MHz) were recorded for CDCl$_3$ solution of 9a and 10 of different temperatures which is calibrated by CIL 4% methanol in methanol-d$_4$, respectively. The resonance at 6.26 ppm (9a) and 6.27 ppm (10) were analyzed to give half-peak width ($w_{1/2}$). The plot of $\ln(k/T)$ (where $k=\pi\times\Delta w_{1/2}$) against 1/T gives $\Delta H^\circ$.

Acknowledgment. Mr Yao Zhang’s contribution for Chapter 4. Zhang performed some the solution dynamic research work and characterization of NMR Spectrum.
4.5 References


Organometallics 2003, 22, 1663.


Chapter 5. Pyridine-Based N-Heterocyclic Carbene Hydride Complexes of Iridium
via C–H Activation

5.1 Introduction

Ever since the isolation of imidazole-based carbenes in the free state,¹ N-heterocyclic carbenes (NHCs) have become powerful ligands to stabilize transition metals in organometallic chemistry and in catalysis.²⁻⁴ The high catalytic activities of NHC complexes may be attributed to the strong σ-donating and weak π-accepting characters of imidazole-2-ylidenes.⁵⁻⁶ As typical electron-rich carbon-centered neutral donors, NHCs on various platforms and with different substituents have been developed to demonstrate their electronic and steric tenability.⁷⁻⁸ In addition to the normal imidazole-derived NHCs, the “abnormal” carbenes, first discovered by Crabtree and coworkers,⁹ which have a carbenoid center adjacent to only one nitrogen, have proven to be more donating than the normal ones.¹⁰⁻¹¹ Analogous to abnormal NHCs, NHCs derived from the deprotonation of pyridiniums at the 2- position are also stabilized by only one nitrogen atom (Figure 1). Previous experimental and theoretical studies have shown that pyridine-based NHCs (py-NHCs) are generally stronger σ-donors and π-acceptors than the more common imidazole-2-ylidenes,¹²⁻¹³ although examples of py-NHC complexes are still rather limited. More recently, remote N-heterocyclic carbenes derived from pyridine¹⁴, quinoline,¹⁵ or pyrazoline,¹⁶ where the heteroatom is distal to the carbene carbon (Figure 5.1), have received increasing attentions owing to their unique structures and properties. For instance, Raubenheimer et al have reported that palladium remote py-NHC complexes are more active in catalyzing C–C coupling reactions than their imidazole-2-ylidenes analogues.¹⁷
In comparison to imidazoliums, pyridiniums are much less acidic, which renders their metalation more difficult and thus examples of py-NHC complexes are rather limited. Common methods to access py-NHC complexes include (Scheme 5.1): (i) C-halogen oxidative addition of 2- or 4-halopyridiums when treated with low valent transition metals such as Pd\textsuperscript{14,15,18} or Pt\textsuperscript{19}, (ii) quaternization of iridium or rhodium pyridyl complexes,\textsuperscript{20} (iii) metalation of \textit{in situ} generated carbenes from the deprotonation of pyridiniums by strong bases,\textsuperscript{12} and (iv) C-H oxidative addition of functionalized pyridiniums.\textsuperscript{21} Kinetic studies of the \(\pi\)-accepting ability of these complexes showed distinctive \textit{trans}-labilizing ability of these py-NHCs in ligand substitution reactions.\textsuperscript{21}

\begin{align*}
\text{(i)} & \\
\text{(ii)} & \\
\text{(iii)} & \\
\text{(iv)} & \\
\end{align*}

\textbf{Scheme 5.1} Common methods for py-NHC complexes
Chapter 5

Metalation of pyridiums via C-H activation route might be an advantageous method owing to base-free reaction conditions. We now describe the synthesis of a series of iridium(III) hydride complexes stabilized by chelating py-NHCs or remote py-NHCs via intramolecular C-H activation under mild conditions. The catalytic activities of representative complexes in transfer hydrogenation of ketones and computational assessment of the donating ability of such ligands have also been studied.

5.2 Results and Discussion

5.2.1 The Ligand System

We\textsuperscript{22} and others\textsuperscript{23} have recently reported Ir(I)-mediated intramolecular C-H activation of functionalized imidazoliums to afford iridium(III) NHC hydride complexes. We have also described Ir(I)-induced tautomerization of 2,3-bipyridyls to the corresponding NHCs, a process that involves the activation of the C2–H bond of those pyridium units.\textsuperscript{24} We reason that pyridium ions tethered to pyridinium moieties (1-4, Figure 5.2) should be more reactive toward C–H activation in that ortho-C–H activation should be favored by chelation assistance and the products are chelation-stabilized NHC complexes. We thus synthesized compounds 1-4 as carbene precursors from the selective alkylation of the corresponding heterocycles in high yields.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure5.2}
\caption{Pyridine-tethered pyridinium halides}
\end{figure}
5.2.2 Metalation and Structures

5.2.2.1 C-H Activation of Compound 1.

We have chosen [Ir(COD)$_2$]SbF$_6$ or [Ir(COD)$_2$]PF$_6$ as a metal source owing to the lability of one of the COD (1,5-cyclooctadiene) ligands.$^{24}$ Compound 1 (Figure 2) was allowed to react with one equivalent of [Ir(COD)$_2$]SbF$_6$ in dichloromethane at room temperature, and two hydride species were obtained based on $^1$H NMR analysis. These two hydrides resonate at $\delta$ -12.9 (s) and -14.3 (s) in a 1:5 ratio. In the $^{13}$C NMR spectrum, two corresponding Ir-C$_{\text{carbene}}$ signals were detected at $\delta$ 187.5 and 178.3. The structures of these two products, however, could not be securely assigned since four possible isomers, two regio- (py-NHC or remote py-NHC) and two stereoisomers (trans or cis orientation of the hydride and the iodide), can be possible.

5.2.2.2 C-H Activation of Ligands with Blocking Groups.

To enhance the selectivity of C-H activation of this system, ligands 2 and 3a, b with blocking groups (Figure 5.2) were used as carbene precursors so that only one ortho-C-H bond can be activated. Stirring a solution of 2 or 3a, b and [Ir(COD)$_2$]PF$_6$ or [Ir(COD)$_2$]SbF$_6$ (CH$_2$Cl$_2$, 25 $^\circ$C) led to the decolorization of the solution. With the liberation of one equivalent of COD, the reaction yielded complex 5 or 6a, b, respectively, as the only product in 65–96% isolated yields (Eq 5.1, 5.2). These products have been fully characterized by NMR spectroscopy (Table 5.1) and 5 and 6b were further characterized as cis hydride iodide complexes by X-ray crystallography (vide infra). The hydrides of complexes 5 and 6a-b resonate within a range of $\delta$ -12.96 to -13.79 in the $^1$H NMR spectra (CD$_2$Cl$_2$), and the Ir-C$_{\text{carbene}}$ signals appear within a range of $\delta$ 182.5 to 189.7 in the $^{13}$C NMR spectra (Table 5.1). These $^{13}$C NMR data are comparable to those reported for other py-NHC complexes.$^{21,24}$
Table 5.1. Characteristic NMR Signals (CD$_2$Cl$_2$) of iridium hydride complexes 5-7

<table>
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<tr>
<th></th>
<th>5</th>
<th>6a</th>
<th>6b</th>
<th>7a</th>
<th>7b</th>
<th>7c</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-12.81 (trans)</td>
<td>-14.01 (trans)</td>
<td>-12.62 (trans)</td>
</tr>
<tr>
<td>Ir-C$_{\text{carbene}}$</td>
<td>182.5</td>
<td>189.6</td>
<td>189.7</td>
<td>191.1 (cis)</td>
<td>192.1 (cis)</td>
<td>192.5 (cis)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>191.9 (trans)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5.2.2.3 Remote py-NHC Complexes.

Preparation and NMR Spectroscopy Encouraged by improved selectivity and the single isomer obtained for complexes 5 and 6a,b, ligands 4a-c were allowed to react with [Ir(COD)$_2$]SbF$_6$ (Scheme 5.2), where the products are remote py-NHC complexes. These products represent the first samples of iridium remote py-NHC complexes. In contrast to py-NHC complexes 5 and 6a,b, each reaction yields an equilibrium mixture of two hydride complexes in solution (Scheme 5.2). For instance, in the $^1$H NMR spectra (CD$_2$Cl$_2$) of iridium(III) iodide 7a or 7c, two hydride signals were observed ($\delta$ -14.13 and -12.81 for 7a and -14.11 and -12.62 for 7c), and the corresponding ratio is 10:1 in each case (Table 5.1). These two hydride complexes are assigned to two stereoisomeric products (cis and trans isomers). Pure 7a-cis or 7c-cis could be obtained as single crystals from the recrystallization of the isomeric mixtures using CH$_2$Cl$_2$ and Et$_2$O. Correlations between the solid structure and the $^1$H NMR spectrum could be achieved by dissolution of a pure
sample of 7a-cis at -40 °C, followed by ¹H NMR analysis (Table 5.1). The cis hydride resonates at a higher field and is the major isomer for both 7a and 7c (Table 5.1 and Scheme 5.2). The remote py-NHC carbon atoms resonates at δ 191.1 (7a-cis) and 192.5 (7c-cis) in the ¹³C NMR spectra, which are slightly deshielded than those in complexes 5 and 6a,b. Halide effects have also been observed: the ratio of 7b-cis to 7b-trans decreases to 4.5:1 when bromide is used. One explanation of the higher cis to trans ratio observed for iodide complexes is that the high trans effects of both the hydride and iodide will render the trans product unfavorable.

Scheme 5.2. Synthesis of iridium(III) remote py-NHC hydrides

The Equilibrium between the cis and trans Iridium Hydride Remote py-NHC Complexes. The equilibrium between 7a-cis and 7a-trans was further studied by NMR spectroscopy in CD₃CN. The van’t Hoff plot of this trans to cis equilibrium system gave thermodynamic parameters ΔH° = 1.6 kcal/mol and ΔS° = -0.77 eu (Table 5.2, Figure 5.3), and this reaction is nearly thermoneutral. The equilibrium between 7b-cis and 7b-trans is even less sensitive to temperature so that no thermodynamic parameters could be accurately measured.
Table 5.2 Measurement of $K_{eq}$ of Equilibrium between 7a-cis and 7a-trans

<table>
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<tr>
<th>T (K)</th>
<th>1/T (K$^{-1}$)</th>
<th>$K_{eq}$</th>
<th>ln$K_{eq}$</th>
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<td>297.46</td>
<td>0.003362</td>
<td>10.28</td>
<td>2.33</td>
</tr>
</tbody>
</table>

Figure 5.3 The van’t Hoff Plot of Equilibrium the conversion of 7a-cis to 7a-trans $^a$

$$y = 542.52x - 0.3374$$

$R^2 = 0.9962$

$^a$ The slope of these lines are $-\Delta H^\circ / R$ and the intercept is $\Delta S^\circ / R$
5.2.2.4 X-ray Crystallographic Analyses. Single crystals of 5, 6b, and 7a were analyzed by X-ray crystallography (Figures 5.4-5.6 and Tables 5.3-5.4). Each of these complexes adopts a pseudo-octahedral geometry. In sharp contrast to the trans orientation of hydride and halide in previously reported Ir(III) NHC hydride complexes obtained from C–H activation, the hydrides here are consistently cis to the halides. In all cases, one of the C=C bonds in the COD is trans to the carbene, while the other C=C bond is trans to the halide. The C=C bonds of the COD ligand all adopt upright conformation with respect to the plane defined by the C carbene, Ir, and the halide. The olefin unit trans to the carbene gives Ir-Colefin distances at ca. 0.05Å longer than that trans to the halide, suggestive of the high trans effect of the carbene ligand in each complex. The Ir-C(18) distance (2.006(3) Å) in remote py-NHC complex 7a is slightly shorter than that in py-NHC complex 6b (2.030(4) Å). The C(18)-Ir-N(1) angle (79.05(12)°) in remote py-NHC complex 7a is comparable to the corresponding ones in complexes 5 [78.6(4)°] and 6b [78.98(14)°]. The C(18)-C(19) bonds in py-NHC complexes 5 and 6b are at least 0.04 Å longer than the other three C-C bonds in the same ring, a structural feature reported in other py-NHC complexes.\textsuperscript{21,24}

![Figure 5.4 Molecular structure of 5 (cation only) with ellipsoids shown at 50% thermal probability](image)
Figure 5.5. Molecular structure of 6b (cation only) with ellipsoids shown at 50% thermal probability

Figure 5.6. Molecular structure of 7a (cation only) with ellipsoids shown at 50% thermal probability

Table 5.3. Selected bond lengths and angles for complexes 5, 6b, and 7a

<table>
<thead>
<tr>
<th></th>
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<th>6b</th>
<th>7a</th>
</tr>
</thead>
<tbody>
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<td>Ir-C(18) (Å)</td>
<td>2.013(9)</td>
<td>2.030(4)</td>
<td>2.006(3)</td>
</tr>
<tr>
<td>Ir-N(1) (Å)</td>
<td>2.193(8)</td>
<td>2.204(3)</td>
<td>2.209(3)</td>
</tr>
<tr>
<td>Ir-X (Å)</td>
<td>2.7069(10)</td>
<td>2.5089(4)</td>
<td>2.6901(3)</td>
</tr>
<tr>
<td>C(18)-C(19) (Å)</td>
<td>1.426(14)</td>
<td>1.415(6)</td>
<td>1.415(4)</td>
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<tr>
<td>C(18)-Ir-N(1) (deg)</td>
<td>78.6(4)</td>
<td>78.98(14)</td>
<td>79.05(12)</td>
</tr>
<tr>
<td>C(18)-Ir-X (deg)</td>
<td>91.1(3)</td>
<td>91.53(10)</td>
<td>88.99(9)</td>
</tr>
<tr>
<td>N(1)-Ir-X (deg)</td>
<td>84.8(2)</td>
<td>84.61(8)</td>
<td>85.78(7)</td>
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</table>
### Table 5.4. Crystallographic data for complexes 5, 6b and 7a

<table>
<thead>
<tr>
<th></th>
<th>5</th>
<th>6b•1/3CH₃CN</th>
<th>7a</th>
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<tr>
<td>empirical</td>
<td>C₂₃H₃₁F₆IrN₂P</td>
<td>C₂₇H₂₇BrF₆IrN₂Sb•1/3CH₃CN</td>
<td>C₂₄H₂₉F₆IrN₂Sb</td>
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<tr>
<td>formula</td>
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<td></td>
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<tr>
<td>weight</td>
<td>799.57</td>
<td>901.05</td>
<td>900.34</td>
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<tr>
<td>temperature</td>
<td>173(2) K</td>
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<tr>
<td>crystal system</td>
<td>Monoclinic</td>
<td>Triclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>P₂(1)/n</td>
<td>P-1</td>
<td>P₂(1)/c</td>
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<tr>
<td>a (Å)</td>
<td>11.317(2)</td>
<td>13.016(4)</td>
<td>14.508(4)</td>
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<tr>
<td>b (Å)</td>
<td>12.8037(3)</td>
<td>13.5422(4)</td>
<td>12.9346(3)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>17.9585(4)</td>
<td>24.0445(7)</td>
<td>14.1699(4)</td>
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<tr>
<td>α (deg)</td>
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<td>85.1270(10)</td>
<td>90</td>
</tr>
<tr>
<td>β (deg)</td>
<td>91.1430(10)</td>
<td>82.9790(2)</td>
<td>99.8920(4)</td>
</tr>
<tr>
<td>γ (deg)</td>
<td>90</td>
<td>87.9560(10)</td>
<td>90</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>2601.82(10)</td>
<td>4190.0(2)</td>
<td>2619.67(12)</td>
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<tr>
<td>Z</td>
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<td>6</td>
<td>4</td>
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<td>d&lt;sub&gt;calc&lt;/sub&gt; (g/cm³)</td>
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<td>2.143</td>
<td>2.283</td>
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<td>μ (mm⁻¹)</td>
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<td>7.343</td>
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<td>crystal size</td>
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<tr>
<td>(mm)</td>
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<tr>
<td>total, unique</td>
<td>35948, 4612</td>
<td></td>
<td></td>
</tr>
<tr>
<td>no. of rflns</td>
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<td></td>
<td></td>
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<tr>
<td>R(int)</td>
<td>0.0334</td>
<td>0.0385</td>
<td>0.0237</td>
</tr>
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<td>data, restraints, parameters</td>
<td>4612, 196, 369</td>
<td>41000, 9, 1064</td>
<td>5716, 3, 320</td>
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<tr>
<td>R, R&lt;sub&gt;w&lt;/sub&gt; (all data)</td>
<td>0.0582, 0.1116</td>
<td>0.0848, 0.1210</td>
<td>0.0220, 0.0456</td>
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<tr>
<td>GOF</td>
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<td>peak and hole</td>
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<td>2.722, -2.987</td>
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<td>(eÅ⁻³)</td>
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</table>
5.2.3 Catalysis in Transfer Hydrogenation.

Iridium bis(carbene) dihalide complexes have proven to be robust catalysts for ketone transfer hydrogenation, and Ir(III) monohydrides are also proposed as the active species.\textsuperscript{25} We reason that hydride complexes 5, 6 and 7 could also be active catalysts in this reaction. Indeed, transfer hydrogenation between acetophenone and \textsuperscript{1}PrOH proceeded smoothly in the presence of 10 mol\% Cs\textsubscript{2}CO\textsubscript{3} (Eq 5.3 and Table 5.5) under reflux. Under these conditions, complexes 6a (1 mol\%) and 6b (1 mol\%) exhibited essentially the same catalytic activity, giving 92\% and 90\% yields, respectively, after 6 h. A lower yield (74\%) was obtained when the loading of 6a was reduced to 0.1 mol\% (entry 2). Other methyl aryl ketones could also be reduced to the corresponding alcohols in high NMR yields (82-99\%). In general, substrates with electron-withdrawing groups (entries 5-8) tend to show higher reactivity than those with electron-donating groups (entry 4).

The catalytic reactions were further extended to the transfer hydrogenation of \(\alpha,\beta\)-unsaturated ketones and aldehydes, where chemoselectivity can be an issue.\textsuperscript{26} The results are given in Table 5.5 and both C=C and C=O double bonds are hydrogenated for the substrates examined. Transfer hydrogenation of cinnamaldehyde only afforded 70\% NMR yield (entry 15), although a nearly full conversion was achieved. It is apparently possible that transfer hydrogenation of enones could occur on the C=C bond first then on the C=O group. To further test whether the other stepwise sequence is possible, we then examined an allylic alcohol \textit{trans}-PhCH=CHC(OH)Me, which can be cleanly hydrogenated under the same reaction conditions (entry 13). These results suggest that transfer hydrogenation here can follow either stepwise sequence. In comparison, hydrogenation of \(\alpha,\beta\)-unsaturated carbonyl compounds at the C=C bonds catalyzed by Cu\textsuperscript{27} and Ru\textsuperscript{28} have been reported and this chemo-selectivity complements the traditional hydride reduction protocols.
Table 5.5 Transfer hydrogenation of acetophenones and $\alpha,\beta$-unsaturated ketones and aldehydes $^a$

<table>
<thead>
<tr>
<th>entry</th>
<th>ketone</th>
<th>time (h)</th>
<th>products</th>
<th>yield (%)$^b$</th>
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<tbody>
<tr>
<td>1</td>
<td>Ar = Ph</td>
<td>6</td>
<td></td>
<td>92, 90$^c$</td>
</tr>
<tr>
<td>2</td>
<td>Ar = Ph</td>
<td>6</td>
<td></td>
<td>74$^d$</td>
</tr>
<tr>
<td>3</td>
<td>Ar = 4-MeC$_6$H$_4$</td>
<td>4</td>
<td></td>
<td>93</td>
</tr>
<tr>
<td>4</td>
<td>Ar = 4-MeOC$_6$H$_4$</td>
<td>6</td>
<td></td>
<td>82</td>
</tr>
<tr>
<td>5</td>
<td>Ar = 4-BrC$_6$H$_4$</td>
<td>3</td>
<td></td>
<td>99</td>
</tr>
<tr>
<td>6</td>
<td>Ar = 4-FC$_6$H$_4$</td>
<td>3</td>
<td></td>
<td>99</td>
</tr>
<tr>
<td>7</td>
<td>Ar = 4-ClC$_6$H$_4$</td>
<td>4</td>
<td></td>
<td>95</td>
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<td>8</td>
<td>Ar = 3-BrC$_6$H$_4$</td>
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<td>99</td>
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<td>9</td>
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</tr>
<tr>
<td>18</td>
<td></td>
<td>6</td>
<td></td>
<td>96</td>
</tr>
</tbody>
</table>

$^a$ Reaction condition: 1 mmol of acetophenone; 0.1 mmol Cs$_2$CO$_3$; 1 mol% of catalyst 6a; 3 ml iPrOH. $^b$ NMR yield using 1,3,5-trimethoxybenzene as an internal standard. $^c$ 6b (1 mol%) as the catalyst. $^d$ 6b (0.1 mol%) as the catalyst.
5.2.4 The Electronic Effects of Pyridine-Based NHCs.

The distinctive $\sigma$-donating characters of carbon-centered ligands are undoubtedly relevant to their increasingly important roles in homogeneous catalysis$^{21}$ and major advances have been focused on the development of electron-rich ligands of late transition metal complexes. The IR stretching frequencies of CO groups in dicarbonyl complex such as IrCl(CO)$_2$L or RhCl(CO)$_2$L are commonly used to assess the electronic properties of a given ligand L. A more donating ligand should result in a lower CO stretching frequency. Synthesis of iridium CO complexes with py-NHC or remote py-NHC ligands met with failure. Thus the electronic effects of these py-NHC and remote py-NHC ligands were evaluated for their rhodium complexes and were compared with those of normal and abnormal NHC ligands by theoretical methods (Figure 5.7). The $\nu_{\text{CO}}$ frequencies of complexes 8-11 were calculated at the B3LYP/6-31G*/LANL2DZ (Rh) level and the average $\nu_{\text{CO}}$ values are directly related to their donating ability. Py-NHC and remote py-NHC ligands are essentially the same in donating capacity (2149.3 cm$^{-1}$ for both 8 and 9). Either the normal or abnormal imidazole-based NHCs in 10 (2155.1 cm$^{-1}$) and 11 (2160 cm$^{-1}$) are slightly less donating than the py-NHC and the remote py-NHC. A general order of $\sigma$-donating ability of py-NHC $\cong$ remote py-NHC $>$ abnormal NHC $>$ normal NHC can be concluded, consistent with previous reports.$^{13,21}$

![Image of calculated CO stretching frequencies of complexes 8-11](image)

**Figure 5.7** Calculated CO stretching frequencies of complexes 8-11
5.3 Conclusions

We have described a mild and straightforward synthetic procedure for py-NHC and remote py-NHC hydride complexes of iridium by means of nitrogen-assisted activation of C-H bonds in pyridine-tethered pyridiums. X-ray crystal structures of representative iridium py-NHC and remote py-NHC complexes were determined and in all cases a mutual cis orientation of the halide and hydride ligands were observed in the solid state. For iridium(III) remote py-NHC hydrides, both cis and trans (with respect to the hydride and the halide) isomers have been observed in the solution state and they are in equilibration. These Iridium py-NHC hydride complexes have shown high catalytic activities in ketone transfer hydrogenation. DFT calculations on [Rh(CO)₂(N^NHC)]⁺ complexes have revealed that py-NHCs and remote py-NHCs are more donating than normal and abnormal imidazole-based NHCs. Extension of the synthetic methodology of pyridine-based NHC complexes to other transition metals and widening of the scope of catalytic applications of these py-NHC complexes are currently under investigation in our laboratory.
5.4 Experimental Section

General Procedure  All manipulations were carried out using standard Schlenk techniques or in a nitrogen-filled dry box, except where otherwise noted. All solvents were distilled under \( \text{N}_2 \) before use and were stored in a dry box. \( \text{CDCl}_3 \) was dried by 4Å molecular sieves. \( \text{CD}_2\text{Cl}_2 \), DMSO-\( \text{d}_6 \), or \( \text{CD}_3 \text{CN} \) was obtained in sealed ampoules from CIL and were used without further purification. Air-sensitive compounds were stored and weight in a dry box. NMR spectra were recorded on a Bruker 300 MHz, 500 MHz, or a JEOL 400 MHz spectrometer at 298K unless otherwise specified. Temperatures (\( >295\text{K} \)) of NMR samples for thermodynamic studies were calibrated using 80% ethylene glycol in DMSO-\( \text{d}_6 \). The chemical shift is given as dimensionless \( \delta \) values and is referenced to \( \text{SiMe}_4 \) for \( ^1\text{H} \) and \( ^{13}\text{C} \) NMR spectroscopy. Elemental analyses were performed in the Division of Chemistry and Biological Chemistry, Nanyang Technological University. HRMS spectra were obtained in ESI mode on a Waters Micromass Q-Tof Premier Mass Spectrometer.

**Compound 1.** 2,3'-Bipyridine (160 mg, 1.02 mmol) and 1-iodobutane (188 mg, 1.02 mmol) were dissolved in acetonitrile (5 ml), and the mixture was loaded into a sealed pressure tube and was stirred at 120 °C for 24 hours. The solvent was then removed under reduced pressure. The residue obtained was washed with diethyl ether, gives a light yellow solid which was used without further purification. Yield: 320 mg (0.94 mmol, 92%). 1H (500 MHz, CDCl\(_3\)): \( \delta \) 9.96 (s, 1H), 9.46 (d, \( J = 5.4 \text{ Hz} \), 1H), 9.26 (d, \( J = 8.0 \text{ Hz} \), 1H), 8.74 (d, \( J = 3.9 \text{ Hz} \), 1H), 8.52 (d, \( J = 8.0 \text{ Hz} \), 1H), 8.25 (t, \( J = 6.8 \text{ Hz} \), 1H), 7.97 (t, \( J = 7.6 \text{ Hz} \), 1H), 7.45 (t, \( J = 6.8 \text{ Hz} \), 1H), 5.13 (t, \( J = 7.4 \text{ Hz} \), 2H, N-CH\(_2\)), 2.11 (t, \( J = 7.4 \text{ Hz} \), 2H, CH\(_2\)), 1.50 (q, \( J = 7.5 \text{ Hz} \), 2H, CH\(_2\)), 1.00 (t, \( J = 7.4 \text{ Hz} \), 3H, CH\(_3\)). 13C (100Hz, CDCl\(_3\)): \( \delta \) 150.4, 149.2, 144.3, 142.7, 142.4, 139.7, 138.2, 128.6, 125.4, 122.8, 62.2 (NCH\(_2\)), 34.0 (NCH\(_2\)CH\(_2\)), 19.4 (NCH\(_2\)CH\(_2\)CH\(_2\)), 13.7 (CH\(_3\)). HRMS (ESI\(^+\)): 213.1385, Calc. Mass for [C\(_{14}\)H\(_{17}\)N\(_2\)]\(^+\) 213.1392.

**Compound 2** was synthesized as a yellow powder in 91% (322 mg, 0.91 mmol) yield
by following a method directly analogous to that for 1 starting from 4-methyl-3-(pyridin-2-yl)pyridine (170 mg, 1 mmol) and 1-iodobutane (184 mg, 1 mmol). 

\(^1\)H (400 MHz, CDCl\(_3\)): \(\delta\) 9.30 (d, \(J = 6.4\) Hz, 1H), 9.12 (s, 1H), 8.70 (d, \(J = 5.0\) Hz, 1H), 8.04 (d, \(J = 7.8\) Hz, 1H), 7.99 (d, \(J = 6.4\) Hz, 1H), 7.92 (td, \(J = 7.8, 1.8\) Hz, 1H), 7.41-7.43 (m, 1H), 4.96 (t, \(J = 7.4\) Hz, 2H, N-CH\(_2\)), 2.69 (s, 3H, CH\(_3\)), 2.19 (t, \(J = 7.8\) Hz, 2H, CH\(_2\)), 1.42 (q, \(J = 7.8\) Hz, 2H, CH\(_2\)), 0.92 (t, \(J = 7.3\) Hz, 3H, CH\(_3\)). \(^{13}\)C (100 MHz, CDCl\(_3\)): 157.7, 151.7, 150.0, 143.5, 143.0, 140.0, 137.9, 130.3, 125.6, 124.4, 61.4, 33.7, 21.6, 19.4, 13.7. HRMS (ESI\(^+\)): 227.1543, Calc. Mass for [C\(_{15}\)H\(_{19}\)N\(_2\)]\(^+\) 227.1548.

Compound 3a was synthesized as a white solid in 88% (320 mg, 0.88 mmol) yield by following a method directly analogous to that for 1 starting from 1,9-phenanthroline (180 mg, 1 mmol) and 1-iodobutane (184 mg, 1 mmol). 

\(^1\)H (400 MHz, CDCl\(_3\)): \(\delta\) 10.43 (s, 1H), 9.60 (d, \(J = 6.7\) Hz, 1H), 9.12 (d, \(J = 3.7\) Hz, 1H), 8.73 (d, \(J = 6.7\) Hz, 1H), 8.47 (d, \(J = 8.0\) Hz, 1H), 9.43 (d, \(J = 9.2\) Hz, 1H), 8.20 (d, \(J = 9.2\) Hz, 1H), 7.82 (dd, \(J = 7.9\) Hz, 1H), 5.15 (t, \(J = 7.9\) Hz, 2H, N-CH\(_2\)), 2.17 (t, \(J = 7.3\) Hz, 2H, CH\(_2\)), 1.49 (q, \(J = 7.4\) Hz, 2H, CH\(_2\)), 0.97 (t, \(J = 7.4\) Hz, 3H, CH\(_3\)). \(^{13}\)C (100 MHz, CDCl\(_3\)): \(\delta\) 152.1, 144.2, 143.3, 140.8, 139.6, 137.9, 137.3, 127.8, 127.3, 126.9, 125.5, 124.9, 62.7, 34.0, 19.5, 13.7. HRMS (ESI\(^+\)): 237.1382, Calc. Mass for [C\(_{16}\)H\(_{17}\)N\(_2\)]\(^+\) 237.1392.

3b was synthesized as a white solid in 96% (343 mg, 0.96 mmol) by following a method directly analogous to that for 1 starting from 1,9-phenanthroline (180 mg, 1 mmol) and benzyl bromide (171 mg, 1 mmol). 

\(^1\)H (400 MHz, DMSO-\(d_6\)): \(\delta\) 10.90 (s, 1H), 9.20-9.23 (m, 2H), 8.74 (d, \(J = 6.4\) Hz, 1H), 6.70 (d, \(J = 9.1\) Hz, 1H), 8.62 (d, \(J = 9.1\) Hz, 1H), 8.27 (d, \(J = 8.7\) Hz, 1H), 7.96 (dd, \(J = 8.3, 4.6\) Hz, 1H), 7.62 (d, \(J = 8.3\) Hz, 2H), 7.40-7.43 (m, 3H), 6.19 (s, 2H). \(^{13}\)C (100 MHz, DMSO-\(d_6\)): \(\delta\) 152.5, 145.1, 144.5, 141.0, 139.4, 138.1, 135.2, 129.8, 129.7, 129.5, 128.0, 127.2, 126.9, 125.9, 125.4, 63.8 (CH\(_2\)). HRMS (ESI\(^+\)): 271.1229, Calc. Mass for [C\(_{19}\)H\(_{15}\)N\(_2\)]\(^+\) 271.1235.

4a was synthesized as a white solid in 85% (155 mg, 0.42 mmol) yield by following a method directly analogous to that for 1 starting from 1,7-phenanthroline (90 mg, 0.5 mmol) and 1-iodobutane (92 mg, 0.5 mmol). 

\(^1\)H (400 MHz, CDCl\(_3\)): \(\delta\) 10.27-10.32 (m, 2H), 9.18
(dd, J = 4.1, 1.4 Hz, 1H), 8.60 (dd, J = 9.6, 20.6 Hz, 2H), 8.51 (dd, J = 8.2, 1.4 Hz, 1H),
8.31 (dd, J = 8.2, 5.9 Hz, 1H), 7.83 (dd, J = 8.2, 4.5 Hz, 1H), 5.51 (tr, J = 7.3 Hz, 2H,
N-CH₂), 2.11-2.15 (m, 2H, CH₂), 1.55-1.58 (m, 2H, CH₂), 0.96 (tr, J = 7.4 Hz, 3H, CH₃).

\(^{13}\text{C}\) (100 MHz, CDCl₃): \(\delta\) 152.5, 149.1, 144.2, 142.7, 139.9, 137.5, 137.0, 130.0, 126.4,
\([\text{C}_{16}\text{H}_{17}\text{N}_{2}]^+\): 237.1392.

\(4\text{b}\) was synthesized as a white solid in 95% (167 mg, 0.47 mmol) yield by following a
method directly analogous to that for \(1\) starting from 1,7-phenanthroline (90 mg, 0.5 mmol)
and benzyl bromide (85.5 mg, 0.5 mmol). \(^1\text{H}\) (400 MHz, DMSO-\(d_6\)): \(\delta\) 10.35 (d, J = 8.2
Hz, 1H), 9.90 (d, J = 6.0 Hz, 1H), 9.30 (dd, J = 4.1, 1.4 Hz, 1H), 8.72-8.76 (m, 2H),
8.53-8.58 (m, 2H), 8.01 (dd, J = 8.2, 4.6 Hz, 1H), 7.35-7.42 (m, 5H), 6.55 (s, 2H, NCH₂).

\(^{13}\text{C}\) (100 MHz, DMSO-\(d_6\)): \(\delta\) 153.1, 150.1, 143.8, 143.3, 140.6, 137.9, 137.2, 134.6, 129.9,
129.6, 129.3, 127.8, 126.5, 124.5, 117.8, 60.8 (CH₂). HRMS (ESI⁺): 271.1230, Calc. Mass for
\([\text{C}_{19}\text{H}_{15}\text{N}_{2}]^+\): 271.1235. Analysis calcd for \(4\text{b}\) (C₁₉H₁₅BrN₂) C, 64.97; H, 4.30; N,
7.98, found C, 65.11; H, 4.19; N, 8.08.

Synthesis of \(4\text{c}\). An excess of KI (900 mg, 5.42 mmol) was added to a solution of \(4\text{b}\)
(300 mg, 0.86 mmol) in methanol (10 mL) and the mixture was stirred at room
temperature for 12 h. The solvent was then removed under reduced pressure and to this
residue was added dichloromethane (15 mL). A clear solution was obtained after filtration.
Removal of the solvent followed by addition of diethyl ether gave \(1\text{b}\) as a yellow solid in
81% yield (280 mg, 0.70 mmol). \(^1\text{H}\) (400 MHz, DMSO-\(d_6\)): \(\delta\) 10.35 (d, J = 8.2 Hz, 1H),
9.92 (d, J = 5.0 Hz, 1H), 9.30 (dd, J = 4.6, 1.8 Hz, 1H), 8.72-8.76 (m, 2H), 8.54-8.57 (m,
2H), 8.00 (dd, J = 8.2, 4.6 Hz, 1H), 7.40-7.42 (m, 5H). \(^{13}\text{C}\) (100 MHz, DMSO-\(d_6\)): \(\delta\) 153.1,
150.2, 143.8, 143.3, 140.7, 138.0, 137.3, 134.76, 130.0, 129.7, 129.3, 127.8, 126.5, 125.8,
Analysis calcd for \(4\text{c}\) (C₁₉H₁₅IN₂) C, 57.30; H, 3.80; N, 7.03, found C, 57.39; H, 3.70; N,
7.11.

Synthesis of \(\text{Ir(COD)}_2\text{SbF}_6\): To a solution of \([\text{Ir(COD)}\text{Cl}]_2\) (1.0 g, 1.49 mmol) in
CH$_2$Cl$_2$ (20 mL) was added COD (0.55 mL, 4.47 mmol) under nitrogen, followed by a solution of AgSbF$_6$ (1.03 g, 3.0 mmol) in CH$_2$Cl$_2$ (10 mL). This resulted deep red solution containing a white precipitate was stirred for 30 min and then was filtered through Celite under nitrogen. Removal of dichloromethane under _vacuo_ and washing with diethyl ether (10 mL × 3), a dark orchid (near to black) solid could be obtained. This complex should be preserved under nitrogen in dark at -30°C. Yield: 1.86 g, 97%.

Ir(COD)$_2$PF$_6$ was synthesized as a dark orchid in 93% (780 mg, 1.39 mmol) yield by following a method directly analogous to that for Ir(COD)$_2$SbF$_6$, starting from [Ir(COD)C1]$_2$ (1.0 g, 1.49 mmol) and AgPF$_6$ (760 mg, 3.0 mmol).

**General Procedure for the Synthesis Iridium(III) py-NHC Hydride Complexes.**

To a stirred solution of [Ir(COD)$_2$]PF$_6$ or [Ir(COD)$_2$]SbF$_6$ (0.20 mmol) in CH$_2$Cl$_2$ (5 mL) was added a CH$_2$Cl$_2$ solution (5 mL) of a pyridinium salt (0.20 mmol). The mixture was stirred for 12 h at room temperature, after which time the red solution became light yellow or nearly colorless. The solution was then concentrated to ca. 0.5 mL followed by addition of diethyl ether (8 mL). A pale yellow or off-white precipitate appeared and was filtered and dried. Analytically pure iridium hydrides were obtained after recrystallization using CH$_2$Cl$_2$ and Et$_2$O.

**Complex 5.** Yield: 65% (yellow solid, 104 mg, 0.13 mmol). Single crystals of 5 suitable for X-ray analysis were obtained by the slow diffusion of diethyl ether into its CH$_2$Cl$_2$ solution after one day at room temperature. $^1$H (300 MHz, CD$_2$Cl$_2$): $\delta$ 9.48 (d, $J$ = 5.8 Hz, 1H), 9.48 (d, $J$ = 6.5 Hz, 1H), 8.23 (d, $J$ = 3.8 Hz, 2H), 7.71-7.76 (m, 1H), 7.36 (d, $J$ = 6.5 Hz, 1H), 5.75 (apparent t, $J$ = 7.8 Hz, 1H, COD), 5.31-5.38 (m, 1H, N-C$_2$H$_5$), 4.86-4.96 (m, 1H, COD), 4.69-4.76 (m, 1H, N-CH$_2$), 4.04-4.11 (m, 1H, COD), 3.28-3.33 (m, 1H, COD), 2.96-3.00 (m, 1H, COD), 2.89 (s, 3H, CH$_3$), 2.53-2.84 (m, 3H, COD), 2.40-2.45 (m, 1H, COD), 2.17-2.25 (m, 2H, CH$_2$), 1.78-2.10 (m, 3H, COD), 1.57-1.69 (m, 2H, CH$_2$), 1.14 (t, $J$ = 7.4 Hz, 3H, CH$_3$CH$_3$), -13.52 (s, 1H, Ir-H). $^{13}$C (75 MHz, CDCl$_3$): $\delta$ 182.5 (Ir-C), 160.8, 153.1, 149.1, 146.1, 141.5, 139.5, 126.5, 126.3, 126.2, 102.9 (CH of
COD), 93.2 (CH of COD), 83.7 (CH of COD), 76.4 (CH of COD), 69.1 (N-CH$_2$), 36.2, 33.0, 32.6, 31.5, 25.3, 24.1 (CH$_3$), 19.9, 15.1, 13.4. Anal. Calcd for C$_{23}$H$_{31}$F$_6$IrN$_2$P: (FW 799.6) C, 34.35; H, 3.91; N, 3.50; Found C, 34.29; H, 3.81; N, 3.44.

**Complex 6a.** Yield: 91% (pale yellow solid, 147.3 mg, 0.182 mmol). $^1$H (300 MHz, CD$_2$Cl$_2$): $\delta$ 9.72 (d, $J = 5.6$ Hz, 1H), 8.81 (dd, $J = 8.2$, 1.1 Hz, 1H), 8.53 (d, $J = 6.9$ Hz, 1H), 8.39 (d, $J = 8.7$ Hz, 1H), 8.09-8.16 (m, 2H), 7.91 (d, $J = 6.8$ Hz, 1H), 5.94 (apparent t, $J = 8.0$ Hz, 1H, COD), 5.37-5.46 (m, 1H, N-CH$_2$), 4.84-5.01 (m, 2H, 1H for N-CH$_2$ and 1H for COD), 4.46-4.53 (m, 1H, COD), 3.23-3.27 (m, 1H, COD), 3.09-3.16 (m, 1H, COD), 2.80-2.93 (m, 1H, COD), 2.55-2.73 (m, 3H, COD), 2.19-2.31 (m, 2H, CH$_3$), 1.94-2.08 (m, 2H, COD), 1.81-1.93 (m, 1H, COD), 1.62-1.70 (m, 2H, CH$_2$), 1.24 (t, $J = 7.4$ Hz, 3H, CH$_2$CH$_3$), -13.8 (s, 1H, Ir-H). $^{13}$C (75 MHz, CDCl$_3$): $\delta$ 186.8 (Ir-C), 153.9, 153.3, 139.9, 139.7, 138.7, 138.8, 134.2, 129.6, 127.4, 125.7, 120.3, 103.0 (CH of COD), 93.0 (CH of COD), 82.4 (CH of COD), 76.6 (CH of COD), 69.8 (N-CH$_2$), 36.8, 33.2, 33.1 31.0, 25.1, 25.0, 11.1 (CH$_3$). Anal. Calcd for C$_{24}$H$_{29}$F$_6$IrN$_2$P (FW 809.6) C, 35.61; H, 3.61; N, 3.46; Found C, 35.79; H, 3.50; N, 3.82.

**Complex 6b.** Yield: 96% (white solid, 170.4 mg, 0.192 mmol). Single crystals suitable for X-ray analysis were obtained by layering its CH$_3$CN/Et$_2$O solution with $n$-pentane after one day at room temperature. $^1$H (400 MHz, CD$_2$Cl$_2$): $\delta$ 9.68 (d, $J = 6.6$ Hz, 1H), 8.82 (d, $J = 7.6$ Hz, 1H), 8.47 (d, $J = 6.1$ Hz, 1H), 8.42 (d, $J = 9.2$ Hz, 1H), 8.15-8.18 (m, 1H), 8.09 (d, $J = 7.6$ Hz, 1H), 7.88 (d, $J = 7.6$ Hz, 1H), 7.55-7.57 (m, 2H), 7.47-7.50 (m, 3H), 6.85 (d, $J = 13.8$ Hz, 1H, N-CH$_2$Ph), 6.31 (d, $J = 13.8$ Hz, 1H, N-CH$_2$Ph), 5.82 (apparent t, $J = 9.2$ Hz, 1H, COD), 5.82 (apparent q, $J = 4.8$ Hz, 1H, COD), 4.07 (apparent q, $J = 4.6$ Hz, 1H, COD), 3.14 (apparent t, $J = 6.1$ Hz, 1H, COD), 3.00-3.05 (m, 1H, COD), 2.80-2.88 (m, 1H, COD), 2.66-2.74 (m, 1H, COD), 2.29-2.40 (m, 2H, COD), 1.85-2.02 (m, 2H, COD), 1.67-1.78 (m, 1H, COD), -13.0 (s, 1H, Ir-H). $^{13}$C (100 MHz, CDCl$_3$): $\delta$ 189.7 (Ir-C), 154.2, 153.3, 140.4, 140.3, 139.3, 137.2, 135.2, 135.1, 130.0, 129.7, 128.8, 127.8, 126.3, 121.0, 105.6 (CH of COD), 94.2 (CH of COD), 80.0 (CH of COD), 75.6 (CH of COD), 70.9 (N-CH$_2$Ph), 36.2 (CH$_2$ of COD), 33.8 (CH$_2$ of COD), 31.4 (CH$_2$ of COD),
24.8 (CH$_2$ of COD). Anal. Calcd for C$_{27}$H$_{27}$BrF$_6$IrN$_2$Sb (FW 887.4) C, 36.54; H, 3.07; N, 3.16; Found C, 36.39; H, 3.01; N, 3.25.

**Complexes 7a.** Yield 82% (white solid, 148 mg, 0.164 mmol). Single crystals of 7a-cis suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into its acetone solution at room temperature. $^1$H (300 MHz, CD$_2$Cl$_2$) for 7a-cis: $\delta$ 9.70 (d, $J = 5.3$ Hz, 1H), 8.81 (dd, $J = 8.1$, 1.0 Hz, 1H), 8.54 (d, $J = 9.4$ Hz, 1H), 8.42 (d, $J = 6.2$ Hz, 1H), 8.11-8.19 (m, 3H), 5.82 (apparent t, $J = 7.8$ Hz, 1H, COD), 4.85-4.94 (m, 1H, COD), 4.69-4.82 (m, 2H, N-C$_2$H$_5$), 4.45-4.52 (m, 1H, COD), 3.01-3.09 (m, 1H, COD), 2.88-2.94 (m, 1H, COD), 2.77-2.85 (m, 1H, COD), 2.60-2.74 (m, 1H, COD), 2.24-2.29 (m, 1H, COD), 1.91-2.12 (m, 6H, 2H for C$_2$H$_5$ and 4H for COD), 1.47-1.59 (m, 2H, CH$_2$), 1.04 (t, $J = 7.3$ Hz, 3H, CH$_2$C$_3$H$_7$), -14.1 (s, 1H, Ir-H). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) for 7a-cis: $\delta$ 191.1 (Ir-C), 154.3, 153.4, 141.6, 140.2, 139.3, 137.2, 135.2, 135.0, 127.9, 125.9, 118.2, 102.6 (CH of COD), 93.5 (CH of COD), 78.0 (CH of COD), 75.7 (CH of COD), 54.0 (N-CH$_3$), 36.2, 33.6, 32.1 31.2, 25.0, 19.9, 12.2 (CH$_3$). Anal. Calcd for C$_{24}$H$_{29}$F$_6$IrN$_2$Sb (FW 900.4) C, 32.02; H, 3.25; N, 3.11; Found C, 32.22; H, 3.29; N, 3.21.

**Observation of the Equilibrium Mixture of Complexes 7b-cis and 7b-trans.**

7b-cis and 7b-trans were observed with 4.5:1 ratio in CD$_2$Cl$_2$ (0.6 ml), starting from compound 4b (15 mg, 0.0427 mmol) and Ir(COD)$_2$SbF$_6$(27.5 mg, 0.0427 mmol). Isolated yield: 34.5 mg, 91%. Selected NMR signals: $^1$H NMR (400 MHz, CD$_2$Cl$_2$): -13.61 (Ir-H, 7b-cis), -14.01 (Ir-H, 7b-trans). $^{13}$C NMR (100 MHz CD$_2$Cl$_2$): 192.1 (Ir-C, 7b-cis), 191.9 (Ir-C, 7b-trans). Anal. Calcd for C$_{27}$H$_{27}$F$_6$BrIrN$_2$Sb (FW 887.4) C, 36.54; H, 3.07; N, 3.16; Found C, 36.31; H, 3.12; N, 3.07.

**Complex 7c.** Yield: 85% (white solid, 159 mg, 0.17 mmol). $^1$H (400 MHz, CD$_2$Cl$_2$) for 7c-cis: $\delta$ 9.70 (d, $J = 6.1$ Hz, 1H), 8.79 (d, $J = 7.6$ Hz, 1H), 8.47 (d, $J = 6.1$ Hz, 1H), 8.42 (d, $J = 9.2$ Hz, 1H), 8.20 (d, $J = 6.1$ Hz, 1H), 8.17 (d, $J = 9.2$ Hz, 1H), 8.10-8.14 (m, 1H), 7.43-7.48 (m, 3H), 7.26-7.28 (m, 2H), 5.95 (q, $J = 15.8$ Hz, 2H, N-CH$_2$), 5.83 (apparent t, $J = 7.6$ Hz, 1H, COD), 4.89-4.94 (m, 1H, COD), 4.50-4.53 (m, 1H, COD),
3.01-3.10 (m, 1H, COD), 2.96-2.99 (m, 1H, COD), 2.77-2.86 (m, 2H, COD), 2.58-2.70 (m, 2H, COD), 2.25-2.30 (m, 1H, COD), 1.98-2.04 (m, 2H, COD), -14.11 (s, 1H, Ir-H). \(^{13}\)C NMR (100 MHz, CD2Cl2) for 7a-cis: \(\delta\) 192.4 (Ir-C), 154.3, 153.3, 141.6, 140.3, 139.3, 137.6, 135.2, 135.0, 132.2, 129.8, 129.7, 128.0, 127.4, 125.9, 118.6, 102.7 (CH of COD), 93.6 (CH of COD), 78.2 (CH of COD), 75.9 (CH of COD), 59.9 (N-CH2), 36.2 (CH2 of COD), 33.5 (CH2 of COD), 31.2 (CH2 of COD), 25.0 (CH2 of COD). Anal. Calcd for C27H27F6IrN2Sb (FW 934.4) C, 34.71; H, 2.91; N, 3.00; Found C, 34.65; H, 3.06; N, 3.11.

**General Procedure for Iridium-Catalyzed Transfer Hydrogenation Reactions.**

An oven-dried flask was charged with acetophenone (1.0 mmol), Cs2CO3 (0.10 mmol), and an internal standard 1,3,5-tri-tert-butylbenzene (0.30 mmol). iPrOH (3 ml) was then added, and the mixture was degassed by bubbling N2 through the solution. An iridium catalyst (1 mol%) was added under a steady flow N2. The mixture was refluxed for a time specified in Table 4. The volatiles were then removed under vacuum. The yields given in Table 4 are based on 1H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. The identity of the products of entries 15-17 (Table 5.5) were confirmed by comparisons with reported NMR data.\(^{26a}\)

**Computational Methods.** All calculations were performed using the Gaussian 2003 program. DFT calculations were carried out using three-parameter hybrid function of Becke with the Lee-Yang-Parr correlation functional theory (B3LYP). The standard basis set 6-31G* is used for C, H, N, O atoms, while the Lanl2dz ECP basis set is adopted for Rh atom. Geometry optimizations were carried out without any geometrical constraints. All geometries were subjected to frequency analysis and characterized as a minimum (no imaginary frequencies).
5.5 References


Chapter 5

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(22) Song, G.; Wang, X.; Li, Y.; Li, X. Organometallics. 2008, 27, 1187.


Chapter 6. Hydrogen Bonding Assisted Tautomerization of Pyridine Moieties in the Coordination Sphere of an Ir(I) Complex

6.1 Introduction

Transition metals can mediate remarkably the behavior of organic molecules. Organic moieties in metal complexes can undergo reactions that are otherwise thermodynamically and kinetically unfavorable. An important illustration is the tautomerization of acetylene to vinylidene (\(\text{C}=\text{CH}_2\)) which has an activation barrier of 76 kcal mol\(^{-1}\) and the vinylidene is thermodynamically less stable by 44 kcal mol\(^{-1}\).\(^1\) Upon coordination to metals, the barrier of this tautomerization can drop significantly and the stabilization of the vinylidene by metals can invert the relative energy of these two tautomers.\(^2\)

The tautomerization of pyridine has been thoroughly studied by computational methods (Scheme 6.1).\(^3\) The N–H tautomer, an N-heterocyclic carbene, lies 45–50 kcal mol\(^{-1}\) higher than the C–H tautomer (pyridine) in energy.\(^3b\) Despite the rather large dissociation energies of many transition metal–carbene bonds,\(^4\) experimental examples of metal-mediated pyridine to carbene tautomerization have not been reported until very recently.\(^5\)–\(^7\) Examples of tautomerization of other heterocycles, such as imidazoles, are also rare\(^8\)\(^,\)\(^9\) (Scheme 6.1). This type of tautomerization is important not only in biological processes, where the energetically less stable tautomer is often responsible for the biological activity,\(^10\) but also in important catalytic C–C coupling reactions of heterocycles, where the N-heterocyclic carbene tautomers are key intermediates.\(^11\)

![Scheme 6.1 Tautomerization of pyridine and imidazole](image-url)
Our group have reported the tautomerization of a substituted imidazole in the coordination sphere of a cationic iridium(III) complex, and the N-bound complex is thermodynamically more stable than the C-bound one. We now report Ir(I)-induced tautomerization of substituted pyridines to N-heterocyclic carbenes.

6.2 Results and Discussion

6.2.1 Bidentate System

Previous theoretical and experimental studies on the tautomerization of imidazoles have shown that either the N-bound imidazole complex or the C-bound carbene complex can be thermodynamically stable, depending on the nature of the metals and the ligands. It is possible that similar thermodynamics may occur in the pyridine system. We reason that ligand 1 is a suitable candidate for this investigation. When bound to metals the carbene tautomer 1a should be thermodynamically more stable (eq 6.1). The C-H tautomer 1 cannot serve as a bidentate chelating ligand, while 1a should allow the formation of a stable metalacycle upon chelation.

\[
\begin{array}{c}
\text{1} \\
\text{1a}
\end{array}
\] (6.1)

The bipyridine-type heterocyclic compounds were synthesized based on Scheme 6.1. Compound 1 was synthesized by Negishi coupling reaction using 3-bromo-pyridine and 2-pyridylzinc bromide as substrates catalyzed by Pd(PPh₃)₄. Compound 2 with methyl group on 4-position could be obtained by Stille coupling by the reaction of 3-bromo-4-methylpyridine and 2-(tributylstannyl)pyridine catalyzed by Pd(PPh₃)₄. Another series of compounds with an amide group at 2-position 3a-e were also prepared by Stille coupling reaction through an analogous method for 2. (Scheme 6.2)
Chapter 6

We have also selected Ir(COD)$_2$BF$_4$ as a metal source owing to the lability of one of the COD ligands, as observed in the rapid formation of Ir(COD)(MeCN)$_2$BF$_4$ from Ir(COD)$_2$BF$_4$ and MeCN. Here the carbene tautomer 1a might readily substitute a COD ligand to give an isolable Ir(I) complex.

6.2.2 Metalation and NMR Spectroscopy

The reaction of ligand 1 and Ir(COD)$_2$BF$_4$ in CD$_2$Cl$_2$ was initially attempted but a complicated mixture was obtained on the basis of $^1$H NMR analysis, which shows at least five hydride species obtained from C–H activation, together with a broad singlet at $\delta$ 12.1 ppm, tentatively ascribed to the NH of the carbene tautomer (eq 6.2). While only the two C–H bonds ortho to the 2-pyridyl group can undergo feasible chelation-assisted C–H activation to give the hydride species, a various number of such species might result from the different stereoisomers of the C–H activation products (eq 6.2). To favor the selectivity
of tautomerization, further improvement was made by using ligand 2 (Scheme 6.2) processing a 4-methyl group, which should prevent any oxidative addition at the 4-position and hence enhance the selectivity of tautomerization over C–H oxidative addition. Indeed we have found that although C–H oxidative addition and its product still exist, there is now only one hydride species (δ -12.95 ppm) with approximately a 5 : 1 molar ratio of the NH tautomer to hydride.

Noting that Carmona and Poveda have proposed that hydrogen bonding in an Ir(III)–OH intermediate stabilizes the carbene tautomer and lowers the barrier of tautomerization,⁶ we reason that an amide group proximal to the incipient NH species should provide a similar stabilization of the NH tautomer in our system. In this regard we then designed ligand 3a (Figure 6.1). This reacted immediately with Ir(COD)₂BF₄ in acetone or CH₂Cl₂ to give a dark green solution, from which complex 4a was isolated in nearly quantitative yield (eq 6.3). Complex 4a was fully characterized. In the ¹H NMR spectrum (CD₂Cl₂), the NH…O resonates at δ 13.88 ppm as a broad singlet and the amide NH appears at δ 10.25 ppm. Two distinct olefinic proton peaks were observed [δ 5.01 (m, 2H) and 3.86 (m, 2H) ppm], suggesting that 4a is Cₜₜ symmetric. The Ir–C carbene resonates at δ 180.0 ppm, comparable to those in related iridium complexes.
In fact, it is not necessary to have a blocking group at the 4-position to prevent the undesired C–H oxidative addition. Directly analogous reactions yielding 4b–e can also be achieved by starting from ligands 3b–e and Ir(COD)₂BF₄, respectively. In all these products the NH···O protons resonate in a range of δ 13.8 to 14.3 ppm in the ¹H NMR spectra and the Ir–C_carbene signals appear in a narrow range of δ 175 to 180 ppm. These comparisons indicate that the presence of an amide group as a hydrogen bond acceptor can remarkably enhance the selectivity of tautomerization over C–H oxidative addition. A hydride species (δ -14.9 ppm in the ¹H NMR spectrum) was observed in the reaction of 3a and [Ir(COD)]BF₄ carried out in CD₂Cl₂ at -20 °C. However, it still remains a question whether the tautomerization proceeds through iridium hydride oxidative addition intermediates¹¹ or goes directly via a concerted mechanism.

6.2.3 X-ray Analysis

The identity of 4a was further confirmed by X-ray crystallography (Figure 6.1 and Table 6.1, 6.2). Complex 4a has a distorted square planar structure. The Ir–carbene bond has a normal length of 1.999(2) Å.⁶,⁷ The calculated NH···O distance is 1.960 Å and is shorter than the sum of the van der Waals radii of hydrogen and nitrogen, suggestive of an intramolecular NH···O hydrogen bond. The amide plane also offsets the adjacent pyridine ring by only 11.09° to allow this hydrogen bond. The length of C(14)–C(15), 1.425(3) Å, is longer than the other three C–C bonds in the carbene ring ranging from 1.377 to 1.407 Å. Similar observations have been found in related pyridine-based carbene complexes.⁶,¹⁴ The Ir(1)–C(1) [2.205(11) Å] and Ir(1)–C(2) [2.212(10) Å] distances are longer than
those of Ir(1)–C(5) [2.123(2) Å] and Ir(1)–C(6) [2.125(2) Å], as a result of the high trans-influence of the carbene. It is clear that ligand 3a can readily isomerize to the corresponding carbene via the activation of the C–H bond adjacent to the N, with the H atom being formally transferred to the nitrogen atom.

Figure 6.1. Molecular structure of the cation of 4a shown at 50% thermal ellipsoid.
Table 6.1 Selected Bond Lengths (Å) and Bond Angles (deg) of 4a

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<td>Ir(1)-C(15)</td>
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## Table 6.2. Crystallographic data for complexes 4a

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6.3 Conclusion

We have demonstrated that Ir(I)-induced tautomerization of a pyridine moiety can be successfully achieved. The carbene tautomer is both stabilized by the chelation effect and by hydrogen bonding with a proximal amide group. The amide group also enhances the selectivity of tautomerization over C–H oxidative addition. These results may find applications in catalyst design featuring non-covalent interactions to enhance the selectivity and reactivity of catalytic reactions, as in molecular recognition. Theoretical investigations of this tautomerization process and the tautomerization of monodentate pyridines are currently in progress.
6.4 Experimental Section

General Considerations.

All manipulations were performed using standard Schlenk techniques or in nitrogen-filled glove-box, except where otherwise noted. All solvent were distilled under N₂ before use and stored glove-box. CDCl₃ was dried by 4Å molecular sieve and CD₂Cl₂, DMSO-d₆ were obtained in sealed ampules from CIL and were used without further purification. Air-sensitive product were stored and weighted in glove-box.

NMR spectra were obtained on a Bruker DPX 300 Mhz, AMX 400 MHz or 500 MHz spectrometer at 298K unless otherwise specified. The chemical shift is given as dimensionless δ values and is frequency referenced to TMS for ¹H and ¹³C NMR. Elemental analyses were performed in the Division of Chemistry and Biological Chemistry, Nanyang Technological University. HRMS spectra were obtained in EI or ESI mode on a Finnigan MAT95XP GC/HRMS system (Thermo Electron Corp.). X-ray crystallographic analysis was performed on a Bruker X8 APEX diffractometer.

Synthesis of Ligands

**Compound 1.** 3-Bromo-pyridine (300 mg, 1.90 mmol) and Pd(PPh₃)₄ (110 mg, 5 mol%) were dissolved in dry toluene (4 ml) under nitrogen, and 2-pyridylzinc bromide solution in THF (0.5 M, 3.8 ml, 1.90 mmol) was then added by syringe. The mixture was stirred for 24 hours under reflux. After reaction, all volatiles were removed under vacuo and water was added. The aqueous layer was then extracted with dichloromethane twice and the extract was dried over sodium sulfate. Silica gel chromatography (EtOAc/hexane 1:1) gave the compound 1 as brown oil. (225 mg, 1.44 mmol, 76%). ¹H NMR (500 MHz CDCl₃) δ 9.19 (d, J = 2.2 Hz, 1H), 8.73(d, J = 4.7 Hz, 1H), 8.65 (d, J = 4.7 Hz, 1H), 8.33 (d, J = 8.0 Hz, 1H), 7.75-7.82 (m, 2H), 7.41 (dd, J = 8.0, 8.0 Hz, 1H), 729-7.31 (m, 1H). ¹³C NMR (125MHz CDCl₃) 154.8, 150.1, 149.9, 148.2, 137.1, 133.9, 134.4, 123.6, 122.9,120.7. HRMS (EI): 156.0722 (calculated 156.0682)
**Compound 2.** 3-Bromo-4-methylpyridine (200 mg, 1.16 mmol) and Pd(PPh₃)₄ (67 mg, 5 mol%) were dissolved in dry toluene (4 ml) under nitrogen, and 2-(tributylstannyl)pyridine (475 mg, 1.28 mmol) was then added by syringe. The mixture was stirring for 24 h under reflux. After removing toluene by vacuum, the residue was dissolved in dichloromethane and the palladium black was removed by filtration through Celite. The pure product could be obtained as brown oil by chromatography on silica gel using hexanes/ethyl acetate (1:1) as eluent in 70% (139 mg) yield. ¹H NMR (500 MHz CDCl₃) 8.71-8.72 (m, 1H), 8.58 (s, 1H), 8.48 (d, J = 5.1 Hz, 1H), 7.79 (td, J = 7.7, 1.8 Hz, 1H), 7.41 (d, J = 7.8 Hz, 1H), 7.29 (dd, J = 7.5, 4.7 Hz, 1H), 7.20 (d, J = 5.0 Hz, 1H), 2.40 (s, 3H, CH₃). ¹³C NMR (125 MHz, CDCl₃) 156.8, 149.9, 149.6, 149.1, 145.3, 136.6, 136.3, 125.6, 124.1, 122.3, 19.8. HRMS (EI): 170.0833 (calculated 170.0838).

Compounds 3a-e were synthesized Stille coupling reaction through a directly analogous method for 2.

**Compound 3a.** 3a was obtained as white solid starting from N-(5-bromo-4-methylpyridin-2-yl)acetamide (180 mg, 0.786 mmol) and 2-(tributylstannyl)pyridine (321 mg, 0.865 mmol). Yield: 77% (137 mg, 0.603 mmol). ¹H NMR (500 MHz CDCl₃): δ 8.92 (br, 1H, NH), 8.74 (d, J = 4.3 Hz, 1H), 8.31 (s, 1H), 8.19 (s, 1H), 7.80 (td, J = 7.8, 1.8 Hz, 1H), 7.41 (d, J = 7.8 Hz, 1H), 7.28-7.31 (m, 1H), 2.46 (s, 3H), 2.24 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): 168.9, 154.4, 150.1, 150.0, 144.0, 138.2, 147.9, 136.5, 132.8, 124.2, 122.2, 115.3, 24.8, 20.5 ppm. Anal. Calcd for C₁₃H₁₃N₃O (FW 227.3) C, 68.70; H, 5.77; N, 18.49; Found C, 68.88; H, 5.31; N, 18.19.

**Compound 3b.** 3b was obtained as white solid starting from N-(5-bromo-3-methylpyridin-2-yl)acetamide (180 mg, 0.786 mmol) and 2-(tributylstannyl)pyridine (321 mg, 0.865 mmol). Yield: 74% (132 mg, 0.581 mmol). ¹H NMR (500 MHz CDCl₃): δ 8.83 (s, 1H), 8.80 (br, 1H, NH), 8.72 (d, J = 4.8 Hz, 1H), 8.21 (s, 1H), 7.79 (t, J = 6.7 Hz, 1H), 7.72 (d, J = 7.9 Hz, 1H), 7.28-7.30 (m, 1H), 2.38 (s, 3H), 2.33 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 172.1, 154.4, 150.1, 150.0, 144.0, 138.2, 137.0, 132.8, 127.7, 122.6,
Compound 3c. 3c was obtained as white solid starting from N-(5-bromo-3-methylpyridin-2-yl)propionamide (150 mg, 0.617 mmol) and 2-(tributylstannyl)pyridine (252 mg, 0.68 mmol). Yield: 72% (116 mg, 0.483 mmol). 1H NMR (500 MHz, CDCl_3): δ 9.05 (br, 1H, NH), 8.83 (d, J = 2.0 Hz, 1H), 8.70 (d, J = 4.2 Hz, 1H), 8.19 (s, 1H), 7.78 (td, J = 7.8, 1.7 Hz, 1H), 7.71 (d, J = 7.9 Hz, 1H), 7.27-7.29 (m, 1H), 2.56 (q, J = 7.4 Hz, 2H, CH_2), 2.37 (s, 3H), 1.26 (t, J = 7.6 Hz, 3H). 13C NMR (125 MHz, CDCl_3): δ 173.4, 154.4, 150.3, 149.9, 143.9, 138.3, 137.1, 132.8, 128.2, 122.7, 120.4, 29.9, 18.4, 9.7. Anal. Calcd C_{14}H_{15}N_{3}O (FW 241.3) C, 69.69; H, 6.27; N, 17.41; Found C, 69.78; H, 6.01; N, 17.50.

Compound 3d. 3c was obtained as white solid starting from N-(5-bromopyridin-2-yl)acetamide (160 mg, 0.744 mmol) and 2-(tributylstannyl)pyridine (304 mg, 0.82 mmol). Yield: 78% (124 mg, 0.58 mmol). 1H NMR (500 MHz, CDCl_3): δ 8.94 (s, 1H), 8.93 (br, 1H, NH), 8.70 (d, J = 4.7 Hz, 1H), 8.33-8.35 (m, 2H), 7.78 (t, J = 7.9 Hz, 1H), 7.71 (d, J = 7.9 Hz, 1H), 7.26-7.29 (m, 1H), 2.27 (s, 3H). 13C NMR (125 MHz, CDCl_3): δ 168.9, 154.4, 151.9, 150.4, 146.3, 137.0, 136.8, 131.1, 122.5, 120.0, 113.8, 24.8. Anal. Calcd C_{12}H_{11}N_{3}O (FW 213.2) C, 67.59; H, 5.20; N, 19.71; Found C, 67.90; H, 5.31; N, 19.51.

Compound 3e. 3e was obtained as white solid starting from N-(5-bromopyridin-2-yl)propionamide (140 mg, 0.611 mmol) and 2-(tributylstannyl)pyridine (250 mg, 0.67 mmol). Yield: 70% (97.5 mg, 0.43 mmol). 1H NMR (500 MHz, CDCl_3): δ 8.93 (s, 1H), 8.71 (d, J = 4.5 Hz, 1H), 8.67 (br, 1H, NH), 8.32-8.37 (m, 2H), 7.78 (td, J = 7.8, 1.6 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.26-7.29 (m, 1H), 2.48 (q, J = 7.5 Hz, 2H), 1.28 (t, J = 7.5 Hz, 3H). 13C NMR (125 MHz, CDCl_3): δ 172.6, 154.5, 151.9, 149.9, 146.3, 137.0, 136.8, 131.0, 122.5, 120.1, 113.7, 30.8, 9.4. Anal. Calcd C_{13}H_{13}N_{3}O (FW 227.3) C, 68.70; H, 5.77; N, 18.49; Found C, 68.51; H, 5.83; N, 18.64.
Synthesis of Iridium Complex 4

**General Procedure:** To a stirred solution of ligand 3a-e (0.2 mmol) in dry acetone (3 ml) was added the Ir(COD)₂BF₄ (0.2 mmol) solution in acetone (2 ml) at room temperature in glovebox. After stirring 30 min, the mixture became dark green and precipitation was formed. All volatiles were removed under vacuum and the residue was washed with diethyl ether, giving complex 4a-e as green solids.

**Complex 4a.** Yield: 120.4 mg, 98%. Single crystals suitable for X-ray analysis were obtained by slow diffusion of ether into a CH₂Cl₂ solution of 4a after one day at room temperature. ¹H NMR (400 MHz, CD₂Cl₂): δ 13.9 (br, 1H, NH of tautomeration), 10.3 (br, 1H, NH of amide), 8.26 (d, J = 5.2 Hz, 1H), 7.99-8.06 (m, 2H), 7.44 (td, J = 7.8, 1.4 Hz, 1H), 7.05 (d, J = 1.4 Hz, 1H), 5.01 (d, J = 2.4 Hz, 2H, COD), 3.85 (t, J = 2.3 Hz, 2H, COD), 2.71 (s, 3H, CH₃), 2.34 (s, 3H, CH₃), 2.33-2.37 (m, 3H, COD), 2.17-2.25 (m, 3H, COD), 2.12 (s, 2H, COD). ¹³C NMR (75 MHz, CD₂Cl₂): δ 180.0 (Ir-C), 175.2, 164.4, 151.8, 150.7, 146.6, 142.2, 141.0, 124.6, 123.5, 112.6, 91.1, 63.9, 32.8, 30.0, 24.1. Anal. Calcd for C₂₁H₂₅BF₄IrN₃O (FW 614.5): C, 41.05; H, 4.10; N, 6.84; Found: C, 41.21; H, 4.31; N, 6.48.

**Complex 4b.** Yield: 116.8 mg, 95%. ¹H NMR (300 MHz, DMSO-d₆): δ 14.2 (br, 1H, NH of tautomeration), 10.8 (br, 1H, NH of amide), 8.72 (s, 1H), 8.66 (d, J = 5.4 Hz, 1H), 8.33 (d, J = 8.0 Hz, 1H), 8.14 (t, J = 7.7 Hz, 1H), 7.51 (t, J = 6.3 Hz, 1H), 3.80 (br, 4H, COD), 2.35 (s, 3H, CH₃), 2.34 (s, 3H), 2.27-2.29 (m, 3H, COD), 2.01-2.08 (m, 5H, COD). ¹³C NMR (75 MHz, DMSO-d₆): δ 175.4 (Ir-C), 175.0, 160.1, 150.5, 147.4, 140.4, 138.8, 137.8, 124.9, 121.1, 116.3, 33.0 (br), 24.8, 16.3. Anal. Calcd for C₂₁H₂₅BF₄IrN₃O (FW 614.5) C, 41.05; H, 4.10; N, 6.84; Found C, 41.43; H, 4.44; N, 6.61.

**Complex 4c.** Yield: 122 mg, 97%. ¹H NMR (400 MHz, CD₂Cl₂): δ 14.5 (br, 1H, NH of tautomeration), 9.6 (br, 1H, NH of amide), 8.32 (d, J = 4.3 Hz, 1H), 8.06-8.10 (m, 2H), 7.87 (d, J = 8.0 Hz, 1H), 7.48 (t, J = 6.6 Hz, 1H), 4.92 (br, 2H, COD), 3.88 (br, 2H, COD), 2.84 (q, J = 7.4 Hz, 2H, CH₂), 2.69 (s, 3H, CH₃), 2.38-2.56 (m, 4H, COD), 2.18-2.24 (m, 4H, COD), 1.25 (t, J = 7.4 Hz, 1H). ¹³C NMR (100 MHz, CD₂Cl₂): δ 179.6, 177.6 (Ir-C),
163.3, 150.2, 147.2, 142.7, 141.1, 137.7, 125.0, 119.9, 118.4, 90.8, 62.6, 33.1, 30.1, 15.9, 8.3. Anal. Calcd for C$_{22}$H$_{27}$BF$_4$IrN$_3$O (FW 628.5) C, 42.04; H, 4.33; N, 6.69; Found C, 41.91; H, 4.52 N, 6.60.

**Complex 4d.** Yield: 115 mg, 96%. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 13.8 (br, 1H, NH of tautomerization), 12.0 (br, 1H, NH of amide), 8.74 (d, $J = 8.6$ Hz, 1H), 8.64 (d, $J = 5.1$ Hz, 1H), 8.30 (d, $J = 7.9$ Hz, 1H), 8.14 (t, $J = 7.6$ Hz, 1H), 7.52 (t, $J = 6.2$ Hz, 1H), 7.04 (d, $J = 8.5$ Hz, 1H), 3.78 (br, 4H, COD), 2.27 (s, 3H, $CH_3$), 2.25-2.28 (m, 4H, COD), 2.03-2.08 (m, 4H, COD). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 178.7 (Ir-C), 174.2, 160.0, 150.4, 149.0, 140.0, 137.9, 137.4, 124.9, 121.0, 106.4, 32.9, 24.7. Anal. Calcd for C$_{20}$H$_{23}$BF$_4$IrN$_3$O (600.4) C, 40.01; H, 3.86; N, 7.00; Found C, 40.22; H, 3.91; N, 6.85.

**Complex 4e.** Yield: 120.4 mg, 98%. $^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 14.2 (br, 1H, NH of tautomerization), 10.4 (br, 1H, NH of amide), 8.21-8.25 (m, 2H), 8.07 (td, $J = 8.0$, 1.5 Hz, 1H), 7.80 (d, $J = 8.0$ Hz, 1H), 7.48 (t, $J = 6.0$ Hz, 1H), 7.30 (dd, $J = 8.7$, 2.0 Hz, 1H), 5.09 (br, 2H, COD), 3.93 (br, 2H, COD), 2.70 (q, $J = 7.4$Hz, 1H), 2.36-2.41 (m, 4H, COD), 2.19-2.28 (m, 4H, COD), 1.24 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta$ 178.6 (Ir-C), 177.6, 160.0, 150.4, 149.0, 139.9, 137.9, 137.4, 124.8, 121.0, 106.4, 33.0, 31.2, 8.9. Anal. Calcd for C$_{21}$H$_{25}$BF$_4$IrN$_3$O (614.5) C, 41.05; H, 4.10; N, 6.84; Found 41.24; H, 4.01; N, 6.99.
Chapter 6

6.5 References


(4) For a review, see Kunz, D. Angew. Chem.; Int. Ed. 2007, 46, 3405.


10. Guoyong Song, Xingwei Li. Abnormal N-Heterocyclic Carbene Complexes in Catalytic


Conference

Selected $^1$H NMR spectrum in Chapter 2
The detailed kinetic data of CH activation (Page 37)

\[
\begin{array}{cccccccccccc}
\text{At 297.1 K}, & t \text{ (min)} & 0 & 21 & 31 & 36 & 42 & 49 & 54 & 64 & 76 & 87 & 97 \\
\text{Ir(I)} & 1.523 & 1.046 & 0.858 & 0.80 & 0.730 & 0.616 & 0.577 & 0.470 & 0.383 & 0.325 & 0.27 \\
\ln[\text{Ir(I)}] & 0.421 & 0.0447 & -0.152 & -0.223 & -0.315 & -0.485 & -0.55 & -0.756 & -0.96 & -1.123 & -1.31 \\
\end{array}
\]

\[
\begin{array}{cccccccccccc}
\text{At 302.3 K} & t \text{ (min)} & 0 & 8 & 13 & 18 & 23 & 28 & 35 & 43 & 48 \\
\text{Ir(I)} & 1.097 & 0.856 & 0.7305 & 0.6282 & 0.5374 & 0.4663 & 0.3679 & 0.2851 & 0.2587 \\
\ln[\text{Ir(I)}] & 0.0903 & -0.155 & -0.314 & -0.465 & -0.621 & -0.763 & -1 & -1.255 & -1.352 \\
\end{array}
\]

\[
\begin{array}{cccccccccccc}
\text{At 307.6 K} & t \text{ (min)} & 0 & 4 & 8 & 12 & 16 & 20 & 24 \\
\text{Ir(I)} & 0.3308 & 0.2367 & 0.1728 & 0.1228 & 0.08786 & 0.06367 & 0.04209 \\
\ln[\text{Ir(I)}] & -1.1062 & -1.4411 & -1.7557 & -2.097 & -2.432 & -2.754 & -3.168 \\
\end{array}
\]

\[
\begin{array}{cccccccccccc}
\text{At 312.99 K} & t \text{ (min)} & 0 & 5 & 10 & 20 & 25 & 30 & 35 & 40 \\
\text{Ir(I)} & 0.7619 & 0.5963 & 0.4877 & 0.2856 & 0.2194 & 0.1666 & 0.1327 & 0.1013 \\
\ln[\text{Ir(I)}] & -0.272 & -0.517 & -0.718 & -1.253 & -1.517 & -1.792 & -2.02 & -2.29 \\
\end{array}
\]

The concentration of Ir (I) is relative to the internal standard.
Selected $^1$H NMR spectrum in Chapter 3
Selected $^1$H NMR spectrum in Chapter 4
Selected $^1$H NMR spectrum in Chapter 5
Appendix

Selected $^1$H NMR spectrum in Chapter 6