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

Synthesis, Mechanism, Dynamics, and Catalysis

by

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Doctor of Philosophy

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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 $[\text{Ir}(\text{COD})\text{Cl}]_2$ 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 $\text{C}(\text{sp}^3)\text{-H}$ *vs* $\text{C}(\text{sp}^2)\text{-H}$ 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 $[\text{Ir}(\text{COD})_2]^+$. 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.

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Abbreviations and Symbols

Ac	acetyl
Ar	aryl
Å	angstrom
Br	broad
Bu, ^t Bu	butyl, <i>t</i> -butyl
Cal	calories
CIL	Cambridge Isotope Laboratories, Inc
°C	degree Celsius
COD	1,5-cyclooctadiene
Cp*	pentamethylcyclopentadienyl
Δ	chemical shift (parts per million)
D	doublet, day
<i>d</i> , D	deuterium
DFT	density functional theory
E	electron
Eq	equation
eq.	equivalents
Et	Ethyl
H	Hour
Hz	Hertz
IR	infrared

<i>J</i>	coupling constants
J	Joules
K	Kelvin
K	kilo, reaction rate constant
K _{eq}	equilibrium constant
KHMDS	potassium hexamethyldisilazane
L	neutral two electron donors
Λ	wavelength
m	milli, multiplet
M	metal, molar
Me	methyl
Min	Minute
NHC	N-heterocyclic carbene
MS	mass spectrometry
NMR	Nuclear Magnetic Resonance
<i>O</i>	Ortho
<i>P</i>	Para
Ph	Phenyl
PPh ₃	triphenyl phosphine
Py	pyridine, pyridyl
Q	Quartet
R	alkyl or aryl group

RT	room temperature
S	second, singlet
Sept	Septet
T	Triplet
THF	Tetrahydrofuran
TMS	Trimethylsilane
$\gamma_{1/2}$	half-peak-width
X	halogen, anionic two electron donors

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 $[\text{Ir}(\text{COD})\text{Cl}]_2$ 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 $\text{C}(\text{sp}^3)\text{-H}$ *vs* aromatic $\text{C}(\text{sp}^2)\text{-H}$ activation could be adjusted by the steric bulk of the OR ligand. Experimental results also confirmed that a 7-membered iridium $\text{C}(\text{sp}^3)\text{-H}$ activation product is the kinetic product while the 6-membered iridium abnormal carbene product, resulting from the activation of a $\text{C}(\text{sp}^2)\text{-H}$ 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-*a*]pyridiniums *via* silver transmetalation. The donating abilities of these new NHC ligands have been accessed by

analyzing the average CO stretching frequencies of their corresponding iridium dicarbonyl complexes. Both VT NMR studies and CO stretching frequency values support significant π -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)

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 imidazolylidenes⁵ (Figure 1.1, A), also 1,2,4-triazolin-5-ylidenes (B)⁸, saturated imidazolidin-2-ylidenes (C),⁹ tetrahydropyrimid-2-ylidenes (D),¹⁰ acyclic structures (E),¹¹ systems with larger ring sizes (F),¹² constrained geometry (G)¹³ or containing other heteroatom in the cycle (H, I).¹⁴ Pioneering work by Bertrand and others evidenced that singlet carbenes may be isolated also with less pronounced heteroatom stabilization (J, K and L).¹⁵ Reviews of the different synthetic routes from different precursors can be found in the literature.

Figure 1.1 Different classes of N-Heterocyclic Carbenes (NHC)

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^tBu, ⁿBuLi) followed by addition to the metal fragment;¹⁶ 2) transmetalation from a silver–NHC complex prepared from the reaction of an imidazolium precursor and Ag₂O or Ag₂CO₃;¹⁷ 3) Direct metallation in the reaction of a precursor and basic metal sources such as Pd(OAc)₂,¹⁸ Pt(acac)₂¹⁹ or Cp^{*}Ni(acac)₂²⁰; 4) oxidative addition by activation of the C-X (X=Me, I, H) bond of an imidazolium cation;²¹⁻²² 5) insertion of a metal into the C=C bond of bis(imidazolidin-2-ylidene)-containing olefins²³ (Lappert method). (Scheme 1.1)

Scheme 1.1 Pathways for synthesis of NHC metal complexes^{6d}

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.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 P^tBu_3 and the normal NHCs.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.²⁶

Scheme 1.2 Normal and abnormal NHC complexes

Similar to other carbenes that lack extensive heteroatom stabilization, such as pyridylidenes, free C4 carbenes display lower stability than their crystallographically characterized C2 counterparts.³ Energy decomposition analysis predicts that the C2 carbene (**M**) is about 19.1 kcal/mol more stable than C4 carbene (**N**).²⁷ (Scheme 1.2)

1.3.1 Reactivity of CH on NHC Backbone

By the computational studies, the pK_a values of C2-H and C4-H protons of imidazolium are 24.9 and 33.0, respectively.²⁸ Although less acidic than C2, the chlorination of C4/5 position in C2 imidazolidene can be achieved under mild conditions using CCl_4 in THF²⁹ (eq 1.2). The protons (C4 and C5) in C2 imidazolidene also could undergo rapid H/D exchange in $\text{DMSO}-d_6$, D_2O , or CD_3OD .³⁰

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,^{31a} iron^{31b} and Ru^{31c} (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.³²

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 $\text{IrH}_5(\text{PPh}_3)_2$ 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

R	X	Abnormal : Normal
Me	Br	9 : 91
Me	OAc	20 : 80
Me	BF_4	45 : 55
Me	PF_6	50 : 50
Me	SbF_6	89 : 11
<i>i</i> Pr	Br	16 : 84
<i>i</i> Pr	BF_4	100 : 0

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 PPh_3 . 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 aploar anions, such as BF_4^- and SbF_6^- . 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 $OsH_6(P^iPr_3)_2$.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-*a*]pyridine³⁵, imidazo[1,5-*a*]pyridine,³⁶ could also afford abnormal NHC complexes following by this method.

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 $\text{Pd}(\text{OAc})_2$ or with a suitable rhodium precursor proceeded to afford abnormal NHC Pd and Rh complexes, respectively^{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

However, when a bisimidazolium salt with a methylene linker was metallated with $[\text{IrCp}^*\text{Cl}_2]_2$ 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 complex³⁹. 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 moieties³⁹ (Scheme 1.5).

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.

Scheme 1.6

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.²² (Scheme 1.6)

1.4 NHCs Tautomerization

N-H tautomer of pyridine, an N-heterocyclic carbene (NHC), first proposed 70 years ago,⁴⁰ was generated in the gas phase by mass spectrometry.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).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.⁴²

Scheme 1.7

1.4.1 Monodentate System

Tautomerization of Pyridine

Poveda, Carmona and coworkers reported the reaction of 2-substituted pyridines ($R = \text{Me, Ph}$) and $[\text{TpMe}_2\text{IrPh}_2(\text{N}_2)]$ ($\text{TpMe}_2 = \text{hydrotris(3,5-dimethylpyrazolyl)borate}$)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

Scheme 1.8

At the same time, Esteruelas and coworkers treated $\text{OsCl}_2\text{H}_2(\text{P}^i\text{Pr}_3)_2$ or $\text{RuCl}_2\text{H}_2(\text{P}^i\text{Pr}_3)_2$ 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 1.9

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.⁴⁶ 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.⁴⁷ 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).

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.⁴⁸ (scheme 1.11)

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 $(\text{PCy}_3)_2\text{RhCl}$ ⁴⁹ (Scheme 1.12). An N-bound complex was identified along the path to the Rh *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 *via* Rh-H intermediates was proposed in the mechanism.⁴⁹

Scheme 1.12

Based on this mechanism, the scope of heterocycle *ortho*-alkylation has been dramatically expanded to pyridines and quinolines, which contain only one nitrogen⁵⁰ (eq 1.6). The reactions are conducted at a high concentration (0.8 M) with 1 mol% Rh loadings. Substitution *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 $[\text{RuCp}^*\text{Cl}]_4$ 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).

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 $[\text{IrCp}^*\text{Cl}_2]_2$ 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 σ -donors and π -acceptors than the more common imidazole-2-ylidenes.⁵³ More recently, remote N-heterocyclic carbenes derived from pyridine⁵⁴, 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 *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.^{54,55} Bercaw and coworkers also prepared a series of py-NHC complexes of Pt^{57a}, Pd^{57b} and Ni^{57b} *via* intramolecular C-H activation using pyridine tethered pyridinium as precursors. (Scheme 1.16)

Scheme 1.16

1.5.2 NHC-Phosponium Ylide Ligands

As neutral spectator carbon-centered ligands, phosphonium ylides have been represented recently and the catalytic properties of these saturated $sp^3\text{-C}$ ligands have been more illustrated.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.⁵⁹ (Scheme 1.17)

Scheme 1.17

A comparisons of IR spectra of $\text{Rh}(\text{CO})_2\text{L}$ 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.⁵⁹

1.5.3 Carbodicarbenes

Previous research have reported synthesis and structural characterization of carbodiphosphoranes, in which two donor ligands PR_3 coordinate to a carbon(0) atom (Figure 1.2). Alternatively, a heterocumulene $\text{R}_3\text{P}=\text{C}=\text{PR}_3$ 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

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 $[\text{RhCl}(\text{CO})_2\text{L}]$ complexes demonstrate that the carbodicarbene is a stronger σ donor and weaker π acceptor than N-heterocyclic or acyclic diaminocarbenes.

Scheme 1.18

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.⁶³ Fürstner et al. isolated 1,3-dimethyl-2-methyleneimidazoline which could react with $[\text{Au}(\text{PPh}_3)\text{Cl}]$ and $\text{Rh}(\text{CO})_2\text{Cl}$ to yield gold and rhodium complexes, respectively⁶⁴ (Scheme 1.19). The carbodicarbene in Rh complex acts as a very strong σ donor with a donor strength comparable to the cyclic carbodiphosphoranes.

Scheme 1.19

Base treatment of di(2-methylimidazolium salts) with $[\text{IrCp}^*\text{Cl}_2]_2$ could also afford 2-methyleneimidazoline complexes.³⁹ (Scheme 1.5)

1.6 Conclusion

The distinctive σ -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

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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}

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^tBu_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.^{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.^{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.^{17a} Alkylation of 1-*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 KPF₆ in acetone or acetonitrile readily afforded complex **1-PF₆**. 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.^{9d, 17b,18a} This alkylation method proved more selective and took a short reaction time compared to that using CH₂Br-CH₂Br, 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 PF₆⁻ salts **2-PF₆** and **10** 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.^{9d}

Scheme 2.1. Synthesis of phosphine-tethered imidazoliums

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_2Cl_2 solution of **1-(PF₆)** and 0.5 equiv of $[\text{Ir}(\text{COD})\text{Cl}]_2$ 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 $[\text{Ir}(\text{COD})_2]\text{PF}_6$. In the ^1H NMR spectrum (CD_2Cl_2) of **5**, the hydride resonates at δ -15.81 (d, $^2J_{\text{HP}} = 7.5$ Hz) and this small coupling constant here suggests the *cis* orientation of the hydride and the phosphine. A low-field signal at δ 8.57 was also observed in the ^1H NMR spectrum and was ascribed to the C(2)-H of the imidazole ring. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the Ir-C(4/5) resonates at δ 135.4 (d, $^2J_{\text{CP}} = 5.7$ 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)**

	5	8a-(PF₆)
Ir(1)-C9 (Å)	2.049(4)	2.065(6)
Ir(1)-P(1) (Å)	2.585(1)	2.316(1)
Ir(1)-Cl(1) (Å)	2.5097(9)	2.5076(14)
C(9)-Ir(1)-P(1) (deg)	80.98(11)	92.24(16)
P(1)-Ir(1)-Cl(1) (deg)	85.98(3)	90.83(5)
N(2)-C(9)-Ir(1) (deg)	117.9(3)	126.7(4)

Table 2.2 Crystallographic Data for complexes **5** and **8a-(PF₆)**

	5	8a-(PF₆)
empirical formula	C ₂₇ H ₃₄ ClF ₆ IrN ₂ P ₂	C ₂₆ H ₃₂ ClF ₆ IrN ₂ P ₂
formula weight	790.15	776.13
temperature	173(2) K	
crystal system	Orthorhombic	Monoclinic
space group	Pbca	P2(1)/c
<i>a</i> (Å)	12.8370(5)	12.5058(4)
<i>b</i> (Å)	18.8931(8)	7.2918(2)
<i>c</i> (Å)	23.3920(10)	29.6570(11)
<i>α</i> (deg)	90	90
<i>β</i> (deg)	90	95.284(2)
<i>γ</i> (deg)	90	90
<i>V</i> (Å ³)	5673.3(4)	2692.92(15)
<i>Z</i>	8	4
<i>d</i> _{calcd} (g/cm ³)	1.850	1.914
<i>μ</i> (mm ⁻¹)	4.975	5.238
crystal size (mm)	0.25 x 0.10 x 0.06	0.15 x 0.04 x 0.04
total, unique no. of rflns	29836, 5873	38359, 4762
<i>R</i> (int)	0.0365	0.0564
data, restraints, parameters	5873, 66, 358	4762, 0, 356
<i>R</i> , <i>R</i> _w (all data)	0.0356, 0.0650	0.0391, 0.0980
GOF	1.034	1.091
peak and hole (eÅ ⁻³)	1.366, -1.003	4.945, -0.961

The acidity of complex **5** can be demonstrated by base-promoted reductive elimination of HCl using Cs_2CO_3 in acetone or MeCN (Scheme 2.2). Thus complex **6** was isolated (92%) and was spectroscopically characterized. In the ^1H NMR spectrum (CD_3CN), the C(2)-H resonates at δ 8.51 and the Ir-C_{carbene} resonates at δ 130.6 (d, $^2J_{\text{PC}} = 11.7$ Hz) in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. Base-promoted *trans* reductive elimination of HCl from Ir(III) biscarbene complexes has been recently reported.^{11a,b} 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 CDCl_3 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 ($k = 0.0179 \text{ min}^{-1}$), 302.3 K ($k = 0.0306 \text{ min}^{-1}$), 307.6 K ($k = 0.0508 \text{ min}^{-1}$), and 312.9 K ($k = 0.0847 \text{ min}^{-1}$) (Figure 2.2). The Eyring plot from these data gave activation parameters $\Delta H^\ddagger = 17.4 \text{ kcal/mol}$ and $\Delta S^\ddagger = -16 \text{ eu}$ (Figure 2.3). The large negative $\Delta S^\ddagger$ 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

^a The slope of this line is k

Figure 2.3 The Eyring Plot for Activation Parameters of Decay of **4** ^a

^a The slope of this line is $-\Delta H^\ddagger/R$, and the intercept is $[\Delta S^\ddagger/R + \ln(k_b/h)]$

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**

Complex **8a**-(PF₆) 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)° 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**-(PF₆) 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 CD_3CN , and the van't Hoff plots of the equilibration systems for **7a**-(Cl), **7a**-(PF_6), and **7b**-(PF_6) 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 2.3 Measurement of K_{eq} of Equilibrium between **7** and **8**

T (K)	8a-(PF_6)/7a-(PF_6)		8b-(PF_6)/7b-(PF_6)		8a-(Cl)/ 8b-(Cl)	
	K_{eq}	$\ln K_{\text{eq}}$	K_{eq}	$\ln K_{\text{eq}}$	K_{eq}	$\ln K_{\text{eq}}$
298.0	18.17	2.9	15.75	2.757	10.85	2.384
308.0	11.80	2.47	10.85	2.384	8.26	2.112
318.0	8.36	2.123	7.64	2.034	5.93	1.7814
323.0	7.10	1.96	6.11	1.81	5.317	1.671
328.0	6.21	1.826	5.20	1.649	4.711	1.55
330.0			4.63	1.533		
338.0	4.43	1.49	3.97	1.378	3.781	1.33

Figure 2.5 The van't Hoff Plot of Equilibrium between **7** and **8**^a

^a The slope of these lines are $-\Delta H^\circ/R$ and the intercept is $\Delta S^\circ/R$

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.¹³ Here C-H activation consistently occurred at the C(4/5) position regardless of the anions (Cl^- , PF_6^- , or SbF_6^-). The ^{19}F - ^1H HOESY spectra of both complexes **5** (Figure 2.6) and **8a**-(PF_6^-) in CD_2Cl_2 were obtained, and they showed the correlation between the PF_6^- anion and the imidazole C(2)-H, suggesting an ion-pairing interaction between these two moieties in solutions.

Figure 2.6. ^{19}F , ^1H -HOESY NMR Spectra (^{19}F , 282 MHz, 298 K, CD_2Cl_2) of Complex **5**

2.2.3.4 Attempt for C2-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 $[\text{Ir}(\text{COD})\text{Cl}]_2$ (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.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).^{9d} 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).

Scheme 2.6

2.2.5 Catalysis Results

Iridium biscarbene dihalides have been demonstrated as robust catalysts for the ketone transfer hydrogenation,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 ⁱPrOH proceeded smoothly in the presence of 0.1 mol% of complexes **8a-b**-(PF₆) and 10 mol% NaOH (eq 2.2). Comparisons between complexes **8a-b**-(PF₆), **9**, and **12** are displayed in Table 2.5, which shows that complexes **8a**-(PF₆), **8b**-(PF₆), and **9** all have similar activity (Table 2.4, entries 1-3). This fact also indicates that complexes **8a-b**-(PF₆) 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**-(PF₆) for the transfer hydrogenation of α,β -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 α,β -unsaturated aldehydes are not as clean, although a nearly full conversion was achieved. Using a weaker base such as Cs₂CO₃ 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

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.

Table 2.4 Transfer Hydrogenation of Acetophenone and α,β -Unsaturated Ketones and Aldehydes^a

Entry	Substrates	Product	Catalyst (mol%)	Time (h)	Yield (%) ^c
1			8a -(PF ₆) (0.1)	5	92
2			8b -(PF ₆) (0.1)	5	95
3			9 (0.1)	5	94
4			12 (0.1)	5	28
5			8b -(PF ₆) (0.5)	4	98
6			8b -(PF ₆) (0.5)	4	95
7 ^b			8b -(PF ₆) (0.5)	6	68
9			8b -(PF ₆) (0.5)	4	96
10			8b -(PF ₆) (0.5)	3	98
11 ^b			8b -(PF ₆) (0.5)	2	99

^a: *i*PrOH, reflux, 10% KOH

^b: *i*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 $[\text{Ir}(\text{COD})\text{Cl}]_2$ and $\text{Ir}(\text{COD})_2\text{PF}_6$ 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 Cs_2CO_3 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 α,β -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-*d*₆ 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-*d*₆. 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 ^{*i*}Pr), 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, J_{PC} = 10.0 Hz, PPh₂), 129.2 (d, J_{PC} = 12.4 Hz, PPh₂), 127.6 (d, J_{PC} = 103 Hz, *ipso*-PPh₂), 123.7 (s, imidazole C4/5), 119.2 (s, imidazole C4/5), 53.5 (s, CH of ^{*i*}Pr), 49.1 (d, J_{PC} = 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 hygroscopic 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, ² J_{PH} = 5.64 Hz, 2H, N-CH₂-P), 4.65 (heptet, ¹H, J = 6.7 Hz, CH of ^{*i*}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 hygroscopicity. 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 ^{*i*}Pr), 1.34 (d, 6H, 2CH₃). ³¹P {¹H} NMR (161

MHz, DMSO- d_6): δ -11.60 (s, PPh₂), -144.2 (sept, $J_{PF} = 707$ Hz, PF₆⁻). ¹³C {¹H} NMR (100 MHz, DMSO- d_6): δ 135.0 (s, imidazole C2), 134.0 (d, $J_{PC} = 12.5$ Hz, *ipso*-PPh₂), 133.2 (d, $J_{PC} = 19.3$ Hz, PPh₂), 130.5 (s, PPh₂), 129.5 (d, $J_{PC} = 6.7$ Hz, PPh₂), 123.3 (s, imidazole C4/5), 121.4 (s, imidazole C4/5), 52.8 (s, CH of ^{*i*}Pr), 47.9 (d, $J_{PC} = 20$ Hz, N-CH₂-P), 22.7 (s, CH₃). Anal. Calcd for C₁₉H₂₂F₆N₂P₂ (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). ¹H NMR (300 MHz, DMSO- d_6): δ 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-CH₂), 4.07 (t, $^3J = 5.6$ Hz, Cl-CH₂), 3.86 (s, 3H, CH₃). ¹³C NMR (75 MHz, DMSO- d_6): δ 137.2 (s, C2), 124.2 (s, C4/5), 122.2 (s, C4/5), 51.4 (s, N-CH₂), 43.9 (s, Cl-CH₂), 35.8 (s, CH₃). HRMS (ESI⁺): 146.0598. Calcd for [C₆H₁₀³⁵CIN]⁺ 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). ¹H NMR (300 MHz, CDCl₃): δ 10.67(s, 1H, imidazole H2), 7.33-7.52 (m, 12H, PPh₂ + imidazole CH), 4.39-4.45 (m, 2H, N-CH₂), 3.99 (s, 3H, CH₃), 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, *J*_{PC} = 11.6 Hz, *ipso*-PPh₂), 132.7 (d, *J*_{PC} = 19.3 Hz, PPh₂), 129.3 (s, PPh₂), 128.8 (d, *J*_{PC} = 7.0 Hz, PPh₂), 123.4 (s, imidazole C4/5), 122.1 (s, imidazole C4/5), 47.6 (d, *J*_{PC} = 23.2 Hz, N-CH₂), 36.4 (s, CH₃), 29.1 (d, *J*_{PC} = 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-*d*₆): δ 9.12 (s, 1H, imidazole H2), 7.77 (d, *J* = 1.7 Hz, 1H, imidazole H4/5), 7.59 (d, *J* = 1.7 Hz, 1H, imidazole H4/5), 7.39-7.47 (m, 10H, PPh₂), 4.25-4.33 (m, 2H, N-CH₂), 3.78 (s, 3H, CH₃), 2.74 (apparent t, *J* = 7.7 Hz, 2H, P-CH₂). ³¹P{¹H} NMR (121 MHz, DMSO-*d*₆): δ -21.8 (s, PPh₂), -144.5 (sept, *J*_{PF} = 706 Hz, PF₆⁻). ¹³C NMR (100 MHz, CD₃CN): δ 136.8 (d, *J*_{PC} = 12 Hz, *ipso*-PPh₂), 135.8 (s, imidazole C2), 132.6 (d, *J*_{PC} = 19.3 Hz, PPh₂), 129.3 (s, PPh₂), 128.8 (d, *J*_{PC} = 7.0 Hz, PPh₂), 123.6 (s, imidazole C4/5), 122.3 (s, imidazole C4/5), 47.6 (d, *J*_{PC} = 24 Hz, N-CH₂), 35.8 (s, CH₃), 27.9 (d, *J*_{PC} = 15.0 Hz, P-CH₂). Anal. Calcd 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, starting 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-*d*₆): 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, ³*J* = 6.7 Hz, 1H), 4.59 (t, ³*J* = 5.7 Hz, N-CH₂), 4.14 (t, ³*J* = 5.5 Hz, ClCH₂), 1.49 (d, ³*J* = 6.7 Hz, 6H, 2CH₃). ¹³C{¹H} NMR (75 MHz, DMSO-*d*₆): δ 136.2, 123.2, 121.2, 52.8,

50.7, 43.5, 22.8. Due to the hygroscopicity of this chloride salt, no satisfactory microanalysis could be obtained.

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). ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.24 (s, 1H, H2), 7.79-7.82 (m, 2H, H4 and H5), 7.38-7.45 (m, 10H, PPh₂), 4.53 (sept, *J* = 6.6 Hz, 1H, CH of ^{*i*}Pr), 4.25-4.31 (m, 2H, N-CH₂), 2.76 (apparent t, *J* = 7.6 Hz, 2H, P-CH₂), 1.42 (d, *J* = 6.8 Hz, 6H, 2CH₃). ³¹P{¹H} NMR (161 MHz, DMSO-*d*₆): δ -21.96 (s, PPh₂), -144.4 (sept, *J*_{PF} = 707 Hz, PF₆⁻). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 137.2 (d, *J*_{PC} = 12.2 Hz, *ipso*-PPh₂), 135.2 (s, C2), 132.9 (d, *J*_{PC} = 19.2 Hz, *o*-PPh₂), 129.6 (s, *p*-PPh₂), 129.2 (d, *J*_{PC} = 6.8 Hz, *m*-PPh₂), 123.0 (s, C4/5), 120.9 (s, C4/5), 52.68 (s, CH of ^{*i*}Pr), 47.3 (d, *J*_{PC} = 27 Hz, N-CH₂), 36.4 (s, CH₃), 27.6 (d, *J*_{PC} = 14 Hz, P-CH₂), 22.72 (s, CH₃ of ^{*i*}Pr). Anal. Calcd for C₂₀H₂₄F₆N₂P₂ (FW 468.1): C, 51.29; H, 5.17; N, 5.98; Found: C, 51.12; H, 5.42; N, 5.97.

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). ¹H NMR (300 MHz, DMSO-*d*₆): δ 7.90 (s, 1H, imidazole H4/5), 7.85 (s, 1H, imidazole H4/5), 4.60 (t, ³*J* = 4.0 Hz, N-CH₂), 4.08 (t, ³*J* = 4.0 Hz, Cl-CH₂), 3.83 (s, 3H, CH₃), 2.67 (s, 3H, CH₃). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 145.6, 123.0, 121.8, 49.2, 43.7, 35.3, 10.1. HRMS (ESI⁺): 159.0674, Calcd for [C₇H₁₂³⁵ClN₂]⁺ 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). ¹H NMR (300 MHz, CDCl₃): δ 7.92 (s, 1H, imidazole H4/5), 7.71 (s, 1H, imidazole C4/5), 7.34-7.38 (m, 10H, PPh₂), 4.33-4.41 (m, 2H, N-CH₂), 3.88 (s, 3H, CH₃), 2.66 (apparent t,

$J = 7.0$ Hz, 2H, P-CH₂), 2.58 (s, 3H, CH₃). ³¹P {¹H} NMR (121 MHz, CDCl₃): δ -21.79 (s). ¹³C NMR (75 MHz, CDCl₃): δ 143.42 (s, imidazole C2), 136.0 (d, $J_{PC} = 11.6$ Hz, *ipso*-PPh₂), 132.6 (d, $J_{PC} = 21.7$ Hz, PPh₂), 129.4 (s, PPh₂), 128.8 (d, $J_{PC} = 7.0$ Hz, PPh₂), 123.2 (s, imidazole C4/5), 121.3 (s, imidazole C4/5), 46.3 (d, $J_{PC} = 21$ Hz, N-CH₂), 35.7 (s, CH₃), 29.1 (d, $J_{PC} = 16.5$ Hz, P-CH₂), 10.51 (d, $J_{PC} = 3$ Hz, CH₃). No satisfactory microanalysis could be obtained for ligand **2c-(Cl)** due to its hygroscopicity.

Compound 2c-(PF₆): 2c-(PF₆) was obtained as a white solid by anion exchange of **2c-(Cl)** (300 mg, 0.87 mmol) using an excess amount of KPF₆ (800 mg, 4.3 mmol) in acetone. Yield: 92% (363 mg, 0.8 mmol). ¹H NMR (300 MHz, CDCl₃): δ 7.25-7.40 (m, 10H, PPh₂), 7.07 (s, 1H), 7.02 (s, 1H), 4.11 (m, 2H, PCH₂), 3.58 (s, 3H, NCH₃), 2.55 (apparent t, $J = 7.3$ Hz, 2H, PCH₂), 2.33 (s, CH₃). ³¹P {¹H} NMR (121 MHz, CDCl₃): δ -21.77 (s), -144.6 (sept, $J_{PF} = 704$ Hz, PF₆⁻). ¹³C NMR (75 MHz, CDCl₃): δ 143.7 (s, imidazole C2), 136.0 (d, $J_{PC} = 11.4$ Hz, *ipso*-PPh₂), 132.6 (d, $J_{PC} = 21.8$ Hz, PPh₂), 129.4 (s, PPh₂), 128.8 (d, $J_{PC} = 7.0$ Hz, PPh₂), 122.5 (s, imidazole C4/5), 120.6 (s, imidazole C4/5), 46.0 (d, $J_{PC} = 23$ Hz, N-CH₂), 34.9 (s, CH₃), 28.6 (d, $J_{PC} = 15.8$ Hz, P-CH₂), 9.3 (s, CH₃). Anal. Calcd for C₁₉H₂₂F₆N₂P₂ (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). ¹H NMR (300 MHz, DMSO-*d*₆): δ 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-CH₂), 4.10 (s, CH₃), 3.64 (t, $J = 5.9$ Hz, Cl-CH₂), 2.51 (quintet, $J = 6.1$ Hz, CH₂-CH₂-CH₂). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 137.4 (s, imidazole C2), 124.1 (s, C4/5), 122.8 (s, C4/5), 46.8 (s, N-CH₂), 42.2 (s, Cl-CH₂), 36.2 (s, N-CH₃), 32.5 (s, C-CH₂-C). HRMS (ESI⁺): 159.0653; Calcd for [C₇H₁₂³⁵ClN₂]⁺: 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 tetraphenylborate (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, CDCl_3): δ 7.49 (br, 8H, BPh_4), 7.33-7.39 (m, 10H, PPh_2), 6.88-6.92 (m, 8H, BPh_4), 6.69-6.72 (m, 4H, *para*- BPh_4), 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-CH_2), 2.70 (s, 3H, CH_3), 1.79 (apparent t, $d = 7.8$ Hz, 2H, P-CH_2), 1.39-1.46 (m, 2H, $\text{C-CH}_2\text{-C}$). ^{31}P $\{^1\text{H}\}$ NMR (121 MHz, CDCl_3): δ -16.9 (s). ^{13}C NMR (75 MHz, CDCl_3): 164.1 (q, $J_{\text{BC}} = 48.4$ Hz, *ipso*- BPh_4), 137.3 (d, $J_{\text{PC}} = 12.1$ Hz, *ipso*- PPh_2), 135.7 (s, BPh_4), 135.1 (s, imidazole C2), 132.6 (d, $J_{\text{PC}} = 18.7$ Hz, *o*- or *m*- PPh_2), 129.2 (s, PPh_2), 128.7 (d, $J_{\text{PC}} = 6.9$ Hz, *o* or *m*- PPh_2), 126.0 (s, *m*- BPh_4), 122.4 (s, imidazole C4/5), 122.0 (s, *p*- BPh_4), 120.3 (s, imidazole C4/5), 49.7 (d, $J_{\text{PC}} = 13.6$ Hz, N-CH_2), 35.6 (s, CH_3), 26.6 (d, $J_{\text{PC}} = 18.8$ Hz, P-CH_2), 24.5 (d, $J_{\text{PC}} = 13.3$ Hz, $\text{C-CH}_2\text{-C}$). Anal. Calcd for $\text{C}_{43}\text{H}_{42}\text{BN}_2\text{P}$ (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, CDCl_3): δ 10.84 (s, 1H, imidazole H2), 4.72 (t, $^3J = 5.04$ Hz, 2H, N-CH_2), 4.41 (heptet, $J = 6.6$, 1H, CH of *i*Pr), 4.14 (t, $^3J = 5.04$ Hz, Cl-CH_2), 2.29 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 1.63 (d, $J = 6.6$ Hz, 6H, 2CH_3). ^{13}C NMR (75 MHz, CDCl_3): δ 135.6 (s, imidazole C2), 127.3 (s, C4/5), 125.2 (s, C4/5), 50.8 (s, CH of *i*Pr), 48.2 (s, N-CH_2), 43.8 (s, Cl-CH_2), 22.8 (s, CH_3 of *i*Pr), 8.8 (s, CH_3), 8.7 (s, CH_3). 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-dimethyl-imidazolium chloride (200 mg, 0.84 mmol). Yield: 88% (367 mg, 0.74 mmol). ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.10 (s, 1H, imidazole H2), 7.39-7.64 (m, 10H, PPh₂), 4.43 (heptet, J = 6.6 Hz, 1H, CH of ^{*i*}Pr), 4.21-4.27 (m, 2H, N-CH₂), 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-*d*₆): δ -21.60 (s, PPh₂), -144.18 (sept, J_{PF} = 702 Hz, PF₆⁻). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 137.2 (d, J_{PC} = 12.3 Hz, *ipso*-PPh₂), 133.0 (s, PPh₂), 132.8 (s, imidazole C2), 129.6 (s, PPh₂), 129.15 (d, J_{PC} = 6.8 Hz, PPh₂), 126.8 (s, imidazole C4/5), 126.3 (s, imidazole C4/5), 49.8 (s, CH of ^{*i*}Pr), 44.9 (d, J_{PC} = 25 Hz, N-CH₂), 27.3 (d, J_{PC} = 14 Hz, P-CH₂), 22.6 (s, 2CH₃), 8.19 (s, CH₃), 8.16 (s, CH₃). Anal. Calcd for C₂₂H₂₈F₆N₂P₂ (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), 5.03 (m, 1H, COD), 4.98–5.01 (m, 2H, N-CH₂-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, CH₃), 1.49 (d, $J = 6.6$ Hz, 3H, CH₃), -15.81 (d, $J_{P-H} = 7.5$ Hz, 1H, Ir-H). ³¹P{¹H} NMR (202 MHz, CD₂Cl₂): δ 27.47 (s, PPh₂), -144.4 (septet, $J_{P-F} = 709$ Hz, PF₆⁻). ¹³C{¹H} NMR (125 MHz, CD₂Cl₂): δ 135.4 (d, $J_{P-C} = 5.7$ Hz, C-Ir), 133.2 (d, $J_{P-C} = 11.4$ Hz, *o*- or *m*-PPh₂), 132.6 (d, $J_{P-C} = 9.0$ Hz, *o*- or *m*-PPh₂), 132.6 (s, imidazole C2), 132.2 (d, $J_{P-C} = 2.58$ Hz, *p*-PPh₂), 131.1 (d, $J_{P-C} = 11.6$ Hz, *ipso*-PPh₂), 129.5 (d, $J_{P-C} = 11.0$ Hz, *o*- or *m*-PPh₂), 128.9 (d, $J_{P-C} = 11.0$ Hz, *o*- or *m*-PPh₂), 125.7 (d, $J_{P-C} = 59.7$ Hz, *ipso*-PPh₂), 119.1 (s, imidazole C4/5), 95.9 (d, $J_{P-C} = 15.7$ Hz, CH of COD), 94.3 (s, CH of COD), 91.7 (d, $J_{P-C} = 9.7$ Hz, CH of COD), 84.7 (s, CH of COD), 52.7 (s, CH of ⁱPr), 49.0 (d, $J_{P-C} = 48.7$ Hz, N-CH₂-P), 35.7 (d, $J_{P-C} = 2.5$ Hz, CH₂ of COD), 30.1 (s, CH₂ of COD), 29.9 (s, CH₂ of COD), 27.6 (d, $J_{P-C} = 2.8$ Hz, CH₂ of COD), 22.7 (s, CH₃ of ⁱPr), 22.5 (s, CH₃ of ⁱPr). Anal. Calcd for C₂₇H₃₄ClF₆IrN₂P₂ (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 Cs₂CO₃ (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%). ¹H NMR (300 MHz, CD₃CN): δ 8.51 (s, 1H, imidazole C-2), 7.51–7.60 (m, 10H, PPh₂), 6.92 (s, 1H, imidazole H4/5), 4.78 (d, $J_{P-C} = 6.4$ Hz, 2H, N-CH₂-P), 4.46 (sept, $J = 6.7$ Hz, 1H, CH of ⁱPr), 4.31 (br, 3H, COD), 2.09 (m, 9H, COD), 1.46 (d, $J = 6.6$ Hz, 6H, 2CH₃). ³¹P{¹H} NMR (121 MHz CD₃CN): δ 40.23 (s, PPh₂), -143.9 (sept, $J_{P-F} = 704$ Hz, PF₆⁻). ¹³C{¹H} NMR (100 MHz, CD₃CN): δ 133.0 (d, $J_{P-C} = 11.9$ Hz, *o*- or *m*-PPh₂), 131.3 (d, $J_{P-C} = 2.1$ Hz, *p*-PPh₂), 130.9 (d, $J_{P-C} = 48$ Hz, *ipso*-PPh₂), 130.7 (s, imidazole C2), 130.6

(d, $J_{\text{P-C}} = 11.7$ Hz, C-Ir), 129.1 (d, $J_{\text{P-C}} = 10.3$ Hz, *o*- or *m*-PPh₂), 122.9 (s, imidazole C4/5), 76.6 (br, CH of ⁱPr), 52.0 (s, CH of COD), 51.4 (d, $J_{\text{P-C}} = 39.1$ Hz, N-CH₂-P), 31.3 (s, CH₂ of COD), 22.1 (s, CH₃). Anal. Calcd for C₂₇H₃₃F₆IrN₂P₂ (FW 753.7): C, 43.03; H, 4.41; N, 3.72. Found: C, 43.32; H, 4.53; N, 3.96.

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, 0.258mmol). 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-CH₂), 4.66 (br, 1H, COD), 3.93–3.96 (m, 1H, COD), 3.76 (s, 3H, CH₃), 3.42–3.55 (m, 2H, COD), 3.00–3.04 (m, 2H, COD), 2.41–2.65 (m, 5H, 2H of P-CH₂ and 3H of COD), 1.96–1.99 (m, 2H, COD), -15.30 (d, $J_{\text{P-C}} = 8.0$ 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, $J_{\text{P-F}} = 709$ Hz, PF₆⁻). ¹³C NMR (75 MHz, CD₂Cl₂) for Ir(III) only: δ 135.5 (s, C2), 134.1 (d, $J_{\text{P-C}} = 10.6$ Hz, *o*- or *m*-PPh₂), 132.7 (d, $J_{\text{P-C}} = 8.0$ Hz, *o*- or *m*-PPh₂), 132.5 (d, $J_{\text{P-C}} = 2.4$ Hz, *p*-PPh₂), 131.4 (d, $J_{\text{P-C}} = 2.4$ Hz, *p*-PPh₂), 129.5 (d, $J_{\text{P-C}} = 10.6$ Hz, *o*- or *m*-PPh₂), 128.7 (d, $J_{\text{P-C}} = 58.0$ Hz, *ipso*-PPh₂), 128.4 (d, $J_{\text{P-C}} = 57.2$ Hz, *ipso*-PPh₂), 128.1 (d, $J_{\text{P-C}} = 14.0$ Hz, *o*- or *m*-PPh₂), 124.6 (s, imidazole C4/5), 120.6 (d, $J_{\text{P-C}} = 9.2$ Hz, C-Ir), 98.5 (d, $J_{\text{P-C}} = 15.3$ Hz, CH of COD), 94.7 (d, $J_{\text{P-C}} = 9.4$ Hz, CH of COD), 94.4 (s, CH of COD), 84.5 (s, CH of COD), 45.6 (s, N-CH₂), 36.1 (d, $J_{\text{P-C}} = 3.4$ Hz, CH₂ of COD), 35.1 (s, CH₃), 30.1 (s, CH₂ of COD), 29.8 (d, $J_{\text{P-C}} = 2.2$ Hz, CH₂ of COD), 27.6 (d, $J_{\text{P-C}} = 3.7$ Hz, CH₂ of COD), 25.3 (d, $J_{\text{P-C}} = 39.3$ Hz, P-CH₂). Anal. Calcd for C₂₆H₃₂ClF₆IrN₂P₂ (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-CH₂), 3.69 (s, 3H, CH₃), 2.65–2.71 (m, 2H, P-CH₂), 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} = 50.4 Hz, *ipso*-PPh₂), 130.9 (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-CH₂), 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-CH₂), 4.67 (br, 1H, COD), 3.98–4.10 (m, 1H, COD), 3.81 (s, 3H, CH₃), 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-CH₂ 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-CH₂), 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 C₂₆H₃₂Cl₂IrN₂P (FW 666.6): C, 46.84; H, 4.84; N, 4.20. Found: C, 46.53; H, 4.87; N, 3.92.

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, 2CH₃ of ⁱPr), -15.29 (d, $J_{P-H} = 8.1$ 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, $J_{P-F} = 707.6$ Hz, PF₆⁻). ¹³C NMR (75 MHz, CD₂Cl₂) for the Ir(III) only: δ 134.1 (d, $J_{P-C} = 10.6$ Hz, *o*- or *m*-PPh₂), 133.2 (s, C2), 132.6 (d, $J_{P-C} = 8.0$ Hz, *o*- or *m*-PPh₂), 132.4 (d, $J_{P-C} = 2.4$ Hz, *p*-PPh₂), 131.4 (d, $J_{P-C} = 2.3$ Hz, *p*-PPh₂), 129.4 (d, $J_{P-C} = 10.7$ Hz, *o*- or *m*-PPh₂), 128.9 (d, $J_{P-C} = 58.0$ Hz, *ipso*-PPh₂), 128.3 (d, $J_{P-C} = 57.8$ Hz, *ipso*-PPh₂), 128.1 (d, $J_{P-C} = 10.5$ Hz, *o*-PPh₂), 121.1 (s, imidazole C4/5), 120.3 (d, $J_{P-C} = 9.3$ Hz, C-Ir), 98.2 (d, $J_{P-C} = 15.4$ Hz, CH of COD), 94.6 (d, $J_{P-C} = 9.0$ 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-CH₂), 36.1 (d, $J_{P-C} = 3.4$ Hz, CH₂ of COD), 30.0 (s, CH₂ of COD), 29.9 (s, CH₂ of COD), 27.5 (d, $J_{P-C} = 3.5$ Hz, CH₂ of COD), 25.4 (d, $J_{P-C} = 39.2$ 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: 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, $J_{P-H} = 8.4$ 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, $J_{\text{P-F}} = 707.6$ Hz, PF₆⁻). ¹³C NMR (75 MHz, CD₂Cl₂) for the major Ir(III) only: δ 142.2 (s, C2), 134.0 (d, $J_{\text{P-C}} = 10.7$ Hz, *o*- or *m*-PPh₂), 132.6 (d, $J_{\text{P-C}} = 8.0$ Hz, *o*- or *m*-PPh₂), 132.4 (d, $J_{\text{P-C}} = 2.2$ Hz, *p*-PPh₂), 131.4 (d, $J_{\text{P-C}} = 2.4$ Hz, *p*-PPh₂), 129.5 (d, $J_{\text{P-C}} = 10.7$ Hz, *o* or *m*-PPh₂), 128.7 (d, $J_{\text{P-C}} = 57.8$ Hz, *ipso*-PPh₂), 128.3 (d, $J_{\text{P-C}} = 58.0$ Hz, *ipso*-PPh₂), 128.1 (d, $J_{\text{P-C}} = 10.4$ Hz, *o*- or *m*-PPh₂), 123.7 (s, imidazole C4/5), 118.2 (d, $J_{\text{P-C}} = 9.6$ Hz, C-Ir), 99.1 (d, $J_{\text{P-C}} = 15.2$ Hz, CH of COD), 95.7 (d, $J_{\text{P-C}} = 9.3$ Hz, CH of COD), 93.9 (s, CH of COD), 84.3 (s, CH of COD), 43.8 (s, N-CH₂), 36.3 (d, $J_{\text{P-C}} = 2.8$ Hz, CH₂ of COD), 34.5 (s, CH₃), 29.9 (s, CH₂ of COD), 29.7 (s, CH₂ of COD), 27.5 (d, $J_{\text{P-C}} = 3.5$ Hz, CH₂ of COD), 25.5 (d, $J_{\text{P-C}} = 39.5$ Hz, P-CH₂), 9.8 (s, CH₃). No satisfactory microanalysis of **7c**-(PF₆)/**8c**-(PF₆) could be obtained. However, the SbF₆⁻ salt [**8c**-(SbF₆)], prepared using the ligand **2c**-(SbF₆) and [Ir(COD)Cl]₂, gave satisfactory results. The ¹H and ¹³C NMR spectra of this **8c**-(SbF₆) are almost identical to those of **8c**-(PF₆). Anal. Calcd for C₂₇H₃₄ClF₆IrN₂PSb: 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 CD₂Cl₂ (0.6 mL), and the solution was loaded into an NMR tube for examination. ¹H NMR (300 MHz, CD₂Cl₂) for complex **11**: δ 8.59 (s, 1H, C2H), 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-CH₂), 4.33–4.42 (sept, $J = 6.7$ Hz, 1H, CH of ⁱPr), 3.03–3.13 (m, 2H, P-CH₂), 2.65–2.66 (m, 2H, COD), 2.28 (s, 3H, CH₃), 2.24 (s, 3H, CH₃), 2.15–2.27 (m, 2H, COD), 1.90–1.95 (m, 2H, COD), 1.59–1.66 (m, 2H of COD), 1.52 (d, $J = 6.7$ Hz, 6H, 2CH₃). No hydride was observed even after heating for 5 h at 40 °C. ³¹P{¹H} NMR (121 MHz, CD₂Cl₂): δ 14, 29 (s, PPh₂), -143.8 (sept, $J_{\text{P-F}} = 708.0$ Hz, PF₆⁻). ¹³C NMR (75 MHz, CD₂Cl₂): δ 133.5 (d, $J_{\text{P-C}} = 10.7$ Hz, *o*- or *m*-PPh₂), 131.3 (s, imidazole C2), 130.9 (d, $J_{\text{P-C}} = 2.2$ Hz, *p*-PPh₂), 130.4 (d, $J_{\text{P-C}} = 49.0$ Hz, *o*-PPh₂), 127.4 (s, imidazole C4/5), 126.0 (s, imidazole C4/5), 94.6 (d, $J_{\text{P-C}} = 14.0$ Hz, CH of COD), 54.8 (s, CH of ⁱPr), 50.7 (s, CH of COD), 44.3 (d, $J_{\text{P-C}} = 9.5$ Hz, N-CH₂), 33.2 (d, $J_{\text{P-C}} = 3.3$ Hz, CH₂ of COD), 29.4 (d, $J_{\text{P-C}} = 28.5$ Hz, P-CH₂), 29.3 (s, CH₂ of COD), 22.1 (s, 2CH₃), 8.4 (s, CH₃), 8.3 (s, CH₃). 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_2Cl_2 (0.6 mL), and the solution was loaded into a NMR tube for examination. ^1H NMR (300 MHz, CD_2Cl_2): δ 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_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz CD_2Cl_2): δ 15.92 (s). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 164.1 (q, $J_{\text{B-C}} = 48.9$ Hz, *ipso*-BPh₄), 135.7 (s, *o*-BPh₄), 133.5 (d, $J_{\text{P-C}} = 6.5$ Hz, *o*- or *m*-PPh₂), 131.2 (d, $J_{\text{P-C}} = 48.4$ Hz, *ipso*-PPh₂), 130.7 (s, imidazole C2), 128.4 (d, $J_{\text{P-C}} = 9.7$ Hz, *o* or *m*-PPh₂), 125.9 (d, $J_{\text{P-C}} = 2.67$ Hz, *m*-BPh₄), 122.4 (s, imidazole C4/5), 122.0 (s, *p*-BPh₄), 121.6 (imidazole C4/5), 94.8 (d, $J_{\text{P-C}} = 14.1$ Hz, CH of COD), 54.1 (s, CH of COD), 50.1 (d, $J_{\text{P-C}} = 14.5$ Hz, N- CH_2), 36.0 (s, CH_3), 33.2 (d, $J_{\text{P-C}} = 3.1$ Hz, CH_2 of COD), 29.4 (s, CH_2 of COD), 26.4 (s, CH_2), 24.4 (d, $J_{\text{P-C}} = 31.7$ 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 $^t\text{BuOK}$ (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**-(PF₆) (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_2Cl_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%). ^1H NMR (300 MHz, CD_2Cl_2): δ 7.38–7.48 (m, 10H, PPh₂), 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, NCH₂), 4.59 (m, 1H, NCH₂), 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). $^{31}\text{P}\{^1\text{H}\}$ NMR (161 MHz, CD_2Cl_2) δ 17.71 (s, PPh₂),

144.4 (sept, $J_{\text{P-F}} = 707$ Hz). $^{13}\text{C}\{^1\text{H}\}$ (100 MHz, CD_2Cl_2) 171.8 (d, $J_{\text{P-C}} = 13.9$ Hz, C-Ir), 133.0 (br, *ipso*-PPh₂), 131.3 (s, *p*-PPh₂), 129.0 (d, $J_{\text{P-C}} = 10.4$ Hz, *m* or *o*-C of PPh₂), 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, $J_{\text{P-C}} = 2.95$ Hz, NCH₂), 38.0 (s, CH₃), 31.5 (br, CH₂ of COD), 25.4 (d, $J_{\text{P-C}} = 38.3$ Hz, PCH₂). Anal. Calcd for $\text{C}_{26}\text{H}_{31}\text{F}_6\text{IrN}_2\text{P}_2$: 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**-(PF₆) (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 $\Delta H^\ddagger$ and $\Delta S^\ddagger$ based on the Eyring equation $\ln(k/T) = -\Delta H^\ddagger/RT + \ln(k_b/h) + \Delta S^\ddagger/R$ (Figure 2.3).

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

Complex **8a**-(Cl), **8a**-(PF₆), or **8b**-(PF₆) (15 mg) was dissolved in CD_3CN (0.6 mL) and the solution was loaded into a J-Young NMR tube. The $^{31}\text{P}\{^1\text{H}\}$ 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. ΔH° and ΔS° were obtained by the equation $\ln K_{\text{eq}} = -\Delta H^\circ/(RT) + \Delta S^\circ/R$ (Figure 2.5).

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Chapter 3. Iridium and Rhodium 2-Methyleneimidazoline Complexes from Highly Selective Activation of C(sp^3)-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.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. Consequently neutral carbon-centered ligands have been widely used to offer unique properties to compete with ubiquitous phosphine ligands in organometallic chemistry.²⁻⁴ N-heterocyclic carbenes (NHCs) are representative of these ligands⁵ and NHC complexes have shown superior activity in palladium-catalyzed C-C coupling⁶ and ruthenium-catalyzed olefin metathesis reactions.⁷

NHCs on various platforms and with different substituents have been reported to demonstrate their tunability in terms of electronic and steric effects.⁸⁻⁹ In this regard, abnormal carbenes (imidazole-based NHC ligands bound through a backbone C4/5 carbon), first discovered by Crabtree and coworkers,⁴ constitute a new family of NHCs that are with electronic variants of normal NHCs and have received increasing attention.¹⁰⁻¹² Abnormal NHCs (**A**, Figure 3.1), which are essentially zwitterionic ligands, are shown to be more donating than normal C2-bound NHCs.^{12b,13} Analogously, metal complexes of ylides¹⁴ (**B**, Figure 3.1) and 2-methyleneimidazolines¹⁵⁻¹⁶ (**C**, Figure 3.1) with a side-on (η^1) binding mode are all zwitterionic in nature and are structurally related. It has been recently shown that both phosphine ylides¹⁴ and 2-methyleneimidazolines^{15a-b} are highly strong σ -donors towards metals.

Figure 3.1

Despite the simplicity of 2-methyleneimidazoline, there are only very few reports¹⁵⁻¹⁶ 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.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 (*in situ* metalation), where only one example was reported for transition metals by Peris and coworkers for this method (Scheme 3.1).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's report, low selectivity was observed for the methyl C(*sp*³)-H vs the C4/5-H activation of a imidazolium ring in a chelating system bound to a IrCp* fragment.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.

Scheme 3.1

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.^{12a} 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 $[\text{Ir}(\text{COD})\text{Cl}]_2$ followed by addition of the phosphine-imidazolium ligand (Scheme 3.3)^{12a, 17} 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.¹⁸

Scheme 3.2

Scheme 3.3

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 $[\text{Ir}(\text{COD})\text{O}^t\text{Bu}]_2$ that is generated *in situ* from the reaction of $[\text{Ir}(\text{COD})\text{Cl}]_2$ and KO^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_3OD 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.

3.2.3 Metalation and Characterization

3.2.3.1 Synthesis and NMR Spectroscopy

Stirring a solution of **1a** and $[\text{Ir}(\text{COD})\text{O}^t\text{Bu}]_2$ 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 ^1H NMR spectrum ($\text{acetone}-d_6$) of **2a**, the CH_2 protons resonate as a doublet (2H, $^3J_{\text{PH}} = 1.8$ Hz) at δ 2.88 and the imidazolium backbone protons resonate as doublets at δ 6.81 and 6.38 (d, $^3J_{\text{H-H}} = 2.1$ Hz), indicating that no metalation took place at the C4/5 position. The fact that the Ir- CH_2 protons are equivalent also indicates that **2a** is C_s symmetrical in the solution structure. In the ^{13}C NMR spectrum,

the CH₂ signal, confirmed by DEPT135, resonates characteristically at δ 13.9 (d, $^2J_{P-C}$ = 5.0 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 metalation 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

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]₂ to afford the corresponding rhodium(I) phosphine complex *in situ*. Addition of KO^tBu to this solution at a low temperature led to the selective metalation 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 ³¹P NMR spectra. The PPh₂ 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 -CH₂PPh₂ 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 $^2J_{\text{P-H}}$ and $^3J_{\text{Rh-H}}$ values in **5**.

Scheme 3.5

Table 3.1. Characteristic NMR Data of 2-Methyleneimidazoline Complexes (CD_2Cl_2)

	^1H		^{13}C	^{31}P
	M- CH_2	imidazole C4- H or C5- H , $^3J_{\text{HH}}$	M- CH_2	PPh_2
2a	2.88 (d, 1.8 Hz)	6.81, 6.38, 2.1 Hz	13.9 (d, $J_{\text{PC}} = 5.0$ Hz)	15.4 (s)
2b	2.96 (d, 1.7 Hz)	6.97, 6.78, 2.0 Hz	13.9 (d, $J_{\text{PC}} = 5.0$ Hz)	13.2 (s)
3a	2.09 (br)	6.46, 6.03, 2.0 Hz	10.0 (dd, $J_{\text{Rh-C}} = 22.0$, $J_{\text{P-C}} = 8.0$ Hz)	24.5 (d, 164.9 Hz)
3b	2.13 (br)	6.64, 6.35, 2.3 Hz	9.8 (dd, $J_{\text{Rh-C}} = 20.9$, $J_{\text{P-C}} = 8.2$ Hz)	21.0 (d, 165.2 Hz)
3c	2.08 (br)	-	10.9 (dd, $J_{\text{Rh-C}} = 20.7$, $J_{\text{P-C}} = 7.9$ Hz)	23.1 (d, 165.7 Hz)
5	1.82 (t, 3.2 Hz)	6.72, 6.56, 2.2 Hz	12.7 (dd, $J_{\text{Rh-C}} = 19.2$, $J_{\text{P-C}} = 5.0$ Hz)	74.2 (d, 186 Hz)
7	1.65 (t, 4.0 Hz)	-	8.51 (dd, $J_{\text{Rh-C}} = 23.3$, $J_{\text{P-C}} = 8.2$ 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 *sp*³ 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-crystallized in the unit cell and only one is shown here.

Table 3.2. Selected Bond Lengths and Angles for Complexes **2a**, **3a**, and **5**

	2a	3a	5·0.5CH₂Cl₂
M–C(9) (Å)	2.145(3)	2.147(2)	2.141(3)
M–P (Å)	2.2841(6)	2.2816(5)	2.2663(8)
C(9)–C(10) (Å)	1.449(4)	1.450(3)	1.431(4)
C(9)–M–P(1) (deg)	93.47(8)	92.34(6)	88.97(9)
M–C(9)–C(10) (deg)	120.69(19)	121.06(14)	113.2(2)
N(1)–C(10)–N(2) (deg)	106.1(2)	106.33(17)	106.5(3)

Table 3.3 Crystallographic Data for Complexes **2a**, **3a**, and **5·0.5CH₂Cl₂**

	2a	3a	5·0.5CH₂Cl₂
empirical formula	C ₂₇ H ₃₃ F ₆ N ₂ P ₂ Rh	C ₂₇ H ₃₃ F ₆ N ₂ P ₂ Rh	C _{34.5} H ₄₀ ClF ₆ N ₂ P ₂ Rh
molecular weight (g mol ⁻¹)	753.69	664.40	796.98
radiation, λ(Å)	Mo K _α (monochr), 0.71073 Å		
<i>T</i> (K)	173(2)		
cryst syst	monoclinic	monoclinic	orthorhombic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> na2(1)
<i>a</i> (Å)	10.3422(4)	10.3242(4)	19.7387(6)
<i>b</i> (Å)	13.7466(5)	13.7831(6)	12.9197(3)
<i>c</i> (Å)	19.3563(7)	19.3904(8)	27.3939(8)
β(deg)	96.117(2)	96.086(2)	90
<i>V</i> (Å ³)	2736.22(18)	2743.7(2)	6985.9(3)
<i>Z</i>	4	4	8
<i>D</i> _{calcd} (g cm ⁻³)	1.830	1.608	1.516
μ (mm ⁻¹)	5.058	0.800	0.717
crystal size (mm)	0.26 × 0.15 × 0.14	0.22 × 0.16 × 0.12	0.25 × 0.15 × 0.10
total, unique no. of rflns	41855, 10269	69771, 13999	198471, 21335
<i>R</i> _{int}	0.0398	0.0439	0.0541
data, restraints, parameters	10259, 0, 420	13999, 0, 344	21335, 1, 839
<i>R</i> , <i>R</i> _w (all data)	0.0430, 0.0712	0.0540, 0.1125	0.0607, 0.0994
GOF	1.025	1.051	1.132
min., max. resid dens (eÅ ⁻³)	-1.461, 2.212	-1.924, 1.196	-0.556, 0.614

3.2.4 C(sp³)-H vs C(sp²)-H Activation

To further understand the factors controlling the selectivity of the C(sp³)-H vs C(sp²)-H activation, we examined the effects of anionic ligands (OR) in the rhodium system. [Rh(COD)OR]₂ (R = ^tBu, Et, Me, and H) was thus either prepared *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(sp³)-H activation product (**3a**) was obtained for R = ^tBu or Et. However, for R = Me or H, the C(sp²)-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) ¹H 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 CD₂Cl₂ 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 ¹H and ¹³C NMR spectra (CD₂Cl₂) of the mixture. The remaining C4/5-H proton of **8** resonates at δ 6.10 (s) and the NCH₂ signal shows up at δ 5.08 as a characteristic doublet of multiplets. Two methyl groups with the correct signal integration were also detected with δ 2.50 and 3.61. Importantly, the abnormal carbene signal resonate at δ 149.9 (dd, ²J_{Rh-C} = 45 Hz, ³J_{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(sp³)-H vs C(sp²)-H activation is likely controlled by the steric effects of these OR ligands. The 2-CH₃ 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^*IrI_2 fragment tend to indicate that the $\text{C}(\text{sp}^3)\text{-H}$ vs $\text{C}(\text{sp}^2)\text{-H}$ 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

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-CH₂ 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_2Cl_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_2Cl_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 ^1H 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 $[\text{Ir}(\text{COD})\text{Cl}]_2$ 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 $[\text{Ir}(\text{COD})\text{O}^t\text{Bu}]_2$.*

Scheme 3.7

3.2.6 The Electronic Properties

Rhodium dicarbonyl complex $\text{RhCl}(\text{CO})_2\text{L}$ 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 $\Delta_{\text{av.}}(\text{calcd-exp}) \approx 104\text{--}105\text{ cm}^{-1}$, 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 2nd 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}

	10	11	12	13	14	15
calcd (cm ⁻¹)	2123, 2166	2123, 2165	2092	2073, 2143	2130, 2169	2137.5, 2176
av. (calcd)	2144.5	2144	2092	2108	2149.5	2157
exp (cm ⁻¹)				1966, 2040		2023, 2083
av. (exp)				2003		2053

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 $[M(\text{COD})(\text{OR})_2]$ ($M = \text{Rh}$ or Ir and $R = \text{alkyl}$ or H) and representative complexes have been analyzed by X-ray crystallography. The selectivity of aliphatic $\text{C}(\text{sp}^3)\text{-H}$ *vs* aromatic $\text{C}(\text{sp}^2)\text{-H}$ 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 $\text{C}(\text{sp}^3)\text{-H}$ activation product is the kinetic product while the 6-membered iridium abnormal carbene product, resulting from the activation of a $\text{C}(\text{sp}^2)\text{-H}$ 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.

3-(2-chloroethyl)-1-isopropyl-2-methylimidazolium chloride 1-isopropyl-2-methylimidazole (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-methylimidazolium chloride as a white solid in 85% yield (1.53 g, 6.8 mmol). ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 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}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 144.4, 122.8, 118.5, 50.6, 49.1, 43.7, 22.4, 10.2. HRMS (ESI^+): 187.1031; calcd for $[\text{C}_9\text{H}_{16}\text{ClN}_2]^+$ 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 NMR (500 MHz, CDCl_3): δ 7.78 (d, $J = 2.1$ Hz, 1H, imidazole H4/5), 7.35-7.38 (m, 4H, PPh_2), 7.34 (d, $J = 2.1$ Hz, 1H, imidazole H4/5), 7.30-7.32 (m, 6H, PPh_2), 4.63 (sept, $J = 6.6$ Hz, 1H, CH of ^iPr), 4.45-4.50 (m, 2H, N-CH_2), 2.69 (apparent t, $J = 7.2$ Hz, 2H, P-CH_2), 2.68 (s, 3H, CH_3), 1.43 (d, $J = 6.7$ Hz, 6H, 2CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CDCl_3): δ -21.74 (s, PPh_2). ^{13}C NMR (75 MHz, CDCl_3): δ 142.4 (s, imidazole C2), 136.0 (d, $J_{\text{P-C}} = 11.5$ Hz, *ipso*- PPh_2), 132.6 (d, $J_{\text{P-C}} = 19.3$ Hz, PPh_2), 129.4 (s, PPh_2), 128.9 (d, $J_{\text{P-C}} = 7.1$ Hz, PPh_2), 122.7 (s, C4/5), 117.6 (s, C4/5), 51.1 (s, CH of ^iPr), 46.4 (d, $J_{\text{P-C}} = 20.9$ Hz, CH_2), 28.4 (d, $J_{\text{P-C}} = 15.7$ Hz, CH_2), 22.6 (s, CH_3 of ^iPr), 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_3CN (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 NMR (500 MHz, CDCl_3): δ 7.37-7.40 (m, 4H, PPh_2), 7.33-7.35 (m, 6H, PPh_2), 7.15 (d, $J = 2.2$ Hz, 1H, imidazole H4/5), 7.08 (d, $J = 2.2$ Hz, 1H, imidazole H4/5), 4.40 (sept, $J = 6.6$ Hz, 1H, CH of ^iPr), 4.15-4.19 (m, 2H, N-CH_2), 2.57 (apparent t, $J = 7.6$ Hz, 2H, P-CH_2), 2.41 (s, 3H, CH_3), 1.38 (d, $J = 6.6$ Hz, 6H, 2CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3): δ -22.1 (s, PPh_2), -144.6 (sept, $J_{\text{P-F}} = 706$ Hz, PF_6). ^{13}C NMR (125 MHz, CDCl_3): δ 142.5 (s, imidazole C2), 136.0 (d, $J_{\text{P-C}} = 11.5$ Hz, *ipso*- PPh_2), 132.6 (d, $J_{\text{P-C}} = 19.4$ Hz, PPh_2), 129.5 (s, PPh_2), 128.9 (d, $J_{\text{P-C}} = 7.1$ Hz, PPh_2), 121.5 (s, imidazole C4/5), 117.3 (s, imidazole C4/5), 51.0 (s, CH of ^iPr), 46.0 (d, $J_{\text{P-C}} = 23$ Hz, CH_2), 28.4 (d, $J_{\text{P-C}} = 15.6$ Hz, CH_2), 22.1 (s, CH_3 of ^iPr), 9.4 (s, CH_3). Anal. Calcd for $\text{C}_{21}\text{H}_{26}\text{F}_6\text{N}_2\text{P}_2$ (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-tetramethylimidazolium 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. ^1H NMR (500 MHz, $\text{DMSO-}d_6$): δ 4.56 (t, $J = 5.8$ Hz, 2H, N- CH_2), 4.00 (t, $J = 5.7$ 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). ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$): 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 powder in 91% yield. ^1H NMR (400 MHz, CDCl_3): δ 7.15-7.38 (m, 10H, 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, $J = 7.2$ Hz, 2H, P- CH_2), 2.08 (s, 3H, CH_3), 2.07 (s, 3H, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (161 MHz, CDCl_3): δ -21.9 (s, PPh_2). ^{13}C NMR (100 MHz, CDCl_3): 142.6 (s, imidazole C2), 136.1 (d, $J_{\text{P-C}} = 11.5$ Hz, *ipso*- PPh_2), 132.6 (d, $J_{\text{P-C}} = 19.2$ Hz, PPh_2), 129.5 (s, PPh_2), 128.8 (d, $J_{\text{P-C}} = 7.7$ Hz, PPh_2), 126.1 (s, imidazole C4/5), 124.8 (s, imidazole C4/5), 43.4 (d, $J_{\text{P-C}} = 23.0$ Hz, N- CH_2), 32.8 (s, CH_3), 28.8 (d, $J_{\text{P-C}} = 17.3$ Hz, P- CH_2), 11.6 (s, CH_3), 10.1 (s, CH_3), 8.9 (s, CH_3). No satisfactory microanalysis could be obtained for ligand **1c-Cl** due to its hydroscopicity. The microanalysis of the PF_6^- 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 powder in 95% yield. ^1H NMR (300 MHz, CDCl_3): δ 7.34-7.43 (m, 10H, CH of PPh_2), 4.04-4.11 (m, 2H, N- CH_2), 3.45 (s, 3H, N- CH_3), 2.47 (apparent t, $J = 7.9$ Hz, 2H, P- CH_2), 2.39 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 2.07 (s, 3H, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CDCl_3): δ -22.1 (s, PPh_2), -144.1 (sept, $J_{\text{P-F}} = 708$ Hz, PF_6). ^{13}C NMR (75 MHz, CDCl_3): 141.9 (s, imidazole C2), 136.1 (d, $J_{\text{P-C}} = 11.2$ Hz, *ipso*- PPh_2), 132.5 (d, $J_{\text{P-C}} = 19.3$ Hz, PPh_2), 129.5 (s, 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_2), 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 $C_{21}H_{26}F_6N_2P_2$ (482.4): C, 52.29; H, 5.43; N, 5.81; Found C, 52.41; H, 5.48; N, 5.94.

Compound 4-oxide. $Ph_2P(O)CH_2Br$ (1 g, 3.4 mmol) and 1-mesityl-2-methylimidazole (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. Yield: 77% (1.3 g, 2.6 mmol). 1H NMR (400 MHz, $CDCl_3$): δ 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_2), 2.56 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 1.91 (s, 6H, 2 CH_3). $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ 28.1 (s, $P(O)Ph_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 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_2), 21.2, 17.4, 10.9. HRMS (ESI^+): 415.1929; calcd for $[C_{26}H_{28}N_2OP]^+$ 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 (2g, 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, 4H, PPh₂), 7.43-7.45 (m, 6H, PPh₂), 7.27 (d, *J* = 1.8 Hz, 1H, imidazole H4/5), 7.03 (s, 2H, Mesityl), 7.01 (d, *J* = 1.9 Hz, 1H, imidazole H4/5), 5.02 (d, *J*_{P-H} = 5.9 Hz, 2H, N-CH₂), 2.36 (s, 3H), 2.02 (s, 3H, CH₃), 1.91 (s, 6H, 2CH₃). ³¹P{¹H} NMR (161 MHz, CDCl₃): δ -14.4 (s, PPh₂), -144.5 (sept, *J*_{P-F} = 709 Hz, PF₆). ¹³C NMR (100 MHz, CDCl₃): δ 144.9 (s), 141.6 (s), 134.8 (s), 133.2 (d, *J*_{P-C} = 10.8 Hz, *ipso*-PPh₂), 133.1 (d, *J*_{P-C} = 19.4 Hz, PPh₂), 130.5 (s), 130.1 (s), 129.9 (s), 129.3 (*J*_{P-C} = 7.1 Hz, PPh₂), 122.9 (*J*_{P-C} = 3.6 Hz, imidazole C4/5), 121.4 (s), 49.5 (d, *J*_{P-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, 8H), 7.14-7.19 (m, 4H), 7.04-7.07 (m, 1H), 6.91-6.94 (m, 1H), 5.38 (s, 2H, CH₂), 3.71 (s, 3H, N-CH₃), 2.62 (s, 3H,

CH_3), 2.12 (s, 3H, CH_3), 2.03 (s, 3H, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CDCl_3): δ -15.5 (s, PPh_2). ^{13}C NMR (75 MHz, CDCl_3): δ 143.6 (s, imidazole C2), 136.6 (d, $J_{\text{P-C}} = 23.4$ Hz, *ipso*- PPh_2), 135.3 (d, $J_{\text{P-C}} = 16.3$ Hz, PPh_2), 134.3 (s), 134.1 (d, $J_{\text{P-C}} = 7.8$ Hz, PPh_2), 133.8 (d, $J_{\text{P-C}} = 19.7$ Hz, PPh_2), 130.1 (s), 129.5 (s), 129.1 (s), 128.8 (d, $J_{\text{P-C}} = 7.3$ Hz, PPh_2), 127.6 (d, $J_{\text{P-C}} = 5.3$ Hz, PPh_2), 126.2 (s, imidazole C4/5), 125.6 (s, imidazole C4/5), 48.0 (d, $J_{\text{P-C}} = 25.5$ Hz, CH_2), 33.0 (s, N- CH_3), 11.7 (s, CH_3), 9.10 (s, CH_3), 8.92 (s, 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_3CN (10 ml), as a white solid power in 94% yield (235.4 mg, 0.43 mmol). ^1H NMR (300 MHz, CDCl_3): δ 7.30-7.46 (m, 6H), 7.21-7.25 (m, 6H), 6.91-6.97 (m, 2H), 5.31 (s, 2H, CH_2), 3.54 (s, 3H, N- CH_3), 2.37 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 2.02 (s, 3H, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (161 MHz, CDCl_3): δ -16.2 (s, PPh_2), -144.7 (sept, $J_{\text{P-F}} = 710$ Hz, PF_6). ^{13}C NMR (100 MHz, CDCl_3): δ 142.8 (s, imidazole C2), 136.3 (d, $J_{\text{P-C}} = 23.3$ Hz, *ipso*- PPh_2), 135.1 (d, $J_{\text{P-C}} = 16.2$ Hz, PPh_2), 134.2 (s), 134.0 (d, $J_{\text{P-C}} = 6.2$ Hz, PPh_2), 133.8 (d, $J_{\text{P-C}} = 19.7$ Hz, PPh_2), 130.4 (s), 129.6 (s), 129.1 (s), 128.8 (d, $J_{\text{P-C}} = 7.3$ Hz, PPh_2), 127.0 (d, $J_{\text{P-C}} = 5.1$ Hz, PPh_2), 126.5 (s, imidazole C4/5), 125.6 (s, imidazole C4/5), 48.0 (d, $J_{\text{P-C}} = 25.5$ Hz, CH_2), 32.0 (s, N- CH_3), 10.4 (s, CH_3), 8.86 (s, CH_3), 8.58 (s, CH_3). Anal. Calcd for $\text{C}_{26}\text{H}_{28}\text{F}_6\text{N}_2\text{P}_2$ (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 $[\text{M}(\text{COD})\text{Cl}]_2$ (M = Rh, Ir, 0.05 mmol) in THF (5 mL) was slowly added KO^tBu (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_2Cl_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 $\times$ 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 CH_2Cl_2 solution of **2a** after 7 days at -20°C . ^1H NMR (300 MHz, acetone- d_6): δ 7.47-7.55 (m, 10H, PPh_2), 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- CH_2), 3.62 (s, 3H, N- CH_3), 3.04-3.11 (m, 2H, P- CH_2), 2.88 (d, $J = 1.6$ Hz, 2H, $\text{CH}_2\text{-Ir}$), 2.81-2.83 (m, 2H, COD), 2.21-2.31 (m, 2H, COD), 1.95-2.15 (m, 4H, COD), 1.66-1.75 (m, 2H, COD). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, acetone- d_6): δ 15.4 (s, PPh_2), -143.6 (sept, $J_{\text{P-F}} = 703.8$ Hz, PF_6). ^{13}C NMR (100 MHz, acetone- d_6): δ 159.9 (s, imidazole C2), 133.5 (d, $J_{\text{P-C}} = 13.0$ Hz, *o*- or *m*- PPh_2), 130.9 (d, $J_{\text{P-C}} = 2.0$ Hz, *p*- PPh_2), 130.3 (d, $J_{\text{P-C}} = 49.3$ Hz, *ipso*- PPh_2), 128.4 (d, $J_{\text{P-C}} = 10.0$ Hz, *o*- or *m*- PPh_2), 118.7 (s, imidazole C4/5), 117.4 (s, imidazole C4/5), 88.9 (d, $J_{\text{P-C}} = 10.0$ Hz, CH of COD), 63.7 (s, CH of COD), 42.8 (s, N- CH_2), 33.5 (s, N- CH_3), 31.7 (d, $J_{\text{P-C}} = 3.0$ Hz, CH_2 of COD), 30.4 (s, CH_2 of COD), 20.1 (d, $J_{\text{P-C}} = 29.4$ Hz, P- CH_2), 13.9 (d, $J_{\text{P-C}} = 5.0$ Hz, Ir- CH_2). Anal. Calcd for $\text{C}_{27}\text{H}_{33}\text{F}_6\text{IrN}_2\text{P}_2$ (FW 753.7): C, 43.03; H, 4.41; N, 3.72; Found C, 43.39; H, 4.53; N, 3.91.

Complex 2b. Yields: 88% (red solid, 68.7 mg, 0.088mmol). ^1H NMR (400 MHz, acetone- d_6): δ 7.48-7.58 (m, 10H, PPh_2), 6.97 (d, $J = 2.0$ Hz, 1H, imidazole H4/5), 6.78 (d, $J = 2.0$ Hz, 1H, imidazole H4/5), 4.82 (br, 2H, COD), 4.52-4.58 (m, 2H, N- CH_2), 3.64 (sept, $J = 6.6$ Hz, 1H, CH of ^iPr), 3.08-3.12 (m, 2H, P- CH_2), 2.96 (d, $J = 1.7$ Hz, 2H, $\text{CH}_2\text{-Ir}$), 2.85 (br, 2H, COD), 2.11-2.29 (m, 2H, COD), 1.98-2.13 (m, 4H, COD), 1.71-1.80 (m, 2H, COD), 1.37 (d, $J = 6.7$ Hz, 6H, 2 CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, acetone- d_6): δ 13.2 (s, PPh_2), -144.7 (sept, $J_{\text{P-F}} = 705$ Hz, PF_6). ^{13}C NMR (75 MHz, acetone- d_6): δ 158.6 (s, imidazole C2), 133.3 (d, $J_{\text{P-C}} = 10.9$ Hz, *o*- or *m*- PPh_2), 130.8 (d, $J_{\text{P-C}} = 2.1$ Hz, *p*- PPh_2), 130.4 (d, $J_{\text{P-C}} = 49.1$ Hz, *ipso*- PPh_2), 128.6 (d, $J_{\text{P-C}} = 9.9$ Hz, *o*- or *m*- PPh_2), 118.7 (s, C4/5), 113.8 (s, C4/5), 88.5 (d, $J_{\text{P-C}} = 13.2$ Hz, CH of COD), 64.1 (s, CH of COD), 49.1 (s, CH of ^iPr), 42.7 (s, N- CH_2), 31.6 (d, $J_{\text{P-C}} = 2.8$ Hz, CH_2 of COD), 30.5 (s, CH_2 of COD), 21.4 (s, CH_3), 19.5 (d, $J_{\text{P-C}} = 29.5$ Hz, P- CH_2), 13.9 (d,

$J_{P-C} = 4.9$ Hz, Ir-CH₂). Anal. Calcd for C₂₉H₃₇F₆IrN₂P₂ (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. ¹H NMR (300 MHz, CD₂Cl₂): δ 7.40-7.51 (m, 10H, PPh₂), 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-CH₂), 3.37-3.38 (m, 2H, COD), 3.35 (s, 3H, N-CH₃), 2.60-2.67 (m, 2H, P-CH₂), 2.43-2.49 (m, 2H, COD), 2.23-2.33 (m, 4H, COD), 2.08-2.09 (m, 2H, Rh-CH₂), 2.02-2.04 (m, 1H, COD), 1.83-1.87 (m, 1H, COD). ³¹P{¹H} NMR (121 MHz, CD₂Cl₂): δ 24.5 (d, $J_{Rh-P} = 164.9$ Hz, PPh₂), -143.8 (sept, $J_{P-F} = 708$ Hz, PF₆). ¹³C NMR (75 MHz, CD₂Cl₂): δ 159.2 (s, imidazole C2), 133.1 (d, $J_{P-C} = 11.9$ Hz, *o*- or *m*-PPh₂), 130.9 (d, $J_{P-C} = 1.9$ Hz, *p*-PPh₂), 130.8 (d, $J_{P-C} = 40.3$ Hz, *ipso*-PPh₂), 128.5 (d, $J_{P-C} = 9.6$ Hz, *o*- or *m*-PPh₂), 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-CH₂), 34.0 (s, CH₃), 31.5 (d, $J_{P-C} = 2.3$ Hz, CH₂ of COD), 30.0 (s, CH₂ of COD), 21.1 (d, $J_{P-C} = 21.6$ Hz, P-CH₂), 10.0 (dd, $J_{P-C} = 8.0$ Hz, $J_{Rh-C} = 20.2$ Hz, Rh-CH₂). Anal. Calcd for C₂₇H₃₃F₆N₂P₂Rh (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). ¹H NMR (300 MHz, CD₂Cl₂): δ 7.40-7.53 (m, 10H, PPh₂), 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-CH₂), 4.21 (septet, $J = 6.7$ Hz, 1H, CH of ^{*i*}Pr), 3.40-3.41 (m, 2H, COD), 2.62-2.69 (m, 2H, P-CH₂), 2.42-2.50 (m, 2H, COD), 2.26-2.30 (m, 4H, COD), 2.13 (apparent t, $J = 2.6$ Hz, 2H, Rh-CH₂), 1.99-2.11 (m, 1H, COD), 1.83-1.86 (m, 1H, COD), 1.38 (d, $J = 6.7$ Hz, 6H, CH₃). ³¹P{¹H} NMR (121 MHz, CD₂Cl₂): δ 21.0 (d, $J_{Rh-P} = 165.2$ Hz, PPh₂), -143.8 (sept, $J_{P-F} = 708$ Hz, PF₆). ¹³C NMR (75 MHz, CD₂Cl₂): δ 157.9 (s, imidazole C2), 133.1 (d, $J_{P-C} = 11.6$ Hz, *o*- or *m*-PPh₂), 131.0 (d, $J_{P-C} = 39.2$ Hz, *ipso*-PPh₂), 130.7 (d, $J_{P-C} = 2.0$ Hz, *p*-PPh₂), 128.7 (d, $J_{P-C} = 9.5$ Hz, *o*- or *m*-PPh₂), 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 ^{*i*}Pr), 42.7 (s, N-CH₂), 31.4 (d, $J_{P-C} = 2.4$ Hz, CH₂ of COD), 30.5 (s, CH₂ of COD), 21.8 (s, CH₃), 20.8 (d, $J_{P-C} = 21.7$

Hz, P-CH₂), 9.8 (dd, $J_{P-C} = 8.2$ Hz, $J_{Rh-C} = 20.9$ Hz, Rh-CH₂). Anal. Calcd 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, CD₂Cl₂): 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. Calcd 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 KO^tBu (0.22 mL, 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 $\times$ 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-CH₂). ³¹P{¹H} NMR (161 MHz, CD₂Cl₂): δ 74.2 (d, $J_{\text{Rh-P}} = 187.3$ Hz, PPh₂), -143.8 (septet, $J_{\text{P-F}} = 714$ Hz, PF₆). ¹³C NMR (100 MHz, CD₂Cl₂): 157.5 (d, $J_{\text{P-C}} = 5.7$ Hz, imidazole C2), 141.0, 135.4, 132.8 (d, $J_{\text{P-C}} = 12.5$ Hz, *o*- or *m*-PPh₂), 131.8, 130.9, 129.9 (d, $J_{\text{P-C}} = 38.3$ Hz, *ipso*-PPh₂), 129.7, 129.5 (d, $J_{\text{P-C}} = 9.6$ Hz, *o*- or *m*-PPh₂), 118.7 (s, imidazole C4/5), 118.5 (s, imidazole C4/5), 102.3 (dd, $J_{\text{P-C}} = 10.5$ Hz, $J_{\text{Rh-C}} = 7.8$ Hz, CH of COD), 82.4 (d, $J_{\text{Rh-C}} = 8.6$ Hz, CH of COD), 49.0 (d, $J_{\text{P-C}} = 20.1$ 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, $J_{\text{P-C}} = 5.3$ Hz, $J_{\text{Rh-C}} = 18.7$ 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, $J_{\text{Rh-P}} = 158.4$ Hz, PPh₂), -143.9 (septet, $J_{\text{P-F}} = 708$ Hz, PF₆). ¹³C NMR (75 MHz, CD₂Cl₂): δ 157.5 (d, $J_{\text{P-C}} = 5.7$ Hz, imidazole C2), 138.8 (d, $J_{\text{P-C}} = 15.6$ Hz, *ipso*-PPh₂), 134.7 (s), 139.9 (d, $J_{\text{P-C}} = 12.1$ Hz, *o*- or *m*-PPh₂), 132.2 (s), 132.1 (d, $J_{\text{P-C}} = 2.1$ Hz, *Ar*-PPh₂), 131.6 (s), 131.3 (d, $J_{\text{P-C}} = 1.7$ Hz, *p*-PPh₂), 129.8 (d, $J_{\text{P-C}} = 5.6$ Hz, *Ar*-PPh₂), 129.5 (d, $J_{\text{P-C}} = 20.6$ Hz, *Ar*-PPh₂), 129.4 (d, $J_{\text{P-C}} = 9.5$ Hz, *o*- or *m*-PPh₂), 123.1 (s, imidazole C4/5), 122.7 (s, imidazole C4/5), 97.9 (apparent tr, $J_{\text{P-C}} = J_{\text{Rh-C}} = 8.9$ Hz, CH of COD), 84.1 (d, $J_{\text{Rh-C}} = 8.6$ Hz, CH of COD), 48.8 ($J_{\text{P-C}} = 17.2$ Hz, N-CH₂), 31.9 (s, N-CH₃), 31.6 (d, $J_{\text{P-C}} = 2.1$ Hz, CH₂ of COD), 31.1 (s, CH₂ of COD), 9.8 (s, CH₃), 9.2 (s, CH₃), 8.5 (dd, $J_{\text{P-C}} = 8.2$ Hz, $J_{\text{Rh-C}} = 23.3$ 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 $[\text{Rh}(\text{COD})(\text{OH})]_2$ (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 $\times$ 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 ^1H NMR. A analogous method was used when $[\text{Rh}(\text{COD})(\text{OMe})]_2$ or $[\text{Rh}(\text{COD})(\text{OEt})]_2$ were allowed to reacted with ligand **1a**. Selected NMR signals: **3a** ^1H NMR (400 MHz, CD_2Cl_2): δ 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** ^1H NMR (400 MHz, CD_2Cl_2): δ 6.55 (s, imidazole H4/5), 5.18 (br, COD), 4.50-4.57 (m, N- CH_2). ^{31}P $\{^1\text{H}\}$ NMR (121 MHz CD_2Cl_2): δ 26.5 (**8**, d, $J_{\text{Rh-P}} = 121.1\text{Hz}$), 23.1 (**3a**, d, $J_{\text{Rh-P}} = 122.7$ Hz), -144.4 (septet, $J_{\text{P-F}} = 706$ Hz, PF_6^-). ^{13}C NMR (100 MHz CD_2Cl_2): δ **3a** 10.1 (dd, $J = 8.8$, 20.6 Hz, Rh- CH_2); **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 μl , 0.10 mmol) were dissolved in CD_2Cl_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 ^1H and $^{31}\text{P}\{^1\text{H}\}$ 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.

^1H NMR (400 MHz CD_2Cl_2): δ 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). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CD_2Cl_2): δ 11.21 (s, PPh_2), -144.4 (septet, $J_{\text{P-F}} = 706$ Hz, PF_6^-). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 149.6 (d, $J_{\text{P-C}} = 12.1$ Hz, Ir-C), 141.7 (s, imidazole C2), 133.2 (d, $J_{\text{P-C}} =$

11.1 Hz, *o*- or *m*-PPh₂), 132.7 (d, $J_{\text{P-C}} = 50.7$ Hz, *ispo*-PPh₂), 130.9 (d, $J_{\text{P-C}} = 2.3$ Hz, *p*-PPh₂), 128.7 (d, $J_{\text{P-C}} = 10.2$ Hz, *o* or *m*-PPh₂), 125.8 (s, imidazole C4/5), 89.5 (d, $J_{\text{P-C}} = 12.3$ Hz, CH of COD), 72.9 (s, CH of COD), 47.8 (d, $J_{\text{P-C}} = 2.4$ Hz, N-CH₂), 34.4 (s, CH₃), 31.6 (d, $J_{\text{P-C}} = 2.9$ Hz, CH₂ of COD), 31.1 ($J_{\text{P-C}} = 1.9$ Hz, CH₂ of COD), 26.8 (d, $J_{\text{P-C}} = 34.6$ 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.

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3.5 References

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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^tBu_3 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

Figure 4.1 Abnormal NHC complexes.

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*]pyridiniums, structurally analogous to imidazoliums which are commonly used as NHC precursors. Base treatment of an imidazol[1,2-*a*]pyridiniums 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 pyridine 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.

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.¹² Therefore, initial attempts were made by reacting 1-benzylimidazo[1,2-*a*]pyridinium chloride with Ag₂O, 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.^{12a}

Hence 3-methylimidazo[1,2-*a*]pyridine and 1-methyl-imidazo[1,2-*a*]quinoline were synthesized according to literature reports.^{19,20} Alkylation using *para* substituted benzyl chlorides gives imidazo[1,2-*a*]pyridinium ions **1a-d** and **4** (eq 4.2, 4.3). Indeed, stirring a mixture of Ag₂O (0.5 equiv) and **1a-d** in CH₂Cl₂ afforded the corresponding silver carbene

chlorides, which were used as transmetalation reagents without isolation (Scheme 4.1).¹² Addition of 0.5 equiv of $[M(COD)Cl]_2$ ($M = Ir$ 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_2O . The higher acidity of the C(2)-*H* in **1a-d** might be accountable.

Scheme 4.1. Synthesis of Ir and Rh Abnormal NHC Complexes *via* Silver

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 ^1H 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 $\text{Ir-C}_{\text{carbene}}$ carries quite a high barrier.^{12a} However, when measured in CD_2Cl_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 δ 6.18 (s, 2H) in CD_2Cl_2 , while an AB pattern (δ 6.40 and 6.10, $^2J_{\text{HH}} = 16$ Hz) was observed for them in CDCl_3 . In the ^{13}C NMR spectra, the carbene C atoms resonate in a narrow range of δ 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_2Cl_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-Ccarbene 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**.

	3a	3d
Bond lengths (Å)		
Rh(1)-C(9)	2.039(2)	2.021(5)
Rh(1)-C(1)	2.097(2)	2.101(5)
Rh(1)-C(2)	2.110(2)	2.103(6)
Rh(1)-C(5)	2.194(2)	2.222(6)
Rh(1)-C(6)	2.218(2)	2.189(6)
C(9)-N(1)	1.412(2)	1.422(7)
C(9)-C(10)	1.380(2)	1.368(8)
N(2)-C(16)	1.368(2)	1.383(7)
Bond angles (deg)		
C(9)-Rh(1)-Cl(1)	89.83(5)	89.72(14)
N(1)-C(9)-C(10)	104.62(15)	104.3(4)
Torsion angle (deg)		
N(1)-C(9)-Rh(1)-Cl(1)	-70.6	-81.3

Table 4.2 Crystallographic Data for Complexes **3a**, **3d**, and **9d**

	3a	3d	9d
empirical formula	C ₂₃ H ₂₆ ClN ₂ Rh	C ₂₄ H ₂₅ ClF ₃ N ₂ Rh	C ₁₈ H ₁₃ ClF ₃ IrN ₂ O ₂
formula weight	468.82	536.82	573.95
temperature	173(2) K	223(2)	173(2) K
crystal system	Monoclinic	Monoclinic	Monoclinic
space group		P2(1)/c	
<i>a</i> (Å)	15.6914(6)	11.7872(4)	14.2118(6)
<i>b</i> (Å)	8.8419(3)	16.2148(6)	8.7062(3)
<i>c</i> (Å)	14.6448(6)	11.9178(4)	15.8811(6)
α (deg)	90	90	90
β (deg)	95.747(2)	102.218(2)	110.789(2)
γ (deg)	90	90	90
<i>V</i> (Å ³)	2021.63(13)	2226.22(13)	1837.05(12)
<i>Z</i>	4	4	4
<i>d</i> _{calcd} (g/cm ³)	1.540	1.602	2.075
μ (mm ⁻¹)	0.987	0.926	7.458
crystal size (mm)	0.30 x 0.20 x 0.20	0.26 x 0.24 x 0.14	0.14 x 0.12 x 0.10
total, unique no. of rflns	25614, 6127	23557, 4382	20651, 4816
<i>R</i> (int)	0.0274	0.0562	0.0334
data, restraints, parameters	6127, 0, 245	4382, 85, 309	4816, 129, 249
<i>R</i> , <i>R</i> _w (all data)	0.0261, 0.0338	0.0555, 0.0645	0.0287, 0.0365
GOF	1.089	1.194	1.044
peak and hole (eÅ ⁻³)	0.577, -0.573	1.354, -0.888	1.651, -1.042

4.2.3 Metalation at the Complementary Position

Although H-3 is less acidic than H-2 in imidazo[1,2-*a*]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 (CD₂Cl₂) at -20 °C, all the methylene protons in the ⁿBu group are sharp and diastereotopic, while they are all broad at 25 °C and coalescence of the NCH₂ signals was observed. This clearly shows that the barrier of the Ir-Ccarbene bond rotation is lower. In the ¹³C NMR spectrum of **8**, the carbene C atom resonates at δ 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-*a*]pyridinium chloride was treated with Ag₂O. 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-*a*]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 $\text{Ir}(\text{NHC})(\text{CO})_2\text{Cl}$ 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. Inequivalent CO carbon atoms have also been observed by ^{13}C NMR spectroscopy.

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 CH_2Cl_2 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-Ccarbene distance is 2.075(4) Å and is comparable to those in Ir-NHC complexes.^{12a,c,22} 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**

Bond lengths (Å)	
Ir(1)-C(1)	2.075(4)
Ir(1)-C(18)	1.899(4)
Ir(1)-C(17)	1.841(6)
Ir(1)-Cl(1)	2.075(4)
C(1)-C(2)	1.364(5)
C(1)-N(1)	1.413(5)
Bond angles (deg)	
C(17)-Ir(1)-C(18)	90.3(2)
C(1)-Ir(1)-Cl(1)	88.53(11)
Torsion angle (deg)	
N(1)-C(1)-Ir(1)-Cl(1)	91.72

4.2.4.3 Solution Dynamics

The methylene protons of complexes **9a-d** and **11** all showed broad singlet signals in the ^1H NMR spectrum at room temperature (CDCl_3), indicated that the rotation along the Ir-C_{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 $\Delta H^\ddagger = 14.4$ 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**

T (K)	1/T×1000 (1/K)	$\Delta(w_{1/2})$ (Hz) ^a	k (Hz)	ln(k/T)
241.19	4.146	1.17	3.676	-4.187
245.18	4.0786	2.14	6.723	-3.596
249.29	4.0114	3.39	10.65	-3.153
253.35	3.947	5.28	16.59	-2.726

^a $w_0=3.740\text{Hz}$ (228.8K)

Figure 4.7 The Eyring Plot for the Fluxionality of Complex **9a**^a

^a The slope of this line is $\Delta H^\ddagger/R$, and the intercept is $[\Delta S^\ddagger/R + \ln(k_b/h)]$

The appearance of methylene protons signals for **10** is, however, significantly different from that of **9a-d** or **11**. Although they are broad ($W_{1/2} = 12.4$ Hz) at room temperature, these signals are not coalesced and an AB pattern was observed (δ 6.27 and 5.82, $^2J_{\text{HH}} = 15.4$ Hz), indicating a higher barrier of rotation along the Ir-C_{carbene} here. Indeed, VT NMR (-10 to 25 °C) line shape analysis of those CH₂ signals of **10** afforded $\Delta H^\ddagger = 17.9$ kcal/mol for the rotation along the Ir-C_{carbene} bond. (Table 4.5, Figure 4.8)

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

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

^a $w_0 = 2.805$ Hz (266K)

Figure 4.8 The Eyring Plot for the Fluxionality of Complex **10**^a

^a The slope of this line is $\Delta H^\ddagger/R$, and the intercept is $[\Delta S^\ddagger/R + \ln(k_b/h)]$

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.^{21a} Herrmann^{4a} reported that π -back-bonding in NHC-transition metal complexes was negligible, and this conclusion was supported by theoretical studies.^{21b} This idea of negligible back-donation is, however, challenged by some recent reports.^{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,^{21e,f} a scenario directly analogous to ours in abnormal NHC complexes.

Figure 4.9 Back-donation to an abnormal NHC derived from imidazo[1,2-*a*]quinoline.

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 $\nu(\text{CO})$ 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 [$\nu_{\text{av}}(\text{CO}) = 1999 \text{ cm}^{-1}$] 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 $\nu_{\text{av}}(\text{CO})$ 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 CF₃ group is introduced to the *para* position of the benzyl group. The difference between the $\nu_{\text{av}}(\text{CO})$ 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 constant²³ (σ_{I}) 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

Ir(L)(CO)₂Cl	$\nu(\text{CO})$ (cm⁻¹)	$\nu_{\text{av}}(\text{CO})$ (cm⁻¹)	Ref.
2041, 1957	1999	this work
2054, 1986	2020	this work
2049, 1967	2008	this work
2050, 1984	2017	this work
2050, 1981	2015	this work
2046, 1965	2006	this work
2045, 1961	2003	12a
2059, 1974	2017	12c
2062, 1978	2020	24
2072, 1989	2031	24
2058, 1973	2016	9
PCy ₃	2072, 1984	2028	12c

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 $\nu_{\text{av}}(\text{CO})$ 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 π -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-*d*₄. The chemical shift is given as dimensionless δ values referenced to TMS for ¹H and ¹³C. 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 CH₃CN (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 mmg 0.974 mmol). ¹H NMR (400 MHz, DMSO-*d*₆) δ 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, CH₂), 2.59 (s, 3H, CH₃). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 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 Calcd for [C₁₅H₁₅N₂⁺]: 223.1235.

Compound 1b. Yield 91% (white solid, 298 mg, 1.03 mmol). ¹H NMR (300 MHz, DMSO-*d*₆) δ 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, CH_2), 3.74 (s, 3H, OCH_3), 2.58 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$) 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 $[\text{C}_{16}\text{H}_{17}\text{N}_2\text{O}^+]$: 253.1341.

Compound 1c. Yield 87% (white solid, 273 mmol, 0.99 mmol). ^1H NMR (300 MHz, $\text{DMSO}-d_6$) 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, CH_2), 2.57 (d, $J = 0.7$ Hz, 3H, CH_3). ^{19}F NMR (282 MHz, $\text{DMSO}-d_6$) δ -113.4. ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$) δ 162.6 (d, $J_{\text{F-C}} = 243.5$ Hz), 138.9, 133.8, 131.7 (d, $J_{\text{F-C}} = 3.1$ Hz), 130.9 (d, $J_{\text{F-C}} = 8.4$ Hz), 128.1, 124.1, 122.7, 117.4, 116.2 (d, $J_{\text{F-C}} = 21.5$ Hz), 111.5, 49.3, 9.0. HRMS (ESI^+): 241.1114. Calcd for $[\text{C}_{15}\text{H}_{14}\text{N}_2\text{F}^+]$: 241.1141.

Compound 1d. Yield 93% (white solid, 345 mg, 1.06 mmol). ^1H NMR (400 MHz, $\text{DMSO}-d_6$) 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, CH_2), 2.60 (s, 3H, CH_3). ^{19}F NMR (282 MHz, $\text{DMSO}-d_6$) δ -61.1 ppm. ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 140.2, 139.2, 133.9, 129.4 (q, $J_{\text{F-C}} = 31.7$ Hz), 129.1, 128.2, 126.2 (q, $J_{\text{F-C}} = 3.7$ Hz), 124.5 (q, $J_{\text{F-C}} = 270.6$ Hz, CF_3), 124.3, 122.9, 117.5, 111.5, 49.4, 9.1. HRMS (ESI^+): 291.1058. Calcd for $[\text{C}_{16}\text{H}_{14}\text{N}_2\text{F}_3^+]$: 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, CDCl_3): δ 10.84 (d, $J = 11.0$ Hz, 1H), 8.50 (d, $J = 12.3$ Hz, 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, $J = 8.7$ Hz, 1H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) 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). ^1H NMR (400 Hz, CDCl_3): δ 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). ^1H NMR (400 Hz, $\text{DMSO}-d_6$): δ 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, $\text{DMSO}-d_6$) δ 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 $[\text{C}_{19}\text{H}_{17}\text{N}_2]^+$: 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). ^1H NMR (400 Hz, CDCl_3): δ 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): δ 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 $[\text{C}_{14}\text{H}_{12}\text{N}_2]$: 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 CH_2Cl_2 (20 mL). A clear solution was obtained after filtration. Product **7** was obtained as a white solid after the removal of CH_2Cl_2 . Yield: 148 mg (97%). ^1H NMR (400 MHz, CDCl_3): 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- CH_2), 2.63 (s, 3H, Ph- CH_3), 1.61-1.68 (m, 2H, CH_2), 1.17-1.23 (m, 2H, CH_2), 0.76 (t, $J = 7.3$ Hz, 3H, CH_3). ^{13}C NMR (100MHz, CDCl_3) 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 $[\text{C}_{18}\text{H}_{21}\text{N}_2]$: 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 $[\text{M}(\text{COD})\text{Cl}]_2$ ($\text{M} = \text{Ir}$ 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 Al_2O_3 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, CD_2Cl_2) 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, CH_2), 6.00 (d, $J = 15.8$ Hz, 1H, CH_2), 5.32 (t, $J = 1.0$ Hz, 2H, COD), 3.07 (m, 1H, COD), 2.71 (s, 3H, CH_3), 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). ^{13}C NMR (75 MHz, CD_2Cl_2) 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- CH_2), 52.9 (CH of COD), 50.8 (CH of COD), 33.7 (CH_2 of COD), 33.3 (CH_2 of COD), 29.9 (CH_2 of COD), 29.5 (CH_2 of COD), 11.0 (CH_3). Anal. Calcd for $\text{C}_{23}\text{H}_{26}\text{ClIrN}_2$ (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). ^1H NMR (300 MHz, CDCl_3) δ 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) δ 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 $\text{C}_{24}\text{H}_{28}\text{ClIrN}_2\text{O}$ (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). ^1H NMR (400 MHz, CDCl_3) δ 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) δ -114.2. ^{13}C NMR (100 MHz CDCl_3) δ 169.1 (C-Ir), 162.3 (d, $J_{\text{F-C}}$ = 245.2 Hz, C-F), 140.2, 132.1 (d, $J_{\text{F-C}}$ = 3.2 Hz), 129.1 (d, $J_{\text{F-C}}$ = 8.1 Hz), 124.9, 122.4, 121.9, 115.7 (d, $J_{\text{F-C}}$ = 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_2), 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 $\text{C}_{23}\text{H}_{25}\text{ClFIrN}_2$ (FW 576.1) 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). ^1H NMR (300 MHz, CD_2Cl_2) δ 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, CD₂Cl₂) δ -62.9. ¹³C NMR (75 MHz CD₂Cl₂) δ 168.6 (Ir-C), 140.7, 140.3, 129.7 (q, $J_{\text{F-C}}$ = 32.2 Hz), 127.7, 125.5 (q, $J_{\text{F-C}}$ = 3.8 Hz), 125.4, 124.2 (q, $J_{\text{F-C}}$ = 270.4 Hz, CF₃), 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 (CH₂), 50.8 (CH of COD), 33.8 (CH₂ of COD), 33.3 (CH₂ of COD), 29.9 (CH₂ of COD), 29.4 (CH₂ of COD), 10.0 (CH₃). Anal. Calcd for C₂₄H₂₅ClF₃IrN₂ (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). ¹H NMR (300 MHz, CD₂Cl₂) 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, CH₂), 6.10 (d, J = 15.9 Hz, 1H, CH₂), 4.84 (br, 2H, COD), 3.41 (br, 1H, COD), 3.03 (br, 1H, COD), 2.78 (s, 3H, CH₃), 2.20-2.49 (m, 3H, COD), 1.83-1.93 (m, 4H, COD), 1.72 (br, 1H, COD). ¹³C NMR (75 MHz, CD₂Cl₂) δ 169.3 (d, $J_{\text{Rh-C}}$ = 46.0 Hz, Rh-C), 140.4, 136.8, 128.7, 127.7, 127.2, 124.8, 121.8, 121.6 (d, $J_{\text{Rh-C}}$ = 2.5 Hz), 114.3, 108.7, 96.9 (d, $J_{\text{Rh-C}}$ = 6.7 Hz, CH of COD), 96.2 (d, $J_{\text{Rh-C}}$ = 6.6 Hz, CH of COD), 68.8 (d, $J_{\text{Rh-C}}$ = 14.7 Hz, CH of COD), 67.0 (d, $J_{\text{Rh-C}}$ = 14.7 Hz, CH of COD), 54.0 (Ph-CH₂), 32.9 (d, $J_{\text{Rh-C}}$ = 14.3 Hz, CH₂ of COD), 28.9 (s, CH₂ of COD), 11.3 (CH₃). Anal. Calcd for C₂₃H₂₆ClN₂Rh (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). ¹H NMR (300 MHz, CDCl₃) 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, CH₂), 5.93 (d, J = 15.7 Hz, 1H, CH₂), 4.95 (br, 2H, COD), 3.79 (s, 3H, OCH₃), 3.41-3.46 (m, 1H, COD), 3.07-3.12 (m, 1H, COD), 2.78 (s, 3H, CH₃), 2.26-2.55 (m, 3H, COD), 2.01-2.06 (m, 1H, COD), 1.85-1.92 (m, 4H, COD). ¹³C NMR (75 MHz CDCl₃): δ 168.9 (d, $J_{\text{Rh-C}}$ = 45.8 Hz, Rh-C), 158.2, 139.2, 127.6, 127.5, 123.5, 120.6 (d, $J_{\text{Rh-C}}$ = 2.3 Hz), 120.5, 113.2, 113.1, 107.9, 96.3 (d, $J_{\text{Rh-C}}$ = 6.8 Hz, CH of COD), 95.6 (d, $J_{\text{Rh-C}}$ = 6.8 Hz, CH of COD), 67.9 (d, $J_{\text{Rh-C}}$ = 15.0 Hz, CH of COD), 65.9 (d, $J_{\text{Rh-C}}$ = 14.8 Hz, CH of COD), 55.3, 54.3 (Ph-CH₂), 32.0 (d, $J_{\text{Rh-C}}$ = 17.9 Hz, CH₂ of COD), 28.9 (d, $J_{\text{Rh-C}}$ = 13.3 Hz, CH₂ of COD), 10.6 (CH₃). Anal. Calcd for C₂₄H₂₈ClN₂ORh (FW 498.9) C, 57.78; H, 5.66; N, 5.62; Found: C, 57.35; H,

5.71; N, 5.55.

Complex 3c. Yield: 91% (yellow solid, 88.6 mg, 0.182 mmol). ^1H NMR (400 MHz, CDCl_3) δ 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) δ -114.3. ^{13}C NMR (100 MHz, CDCl_3) δ 169.9 (d, $J_{\text{Rh-C}}$ = 45.9 Hz, Rh-C), 162.3 (d, $J_{\text{F-C}}$ = 245.0 Hz, C-F), 140.2, 132.3 (d, $J_{\text{F-C}}$ = 3.1 Hz), 128.9 (d, $J_{\text{F-C}}$ = 8.0 Hz), 124.7, 121.8 (d, $J_{\text{Rh-C}}$ = 2.2 Hz), 121.6, 115.8 (d, $J_{\text{F-C}}$ = 21.4 Hz), 114.4, 108.7, 97.5 (d, $J_{\text{Rh-C}}$ = 6.9 Hz, CH of COD), 96.7 (d, $J_{\text{Rh-C}}$ = 6.9 Hz, CH of COD), 69.0 (d, $J_{\text{Rh-C}}$ = 15.0 Hz, CH of COD), 67.0 (d, $J_{\text{Rh-C}}$ = 14.9 Hz, CH of COD), 53.6 (Ph- CH_2), 33.0 (d, $J_{\text{Rh-C}}$ = 13.9 Hz, CH_2 of COD), 28.9 (d, $J_{\text{Rh-C}}$ = 11.6 Hz, CH_2 of COD), 11.7 (CH_3). Anal. Calcd for $\text{C}_{23}\text{H}_{25}\text{ClF}_3\text{N}_2\text{Rh}$ (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). ^1H NMR (400 MHz, CD_2Cl_2) δ 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_2Cl_2) δ -62.8. ^{13}C NMR (100 MHz, CD_2Cl_2) δ 169.4 (d, $J_{\text{Rh-C}}$ = 45.8 Hz, C-Rh), 141.1, 140.3, 129.7 (q, $J_{\text{C-F}}$ = 32.0 Hz), 127.7, 125.5 (q, $J_{\text{C-F}}$ = 3.6 Hz), 125.4, 124.8 (q, $J_{\text{C-F}}$ = 272.0 Hz, CF_3), 122.0, 121.9 (d, $J_{\text{Rh-C}}$ = 2.3 Hz), 114.6, 108.5, 97.2 (d, $J_{\text{Rh-C}}$ = 6.7 Hz, CH of COD), 96.5 (d, $J_{\text{Rh-C}}$ = 6.7 Hz, CH of COD), 69.0 (d, $J_{\text{Rh-C}}$ = 14.9 Hz, CH of COD), 67.1 (d, $J_{\text{Rh-C}}$ = 14.9 Hz, CH of COD), 53.4 (Ph- CH_2), 32.9 (d, $J_{\text{Rh-C}}$ = 14.1 Hz, CH_2 of COD), 28.8 (s, CH_2 of COD), 11.3 (CH_3). Anal. Calcd for $\text{C}_{24}\text{H}_{25}\text{ClF}_3\text{N}_2\text{Rh}$ (FW 536.8) C, 53.70; H, 4.69; N, 5.22; Found: C, 53.61; H, 4.47; N, 5.39.

Complex 5. Yield: 85% (red solid, 103 mg, 0.17 mmol) ^1H NMR (300 MHz, CD_2Cl_2)

δ 8.67 (d, J = 8.8 Hz, 1H), 7.87 (dd, J = 7.9, 1.3 Hz, 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, CH_2), 4.36 (br, 2H, COD), 3.32 (s, 3H, CH_3), 3.09 (td, J = 6.9, 2.5 Hz, 1H, COD), 2.572 (td, J = 7.2, 3.1 Hz, 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). ^{13}C NMR (75 MHz, CD_2Cl_2) 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 (CH_2), 53.4 (CH of COD), 51.3 (CH of COD), 34.2 (CH_2 of COD), 33.8 (CH_2 of COD), 30.3 (CH_2 of COD), 30.3 (CH_2 of COD), 18.2 (CH_3) ppm. Anal. Calcd for $\text{C}_{27}\text{H}_{28}\text{ClIrN}_2$ (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, CD_2Cl_2 , 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- CH_2), 2.80-2.83 (m, 1H, COD), 2.52 (s, CH_3), 2.31-2.34 (m, 1H, COD), 1.90-2.13 (m, 3H, COD), 1.72-1.77 (m, 2H, CH_2), 1.44-1.50 (m, 4H, COD), 1.27-1.30 (m, 2H, CH_2), 1.24-1.27 (m, 1H, COD), 0.86 (t, J = 7.3 Hz, 3H, CH_2CH_3). ^{13}C NMR (75 MHz, CD_2Cl_2 , 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 $\text{C}_{26}\text{H}_{32}\text{ClIrN}_2$ (FW 600.2) C, 52.03; H, 5.37; N, 4.67; Found: C, 51.90; H, 5.42; N, 4.55.

General Method for the Synthesis of Bicarboxyl 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, CD_2Cl_2): 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, CH_2), 2.66 (s, 3H, CH_3). ^{13}C NMR (75 MHz, CD_2Cl_2): 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), ν_{CO} = 2041, 1957 cm^{-1} . Anal. Calcd for $\text{C}_{17}\text{H}_{14}\text{ClIrN}_2\text{O}_2$ (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%. ^1H NMR (300 MHz, CD_2Cl_2): δ 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_2Cl_2): δ 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), ν_{CO} = 2048, 1966 cm^{-1} . Anal. Calcd for $\text{C}_{18}\text{H}_{16}\text{ClIrN}_2\text{O}_3$ (FW 536.0) C, 40.33; H, 3.01; N, 5.23; Found C, 40.26; H, 3.29; N, 5.47.

Complex 9c. Yield: 51 mg, 97%. ^1H NMR (400MHz, CDCl_3) δ 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) 182.7 (CO), 169.3 (Ir-C), 162.5 (d, $J_{\text{F-C}}$ = 246 Hz), 160.6 (CO), 140.1, 131.2 (d, $J_{\text{F-C}}$ = 3.0 Hz), 129.1 (d, $J_{\text{F-C}}$ = 8.1 Hz), 127.5, 126.5, 123.4, 115.9 (d, $J_{\text{F-C}}$ = 21.6 Hz), 115.4, 109.9, 52.7, 11.5. FTIR (Nujol), ν_{CO} = 2054, 1986 cm^{-1} . Anal. Calcd for $\text{C}_{17}\text{H}_{13}\text{ClIrN}_2\text{O}_2$ (FW 524.0) C, 38.97; H, 2.50; N, 5.35; Found C, 39.02; H, 2.66; N, 5.21.

Complex 9d. Yield: 53 mg, 93%. ^1H NMR (300 MHz, CDCl_3): δ 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, 3H, CH_3). ^{13}C NMR (75 MHz, CDCl_3): δ 183.4 (CO), 169.2 (Ir-C), 160.8(CO), 140.2, 139.2, 130.5 (q, $J_{\text{F-C}}$ = 32.4 Hz), 127.8, 127.5, 126.7, 125.9 (q, $J_{\text{F-C}}$ = 3.8 Hz), 123.8 (q, $J_{\text{F-C}}$ = 270 Hz), 123.5, 115.6, 109.7, 52.9, 11.5. FTIR (Nujol), ν_{CO} = 2050, 1984 cm^{-1} . Anal. Calcd for $\text{C}_{18}\text{H}_{13}\text{ClF}_3\text{IrN}_2\text{O}_2$ (FW 574.0) C, 37.67; H, 2.28; N, 4.88; Found C, 37.39; H, 2.45; N, 4.96.

Complex 10. Yield: 52 mg, 94%. ^1H NMR (300 MHz, CD_2Cl_2): δ 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_2Cl_2): δ 183.2 (CO), 169.5 (Ir-C), 158.9(CO), 139.3, 135.6, 133.2, 130.6, 130.5, 130.0, 129.6, 128.8, 128.1, 127.0, 126.5, 124.6, 117.4, 108.5, 53.5, 18.1. FTIR (Nujol), ν_{CO} = 2050, 1981 cm^{-1} . Anal. Calcd for $\text{C}_{21}\text{H}_{16}\text{ClIrN}_2\text{O}_2$ (FW 556.0) C, 45.36; H, 2.90; N, 5.04; Found C, 45.45; H, 3.11; N, 4.94.

Complex 11. Yield: 51.5 mg, 94%. ^1H NMR (300 MHz, CDCl_3): δ 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), 1.19-1.27 (m, 2H, CH_2), 0.82 (t, $J=7.3\text{Hz}$, 3H, $\text{CH}_2\text{-CH}_3$). ^{13}C NMR (75 MHz, CDCl_3): δ 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), $\nu_{\text{CO}} = 2046, 1965\text{ cm}^{-1}$. Anal. Calcd for $\text{C}_{20}\text{H}_{20}\text{ClIrN}_2\text{O}_2$ (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 $\Delta H^\ddagger$.

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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

Figure 5.1. NHCs, abnormal NHCs, Py-NHCs, and remote py-NHCs

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-halopyridiniums when treated with low valent transition metals such as Pd^{14,15,18} or Pt¹⁹, (ii) quaternization of iridium or rhodium pyridyl complexes,²⁰ (iii) metalation of *in situ* generated carbenes from the deprotonation of pyridiniums by strong bases,¹² and (iv) C-H oxidative addition of functionalized pyridiniums.²¹ Kinetic studies of the π -accepting ability of these complexes showed distinctive *trans*-labilizing ability of these py-NHCs in ligand substitution reactions.²¹

Scheme 5.1 Common methods for py-NHC complexes

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.

We²² and others²³ 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.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.

Figure 5.2. Pyridine-tethered pyridinium halides

5.2.2 Metalation and Structures

5.2.2.1 C-H Activation of Compound 1.

We have chosen $[\text{Ir}(\text{COD})_2]\text{SbF}_6$ or $[\text{Ir}(\text{COD})_2]\text{PF}_6$ 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 $[\text{Ir}(\text{COD})_2]\text{SbF}_6$ in dichloromethane at room temperature, and two hydride species were obtained based on ^1H NMR analysis. These two hydrides resonate at δ -12.9 (s) and -14.3 (s) in 1:5 ratio. In the ^{13}C NMR spectrum, two corresponding Ir-C_{carbene} signals were detected at δ 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 $[\text{Ir}(\text{COD})_2]\text{PF}_6$ or $[\text{Ir}(\text{COD})_2]\text{SbF}_6$ (CH_2Cl_2 , 25 °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 δ -12.96 to -13.79 in the ^1H NMR spectra (CD_2Cl_2), and the Ir-C_{carbene} signals appear within a range of δ 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 (CD₂Cl₂) of iridium hydride complexes **5-7**

	5	6a	6b	7a	7b	7c
Ir- <i>H</i>	-13.52	-13.79	-12.96	-14.13 (<i>cis</i>) -12.81 (<i>trans</i>)	-13.61 (<i>cis</i>) -14.01 (<i>trans</i>)	-14.11 (<i>cis</i>) -12.62 (<i>trans</i>)
Ir- <i>C</i> _{carbene}	182.5	189.6	189.7	191.1 (<i>cis</i>)	192.1 (<i>cis</i>) 191.9 (<i>trans</i>)	192.5 (<i>cis</i>)

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]₂SbF₆ (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 ¹H NMR spectra (CD₂Cl₂) of iridium(III) iodide **7a** or **7c**, two hydride signals were observed (δ -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 CH₂Cl₂ and Et₂O. Correlations between the solid structure and the ¹H NMR spectrum could be achieved by dissolution of a pure

sample of **7a-cis** at $-40\text{ }^{\circ}\text{C}$, 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 ^{13}C 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 CD_3CN . The van't Hoff plot of this *trans* to *cis* equilibrium system gave thermodynamic parameters $\Delta H^\circ = 1.6\text{ kcal/mol}$ and $\Delta S^\circ = -0.77\text{ eu}$ (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**

T (K)	1/T (K^{-1})	K_{eq}	$\ln K_{eq}$
345.29	0.002896	7.05	1.953
334.07	0.002993	7.69	2.0399
323.95	0.003087	8.18	2.1017
313.12	0.003194	9.05	2.2028
297.46	0.003362	10.28	2.33

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

^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,^{22,23} 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-C_{olefin} distances at ca. 0.05 Å 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.^{21,24}

Figure 5.4 Molecular structure of **5** (cation only) with ellipsoids shown at 50% thermal probability

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**

	5	6b	7a
Ir-C(18) (Å)	2.013(9)	2.030(4)	2.006(3)
Ir-N(1) (Å)	2.193(8)	2.204(3)	2.209(3)
Ir-X (Å)	2.7069(10)	2.5089(4)	2.6901(3)
C(18)-C(19) (Å)	1.426(14)	1.415(6)	1.415(4)
C(18)-Ir-N(1) (deg)	78.6(4)	78.98(14)	79.05(12)
C(18)-Ir-X (deg)	91.1(3)	91.53(10)	88.99(9)
N(1)-Ir-X (deg)	84.8(2)	84.61(8)	85.78(7)

Table 5.4. Crystallographic data for complexes **5**, **6b** and **7a**

	5	6b •1/3CH ₃ CN	7a
empirical formula	C ₂₃ H ₃₁ F ₆ IrN ₂ P	C ₂₇ H ₂₇ BrF ₆ IrN ₂ Sb•1/3CH ₃ CN	C ₂₄ H ₂₉ F ₆ IrN ₂ Sb
formula weight	799.57	901.05	900.34
temperature		173(2) K	
crystal system	Monoclinic	Triclinic	Monoclinic
space group	<i>P</i> 2(1)/n	<i>P</i> -1	<i>P</i> 2(1)/c
<i>a</i> (Å)	11.3177(2)	13.0166(4)	14.5088(4)
<i>b</i> (Å)	12.8037(3)	13.5422(4)	12.9346(3)
<i>c</i> (Å)	17.9585(4)	24.0445(7)	14.1699(4)
<i>α</i> (deg)	90	85.1270(10)	90
<i>β</i> (deg)	91.1430(10)	82.9790(2)	99.8920(4)
<i>γ</i> (deg)	90	87.9560(10)	90
<i>V</i> (Å ³)	2601.82(10)	4190.0(2)	2619.67(12)
<i>Z</i>	4	6	4
<i>d</i> _{calcd} (g/cm ³)	2.041	2.143	2.283
<i>μ</i> (mm ⁻¹)	6.437	7.219	7.343
crystal size (mm)	0.30 x 0.26 x 0.16	0.30 x 0.12 x 0.10	0.30 x 0.18 x 0.06
total, unique no. of rflns	35948, 4612	176183, 41000	40906, 5716
<i>R</i> (int)	0.0334	0.0385	0.0237
data, restraints, parameters	4612, 196, 369	41000, 9, 1064	5716, 3, 320
<i>R</i> , <i>R</i> _w (all data)	0.0582, 0.1116	0.0848, 0.1210	0.0220, 0.0456
GOF	1.206	1.035	1.055
peak and hole (eÅ ⁻³)	3.278, -2.246	2.722, -2.987	2.619, -1.099

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.²⁵ We reason that hydride complexes **5**, **6** and **7** could also be active catalysts in this reaction. Indeed, transfer hydrogenation between acetophenone and ⁱPrOH proceeded smoothly in the presence of 10 mol% Cs₂CO₃ (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 α,β -unsaturated ketones and aldehydes, where chemoselectivity can be an issue.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 *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 α,β -unsaturated carbonyl compounds at the C=C bonds catalyzed by Cu²⁷ and Ru²⁸ have been reported and this chemo-selectivity complements the traditional hydride reduction protocols.

Table 5.5 Transfer hydrogenation of acetophenones and α,β -unsaturated ketones and aldehydes^a

entry	ketone	time (h)	products	yield (%) ^b
1	Ar = Ph	6		92, 90 ^c
2	Ar = Ph	6		74 ^d
3	Ar = 4-MeC ₆ H ₄	4		93
4	Ar = 4-MeOC ₆ H ₄	6		82
5	Ar = 4-BrC ₆ H ₄	3		99
6	Ar = 4-FC ₆ H ₄	3		99
7	Ar = 4-ClC ₆ H ₄	4		95
8	Ar = 3-BrC ₆ H ₄	4		99
9		6		95
10		4		99
11		8		82
12		13		86
13		6		95
14		10		88
15		10		70
16		4		96
17		10		92
18		6		96

^a Reaction condition: 1 mmol of acetophenone; 0.1 mmol Cs₂CO₃; 1 mol% of catalyst **6a**; 3 ml *i*PrOH. ^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 σ -donating characters of carbon-centered ligands are undoubtedly relevant to their increasingly important roles in homogeneous catalysis²¹ 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 $\text{IrCl}(\text{CO})_2\text{L}$ or $\text{RhCl}(\text{CO})_2\text{L}$ 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 ν_{CO} frequencies of complexes **8-11** were calculated at the B3LYP/6-31G*/LANL2DZ (Rh) level and the average ν_{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 σ -donating ability of py-NHC $\cong$ remote py-NHC $>$ abnormal NHC $>$ normal NHC can be concluded, consistent with previous reports.^{13,21}

	8 py-NHC	9 remote py-NHC	10 abnormal NHC	11 normal NHC
$\nu_{\text{CO}}\text{ (cm}^{-1}\text{)}$	2124.8, 2173.8	2127.0, 2171.6	2134.5, 2175.7	2138.0, 2182.1
average (cm ⁻¹)	2149.3	2149.3	2155.1	2160

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 $[\text{Rh}(\text{CO})_2(\text{N}^{\wedge}\text{NHC})]^+$ 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 N₂ before use and were stored in a dry box. CDCl₃ was dried by 4Å molecular sieves. CD₂Cl₂, DMSO-*d*₆, or CD₃CN 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 (>295K) of NMR samples for thermodynamic studies were calibrated using 80% ethylene glycol in DMSO-*d*₆. The chemical shift is given as dimensionless δ values and is referenced to SiMe₄ for ¹H and ¹³C 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, CDCl₃): δ 9.96 (s, 1H), 9.46 (d, *J* = 5.4 Hz, 1H), 9.26 (d, *J* = 8.0 Hz, 1H), 8.74 (d, *J* = 3.9 Hz, 1H), 8.52 (d, *J* = 8.0 Hz, 1H), 8.25 (t, *J* = 6.8 Hz, 1H), 7.97 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 6.8 Hz, 1H), 5.13 (t, *J* = 7.4 Hz, 2H, N-CH₂), 2.11 (t, *J* = 7.4 Hz, 2H, CH₂), 1.50 (q, *J* = 7.5 Hz, 2H, CH₂), 1.00 (t, *J* = 7.4 Hz, 3H, CH₃). ¹³C (100Hz, CDCl₃): δ 150.4, 149.2, 144.3, 142.7, 142.4, 139.7, 138.2, 128.6, 125.4, 122.8, 62.2 (NCH₂), 34.0 (NCH₂CH₂), 19.4 (NCH₂CH₂CH₂), 13.7 (CH₃). HRMS (ESI⁺): 213.1385, Calc. Mass for [C₁₄H₁₇N₂]⁺ 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). ^1H (400 MHz, CDCl_3): δ 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, $^3J = 7.8$ Hz, $^2J = 1.8$ 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 $[\text{C}_{15}\text{H}_{19}\text{N}_2]^+$ 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). ^1H (400 MHz, CDCl_3): δ 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, $J = 4.3$ Hz, 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): δ 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 $[\text{C}_{16}\text{H}_{17}\text{N}_2]^+$ 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). ^1H (400 MHz, $\text{DMSO}-d_6$): δ 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, $\text{DMSO}-d_6$): δ 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 $[\text{C}_{19}\text{H}_{15}\text{N}_2]^+$ 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). ^1H (400 MHz, CDCl_3): δ 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). ¹³C (100 MHz, CDCl₃): δ 152.5, 149.1, 144.2, 142.7, 139.9, 137.5, 137.0, 130.0, 126.4, 125.2, 123.4, 116.8, 59.0, 32.7, 19.9, 13.8. HRMS (ESI⁺): 237.1388, Calc. Mass for [C₁₆H₁₇N₂]⁺ 237.1392.

4b 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). ¹H (400 MHz, DMSO-*d*₆): δ 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).. ¹³C (100 MHz, DMSO-*d*₆): δ 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, 125.8, 124.5, 117.8, 60.8 (CH₂). HRMS (ESI⁺): 271.1230, Calc. Mass for [C₁₉H₁₅N₂]⁺: 271.1235. Analysis calcd for **4b** (C₁₉H₁₅BrN₂) C, 64.97; H, 4.30; N, 7.98, found C, 65.11; H, 4.19; N, 8.08.

Synthesis of **4c**. An excess of KI (900 mg, 5.42 mmol) was added to a solution of **4b** (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 **1b** as a yellow solid in 81% yield (280 mg, 0.70 mmol). ¹H (400 MHz, DMSO-*d*₆): δ 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). ¹³C (100 MHz, DMSO-*d*₆): δ 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, 124.5, 117.8, 60.8 (CH₂). HRMS (ESI⁺): 271.1226, Calc. Mass for [C₁₉H₁₅N₂]⁺: 271.1235. Analysis calcd for **4c** (C₁₉H₁₅IN₂) C, 57.30; H, 3.80; N, 7.03, found C, 57.39; H, 3.70; N, 7.11.

Synthesis of **Ir(COD)₂SbF₆**: To a solution of [Ir(COD)Cl]₂ (1.0 g, 1.49 mmol) in

CH_2Cl_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_2Cl_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 $\times$ 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%.

$\text{Ir}(\text{COD})_2\text{PF}_6$ was synthesized as a dark orchid in 93% (780 mg, 1.39 mmol) yield by following a method directly analogous to that for $\text{Ir}(\text{COD})_2\text{SbF}_6$, starting from $[\text{Ir}(\text{COD})\text{Cl}]_2$ (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 $[\text{Ir}(\text{COD})_2]\text{PF}_6$ or $[\text{Ir}(\text{COD})_2]\text{SbF}_6$ (0.20 mmol) in CH_2Cl_2 (5 mL) was added a CH_2Cl_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_2Cl_2 and Et_2O .

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_2Cl_2 solution after one day at room temperature. ^1H (300 MHz, CD_2Cl_2): δ 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- CH_2), 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_2CH_3), -13.52 (s, 1H, Ir- H). ^{13}C (75 MHz, CDCl_3): δ 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-CH₂), 36.2, 33.0, 32.6, 31.5, 25.3, 24.1 (CH₃), 19.9, 15.1, 13.4. Anal. Calcd for C₂₃H₃₁F₆IrN₂P: (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). ¹H (300 MHz, CD₂Cl₂): δ 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-CH₂), 4.84-5.01 (m, 2H, 1H for N-CH₂ 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, CH₂), 1.94-2.08 (m, 2H, COD), 1.81-1.93 (m, 1H, COD), 1.62-1.70 (m, 2H, CH₂), 1.24 (t, *J* = 7.4 Hz, 3H, CH₂CH₃), -13.8 (s, 1H, Ir-*H*). ¹³C (75 MHz, CDCl₃): δ 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-CH₂), 36.8, 33.2, 33.1, 31.0, 25.1, 25.0, 11.1 (CH₃). Anal. Calcd for C₂₄H₂₉F₆IrN₂P (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 CH₃CN/Et₂O solution with *n*-pentane after one day at room temperature. ¹H (400 MHz, CD₂Cl₂): δ 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-CH₂Ph), 6.31 (d, *J* = 13.8 Hz, 1H, N-CH₂Ph), 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*). ¹³C (100 MHz, CDCl₃): δ 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-CH₂Ph), 36.2 (CH₂ of COD), 33.8 (CH₂ of COD), 31.4 (CH₂ of COD),

24.8 (CH₂ of COD). Anal. Calcd for C₂₇H₂₇BrF₆IrN₂Sb (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. ¹H (300 MHz, CD₂Cl₂) for **7a-cis**: δ 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-CH₂), 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 CH₂ and 4H for COD), 1.47-1.59 (m, 2H, CH₂), 1.04 (t, *J* = 7.3 Hz, 3H, CH₂CH₃), -14.1 (s, 1H, Ir-*H*). ¹³C NMR (100 MHz, CD₂Cl₂) for **7a-cis**: δ 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-CH₂), 36.2, 33.6, 32.1 31.2, 25.0, 19.9, 12.2 (CH₃). Anal. Calcd for C₂₄H₂₉F₆IrN₂Sb (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 CD₂Cl₂ (0.6 ml), starting from compound **4b** (15 mg, 0.0427 mmol) and Ir(COD)₂SbF₆ (27.5 mg, 0.0427 mmol). Isolated yield: 34.5 mg, 91%. Selected NMR signals: ¹H NMR (400 MHz, CD₂Cl₂): -13.61 (Ir-*H*, **7b-cis**), -14.01 (Ir-*H*, **7b-trans**). ¹³C NMR (100 MHz CD₂Cl₂): 192.1 (Ir-C, **7b-cis**), 191.9 (Ir-C, **7b-trans**). Anal. Calcd for C₂₇H₂₇F₆BrIrN₂Sb (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). ¹H (400 MHz, CD₂Cl₂) for **7c-cis**: δ 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-CH₂), 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*). ¹³C NMR (100 MHz, CD₂Cl₂) for **7a-cis**: δ 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). ¹PrOH (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).

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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 (:C=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 $45\text{--}50 \text{ kcal mol}^{-1}$ 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

Our group have reported the tautomerization of a substituted imidazole in the coordination sphere of a cationic iridium(III) complex,⁸ 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.^{8,9,12} 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.

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 $\text{Pd}(\text{PPh}_3)_4$. 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 $\text{Pd}(\text{PPh}_3)_4$. 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)

Scheme 6.2. Synthesis of ligands for tautomerization studies

We have also selected $\text{Ir(COD)}_2\text{BF}_4$ as a metal source owing to the lability of one of the COD ligands, as observed in the rapid formation of $\text{Ir(COD)(MeCN)}_2\text{BF}_4$ from $\text{Ir(COD)}_2\text{BF}_4$ 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 $\text{Ir(COD)}_2\text{BF}_4$ in CD_2Cl_2 was initially attempted but a complicated mixture was obtained on the basis of ^1H NMR analysis, which shows at least five hydride species obtained from C–H activation, together with a broad singlet at δ 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 C_s 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 $\text{Ir}(\text{COD})_2\text{BF}_4$, respectively. In all these products the $\text{NH}\cdots\text{O}$ protons resonate in a range of δ 13.8 to 14.3 ppm in the ^1H NMR spectra and the $\text{Ir}-\text{C}_{\text{carbene}}$ 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 $[\text{Ir}(\text{COD})]\text{BF}_4$ carried out in CD_2Cl_2 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 $\text{NH}\cdots\text{O}$ 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 $\text{NH}\cdots\text{O}$ 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**

Bond lengths (Å)	
Ir(1)-C(15)	1.999(2)
Ir(1)-N(1)	2.0865(19)
Ir(1)-C(1)	2.221(2)
Ir(1)-C(2)	2.204(3)
Ir(1)-C(5)	2.124(2)
Ir(1)-C(6)	2.125(2)
C(14)-C(15)	1.424(3)
O(1)-H[N(2)]	1.959
Bond angles (deg)	
N(1)-Ir(1)-C(15)	78.43(8)
C(14)-C(15)-N(2)	116.7(2)
N(1)-C(1)-Ir(1)-Cl(1)	91.72

Table 6.2. Crystallographic data for complexes **4a**

4a	
empirical formula	C ₂₁ H ₂₅ B F ₄ Ir N ₃ O
formula weight	614.45
Temperature	173(2) K
crystal system	Monoclinic
space group	P2(1)/n
<i>a</i> (Å)	7.7588(2)
<i>b</i> (Å)	16.9174(5)
<i>c</i> (Å)	15.9163(5)
α (deg)	90
β (deg)	103.7470(10)
γ (deg)	90
<i>V</i> (Å ³)	2029.31(10)
<i>Z</i>	4
<i>d</i> _{calcd} (g/cm ³)	2.011
μ (mm ⁻¹)	6.635
crystal size (mm)	0.30 x 0.04 x 0.04
total, unique no. of rflns	32967, 6170
<i>R</i> (int)	0.0256
data, restraints, parameters	6170, 201, 343
<i>R</i> , <i>R</i> _w (all data)	0.0179, 0.0246
GOF	1.061
peak and hole (eÅ ⁻³)	1.377, -0.610

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 N_2 before use and stored glove-box. $CDCl_3$ was dried by 4Å molecular sieve and CD_2Cl_2 , DMSO-*d*₆ 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, AMX400 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 ^{13}C 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 $Pd(PPh_3)_4$ (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 $CDCl_3$) 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), 7.29-7.31 (m, 1H). ^{13}C NMR (125MHz $CDCl_3$) 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 $\text{Pd}(\text{PPh}_3)_4$ (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 CDCl_3) 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, CH_3). ^{13}C NMR (125 MHz, CDCl_3) 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 CDCl_3): 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). ^{13}C NMR (125 MHz, CDCl_3): 168.9, 156.4, 151.1, 149.7, 148.2, 147.9, 136.5, 132.8, 124.2, 122.2, 115.3, 24.8, 20.5 ppm. Anal. Calcd for $\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}$ (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, CDCl_3): 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). ^{13}C NMR (125 MHz, CDCl_3): δ 172.1, 154.4, 150.1, 150.0, 144.0, 138.2, 137.0, 132.8, 127.7, 122.6,

120.4, 24.8, 20.5. Anal. Calcd for $C_{13}H_{13}N_3O$ (FW 227.3) C, 68.70; H, 5.77; N, 18.49; Found C, 68.56; H, 5.38; N, 18.30.

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). ^{13}C 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 $C_{14}H_{15}N_3O$ (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). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.9, 154.4, 151.9, 150.0, 146.3, 137.0, 136.8, 131.1, 122.5, 120.0, 113.8, 24.8. Anal. Calcd $C_{12}H_{11}N_3O$ (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). ^{13}C 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 $C_{13}H_{13}N_3O$ (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 *vacuo* 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 tautomerization), 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-*d*₆): δ 14.2 (br, 1H, *NH* of tautomerization), 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-*d*₆): 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 tautomerization), 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 $C_{22}H_{27}BF_4IrN_3O$ (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%. 1H NMR (400 MHz, $DMSO-d_6$): δ 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, $DMSO-d_6$): δ 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 $C_{20}H_{23}BF_4IrN_3O$ (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%. 1H NMR (300 MHz, CD_2Cl_2): δ 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, $DMSO-d_6$): δ 178.6 (Ir-C), 177.6, 160.0, 150.4, 149.0, 139.9, 137.8, 137.4, 124.8, 121.0, 106.4, 33.0, 31.2, 8.9. Anal. Calcd for $C_{21}H_{25}BF_4IrN_3O$ (614.5) C, 41.05; H, 4.10; N, 6.84; Found C, 41.24; H, 4.01; N, 6.99.

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3. **Guoyong Song**, Yongxin Li, Shanshan Chen, Xingwei Li. Hydrogen Bonding Assisted Tautomerization of Pyridine Moieties in the Coordination Sphere of an Ir(I) Complex. *Chem. Commun.* **2008**, 3558-3560.
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9. **Guoyong Song**, Yan Su, Weiqiao Deng, Xingwei Li. Experimental and Computational Studies of the Tautomerization of Substituted Pyridines Mediated by Iridium. Manuscript in preparation.
10. **Guoyong Song**, Xingwei Li. Abnormal N-Heterocyclic Carbene Complexes in Catalytic

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11. **Guoyong Song**, Xingwei Li. Synthesis and Structures of multidentate phosphine-functionalized N-Heterocyclic Carbene Complexes. Manuscript in preparation.

Conference

“Iridium Hydrides with Non-Classical N-Heterocyclic Carbenes via Highly Selective C-H Activation”. International Symposium on Catalysis & Fine Chemicals 2007, Singapore. Obtained Best Poster Award.

Appendix

Selected ^1H NMR spectrum in Chapter 2

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Appendix

The detailed kinetic data of CH activation (Page 37)

At 297.1 K,

t (min)	0	21	31	36	42	49	54	64	76	87	97
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[Ir(I)]	0.421	0.0447	-0.152	-0.223	-0.315	-0.485	-0.55	-0.756	-0.96	-1.123	-1.31

At 302.3 K

t (min)	0	8	13	18	23	28	35	43	48
Ir(I)	1.097	0.856	0.7305	0.6282	0.5374	0.4663	0.3679	0.2851	0.2587
ln[Ir(I)]	0.0903	-0.155	-0.314	-0.465	-0.621	-0.763	-1	-1.255	-1.352

At 307.6 K

t (min)	0	4	8	12	16	20	24
Ir(I)	0.3308	0.2367	0.1728	0.1228	0.08786	0.06367	0.04209
ln[Ir(I)]	-1.1062	-1.4411	-1.7557	-2.097	-2.432	-2.754	-3.168

At 312.99 K

t (min)	0	5	10	20	25	30	35	40
Ir(I)	0.7619	0.5963	0.4877	0.2856	0.2194	0.1666	0.1327	0.1013
ln[Ir(I)]	-0.272	-0.517	-0.718	-1.253	-1.517	-1.792	-2.02	-2.29

The concentration of Ir (I) is relative to the internal standard.

Appendix

Selected ^1H NMR spectrum in Chapter 3

Appendix

Appendix

Selected ^1H NMR spectrum in Chapter 4

¹H NMR spectrum of [Ir(phen)(py)(CH₂CH₂CH₂)]PF₆ in CDCl₃. The spectrum shows peaks from 1.2 to 9.7 ppm. Integration values are provided below the peaks. The chemical structure of the cation is shown as an inset.

Chemical Shift (ppm)	Integration
9.72	1.02
9.71	1.01
8.82	0.96
8.81	0.95
8.41	1.80
8.38	0.97
8.16	0.96
8.14	2.01
8.13	2.04
8.09	0.98
7.97	1.00
7.93	1.06
7.92	1.19
7.56	2.90
7.54	2.05
7.52	1.98
7.51	1.99
7.49	1.18
7.48	1.29
7.47	2.09
7.46	2.05
7.45	2.09
7.44	2.05
7.43	2.09
7.42	2.05
7.41	2.09
7.40	2.05
7.39	2.09
7.38	2.05
7.37	2.09
7.36	2.05
7.35	2.09
7.34	2.05
7.33	2.09
7.32	2.05
7.31	2.09
7.30	2.05
7.29	2.09
7.28	2.05
7.27	2.09
7.26	2.05
7.25	2.09
7.24	2.05
7.23	2.09
7.22	2.05
7.21	2.09
7.20	2.05
7.19	2.09
7.18	2.05
7.17	2.09
7.16	2.05
7.15	2.09
7.14	2.05
7.13	2.09
7.12	2.05
7.11	2.09
7.10	2.05
7.09	2.09
7.08	2.05
7.07	2.09
7.06	2.05
7.05	2.09
7.04	2.05
7.03	2.09
7.02	2.05
7.01	2.09
7.00	2.05
6.99	2.09
6.98	2.05
6.97	2.09
6.96	2.05
6.95	2.09
6.94	2.05
6.93	2.09
6.92	2.05
6.91	2.09
6.90	2.05
6.89	2.09
6.88	2.05
6.87	2.09
6.86	2.05
6.85	2.09
6.84	2.05
6.83	2.09
6.82	2.05
6.81	2.09
6.80	2.05
6.79	2.09
6.78	2.05
6.77	2.09
6.76	2.05
6.75	2.09
6.74	2.05
6.73	2.09
6.72	2.05
6.71	2.09
6.70	2.05
6.69	2.09
6.68	2.05
6.67	2.09
6.66	2.05
6.65	2.09
6.64	2.05
6.63	2.09
6.62	2.05
6.61	2.09
6.60	2.05
6.59	2.09
6.58	2.05
6.57	2.09
6.56	2.05
6.55	2.09
6.54	2.05
6.53	2.09
6.52	2.05
6.51	2.09
6.50	2.05
6.49	2.09
6.48	2.05
6.47	2.09
6.46	2.05
6.45	2.09
6.44	2.05
6.43	2.09
6.42	2.05
6.41	2.09
6.40	2.05
6.39	2.09
6.38	2.05
6.37	2.09
6.36	2.05
6.35	2.09
6.34	2.05
6.33	2.09
6.32	2.05
6.31	2.09
6.30	2.05
6.29	2.09
6.28	2.05
6.27	2.09
6.26	2.05
6.25	2.09
6.24	2.05
6.23	2.09
6.22	2.05
6.21	2.09
6.20	2.05
6.19	2.09
6.18	2.05
6.17	2.09
6.16	2.05
6.15	2.09
6.14	2.05
6.13	2.09
6.12	2.05
6.11	2.09
6.10	2.05
6.09	2.09
6.08	2.05
6.07	2.09
6.06	2.05
6.05	2.09
6.04	2.05
6.03	2.09
6.02	2.05
6.01	2.09
6.00	2.05
5.99	2.09
5.98	2.05
5.97	2.09
5.96	2.05
5.95	2.09
5.94	2.05
5.93	2.09
5.92	2.05
5.91	2.09
5.90	2.05

Appendix

Appendix

Selected ^1H NMR spectrum in Chapter 6

Appendix