Synthesis and Complexation of Bis(imino)aryl Ligands: Towards the Generation of Iridium Based Water Oxidation Catalysts.

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A dissertation submitted to the faculty of the University of North Carolina at Chapel Hill in partial fulfillment of the requirements for the degree of Master of Arts in the Department of Chemistry.

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ABSTRACT

Mathew Finniss: Synthesis and Complexation of Bis(imino)aryl Ligands: Towards the Generation of Iridium Based Water Oxidation Catalysts.
(Under the direction of Professor Joseph Templeton and Professor Maurice Brookhart)

The *C,C*-trans bis-cyclometalation of 2,6-diphenylpyridine across an iridium center was investigated. Equally the synthesis and complexation of a series of bis(imino)aryl ligands was studied. Installing methyl and fluoro substituents in the backbone of the ligand prevented the C-H activation of the 4- and 6- positions and resulted in metalation of the 2-position. A mixed valent dimer [(4,6-$(CH_3)_2C_6H$-1,3-$(CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$)IrH-μ-Cl_2-Ir(C_8H_{12})] was isolated from the reaction of [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$] and $[Ir(COE)_2Cl]_2$. Using $[Ir(C_2H_4)_2Cl]_2$ as a starting Ir(I) precursor proved to be the most effective way to metalate the ligand. Three clean Ir(III) ethyl chlorides, [(4,6-$(CH_3)_2C_6H$-1,3-$(CHNC_6H_5)_2$)Ir(CH_2CH_3)Cl] [(4,6-$(CH_3)_2C_6H$-1,3-$(CHNC_6H_3$-3,5-$(C(CH_3)_3)_2)_2$)Ir(CH_2CH_3)Cl] and [(4,6-$(CH_3)_2C_6H$-1,3-$(CHNC_6H_4$-4-$(C(CH_3)_3)_2$)Ir(CH_2CH_3)Cl] were isolated and characterized by ^{1}H NMR. The transformation of these complexes into usable water oxidation catalysts is under investigation.

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LIST OF ABBREVIATIONS AND SYMBOLS

°	degree(s)
δ	Greek delta: denotes chemical shift reference scale
η	Greek eta: ligand hapticity
bpy	2,2' – bipyridine
bpm	2,2' – bipyrimidine
bpz	2,2' – bipyrazine
br	broad
C	Celsius
COD	1,5-cyclooctadiene
COE	cyclooctene
Cp^*	pentamethylcyclopentadienyl
d	doublet
DIBAL-H	diisobutylaluminum hydride
dppy	2,6-diphenylpyridine
dpyx	1,3-di(2-pyridyl)-4,6-dimethylbenzene
form	*N,N'*-di-*p*-tolyformamidinatio ion
h	hour(s)
^{i}Pr	isopropyl, $-CH(CH_3)_2$
L	general ligand, usually 2 e^- donor
M	general metal atom
m	multiplet
Me	methyl, $-CH_3$

min	minute(s)
mol	mole
mmol	millimole
NMR	nuclear magnetic resonance
p	para
Ph	phenyl, $-C_6H_5$
ppm	parts per million
ppy	2 – phenylpyridine
PTSA	*p* – toluenesulfonic acid
py	pyridine
q	quartet
R	general alkyl group
s	singlet
t	triplet
^{t}Bu	tertiary butyl, $-C(CH_3)_3$
terpy	2,2';6',2" – terpyridine
tpy	2,2';6,2" – terpyridine
X	general halogen atom

Chapter 1

Synthesis and Complexation of Bis(imino)aryl Ligands: Towards the Generation of Iridium Based Water Oxidation Catalysts.

Introduction

The continual increase in global energy consumption has driven research toward the generation of clean renewable energy sources. Investigations into harnessing natural resources such as sunlight, wind currents and geothermal heat to meet energy demands have been exhaustive. The collection of solar energy by splitting water into its elemental components, H_2 and O_2, has received international attention as an alternative to traditional fuel stocks. The development of an artificial photosynthetic system is a monumental challenge that will require the implementation of delicate techniques on a massive scale. While significant progress has been made towards water oxidation the challenge of routinely mediating four electron transfers remains. Effective water oxidation catalysts must be kinetically fast, have a potential above the requisite thermodynamic value (1.229 – 0.059 pH) as well as be stable to air, water and heat.[1]

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $\quad E_{anodic} = 1.23\ V - 0.059\ (pH)\ V\ vs\ NHE$

$4H^+ + 4e^- \rightarrow 2H_2$ $\quad E_{cathodic} = 0\ V - 0.059\ (pH)\ V\ vs\ NHE$

$2H_2O \rightarrow O_2 + 2H_2$

Figure 1.0: Oxidative and reductive half reactions of water decomposition.[2]

In nature the oxygen-evolving complex of photosystem II catalyzes water oxidation. A tetranuclear manganese cluster delivers electrons to convert metal-aquo species to metal-oxo species capable of releasing oxygen.[3] Despite studies concerning the chemical and physical properties of the oxygen-evolving complex, its structure and mechanism remain

unsolved. Simpler transition metal systems have shown promise as catalysts for water oxidation but the development of a homogenous artificial photosynthetic process remains a complex challenge.

Early attempts at developing homogeneous water oxidation catalysts were modeled after photosystem II. Though many of these complexes proved useful in gleaning information concerning the structure of the cluster, few structural analogues proved capable of oxidizing water.[4,5] Originally reported in 1986, $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3+}$, is one example of a dinuclear manganese catalyst capable of oxidizing water.[6] Failure to develop manganese systems capable of oxidizing water shifted research toward metal oxide and precious metal catalysts.

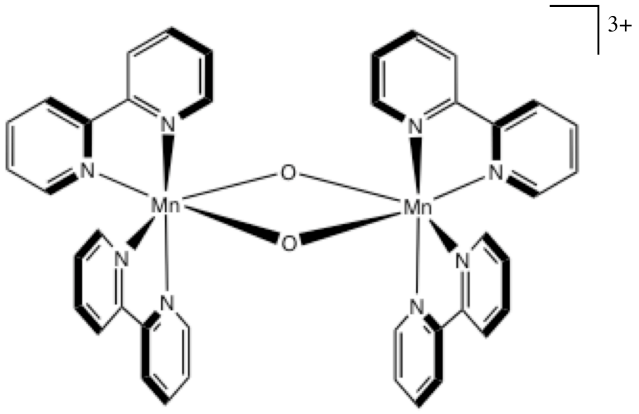


Figure 2.0: $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3+}$ reported by Kaneko *et al*.[6]

Metal oxides typically have a moderate overpotential (< 400 mV) and require concentrated basic solutions (pH > 13) where as precious metal systems require concentrated acidic conditions (pH < 1).[2] Very few catalysts operate under ambient conditions. In 1983 Brunschwig *et al* first demonstrated that Co^{2+} ions are capable of catalyzing water to oxygen

conversion in the presence of neutral phosphates using $Ru(bpy)_3^{3+}$ $E^o = 1.26$ V as a chemical oxidant.[7] In 2008 Nocera and Kanan reported an in-situ water oxidation catalyst generated from Co^{2+} ions in aqueous phosphate solution.[2] The Nocera *et al* system is formed from earth abundant metal ions, has a self repair mechanism, is a carrier for protons in neutral water and generates O_2 under ambient conditions.[2] All these features are desirable attributes for a water oxidation catalyst. More recently Yin *et al* reported a cobalt based water oxidation catalyst, $[Co_4(H_2O)_2(\alpha\text{-}PW_9O_{34})_2]^{10-}$, that is composed of a Co_4O_4 core stabilized by inorganic polyoxotungstate ($PW_9O_{34}^{9-}$) ligands. Using $[Ru(bpy)_3]^{3+}$ as a chemical oxidant, catalytic turnover frequencies for O_2 production ≥ 5 s^{-1} were observed at pH = 8.[1] These are among the highest turnover frequencies reported for heterogeneous cobalt phosphate catalysts. Analogous to Nocera's system, the one pot equilibrium synthesis of $[Co_4(H_2O)_2(\alpha\text{-}PW_9O_{34})_2]^{10-}$ defines a mechanism of self repair.[8]

Initial work by the Meyer and Gratzel groups in the 1980's led to the hypothesis that higher ordered structures were required to achieve water oxidation. In 1982 Meyer *et al* reported the ruthenium blue dimer, a dinuclear oxo-bridged ruthenium catalyst (cis, cis-$[(bpy)_2(H_2O)Ru^{III}ORu^{III}(OH_2)(bpy)_2]^{4+}$) capable of oxidizing water.[9]

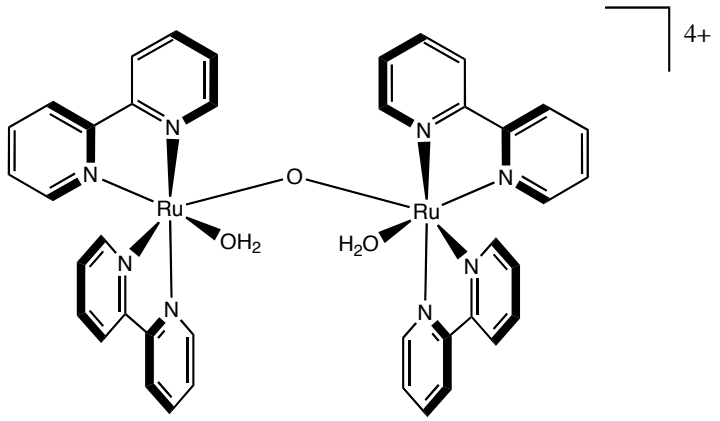


Figure 3.0: cis – $[(bpy)_2(H_2O)Ru^{III}ORu^{III}(OH_2)(bpy)_2]^{4+}$ synthesized by Meyer *et al*.[9]

In 1986 Gratzel *et al* were also successful at catalyzing water oxidation with dinuclear oxo-bridged ruthenium catalysts derived from ruthenium diaqua bis(2,2'-bipyridyl-5,5'-dicarboxylicacid).[10]

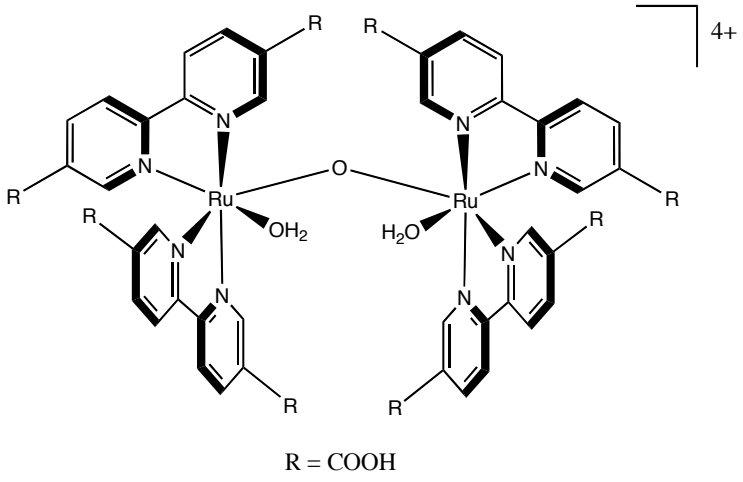


Figure 4.0: Dinuclear oxo-bridged ruthenium dimer from Gratzel *et al*.[10]

In 2005, Thummel *et al* reported a dinuclear chloro-bridged ruthenium water oxidation catalyst with a rate equal to 7.7 (turnover/s x 10^4).[11]

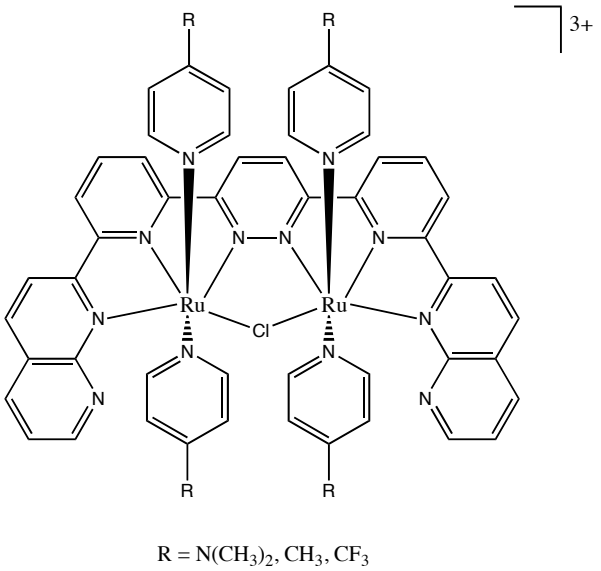


Figure 5.0: Dinuclear chloro-bridged ruthenium dimer from Thummel *et al*.[11]

In 2009 Kohl *et al* reported a new water oxidation system that uses both light and heat to oxidize water.[12,13]. Reaction of a Ru(II) hydrido-hydroxo complex with water at 100^{o}C liberates H_2. Irradiation of the resulting cis-dihydroxo Ru(II) intermediate produces dioxygen and regenerates the catalytic species.[12] Although the Kohl *et al* system provides a complete cycle for the generation of dihydrogen and dioxygen, it is plagued with problems. The Kohl *et al* system is one of the first examples of mononuclear catalyst capable of oxidizing water.

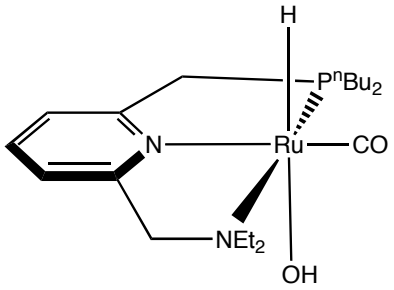
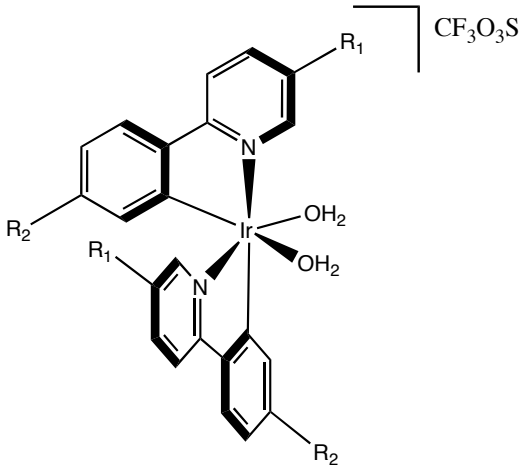


Figure 6.0: Ru(II) hydrido-hydroxide complex generated by Kohl *et al*.[12]

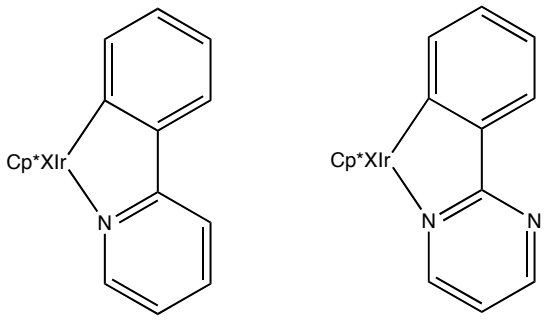
Several other groups have also demonstrated that mononuclear arrangements are sufficient to decompose water. Work from the Bernhard *et al* in 2008 has established mononuclear cyclometalated Ir(III) complexes as simple, robust and highly tunable catalysts for water oxidation.[14]



$R_1 = H, R_2 = H$
$R_1 = CH_3, R_2 = H$
$R_1 = CH_3, R_2 = Ph$
$R_1 = CH_3, R_2 = F$
$R_1 = CH_3, R_2 = Cl$

Figure 7.0: $[Ir(ppy)_2(OH_2)_2]^+$ reported by Bernhard *et al*.[14]

Crabtree *et al* have synthesized some of the most active mononuclear Ir(III) water oxidation catalysts to date. The activities are an order of magnitude greater than those previously reported.[15]



X = Cl, OTf X = Cl

Figure 8.0: $[(Cp^*)Ir(OH_2)(ppy)]^+$ synthesized by Crabtree *et al*.[15]

The Thummel group has also started to explore simple mononuclear ruthenium catalysts for understanding and optimizing water oxidation catalytic systems.[16]

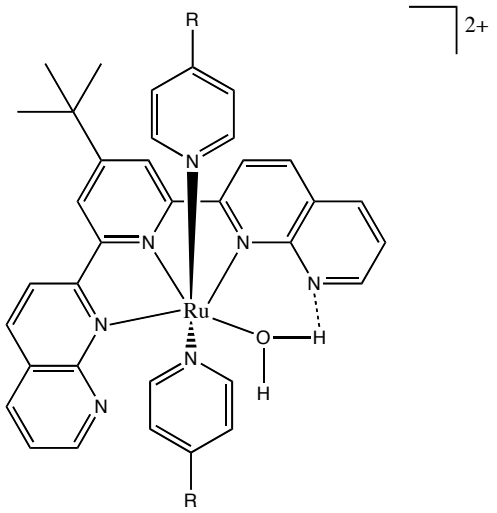
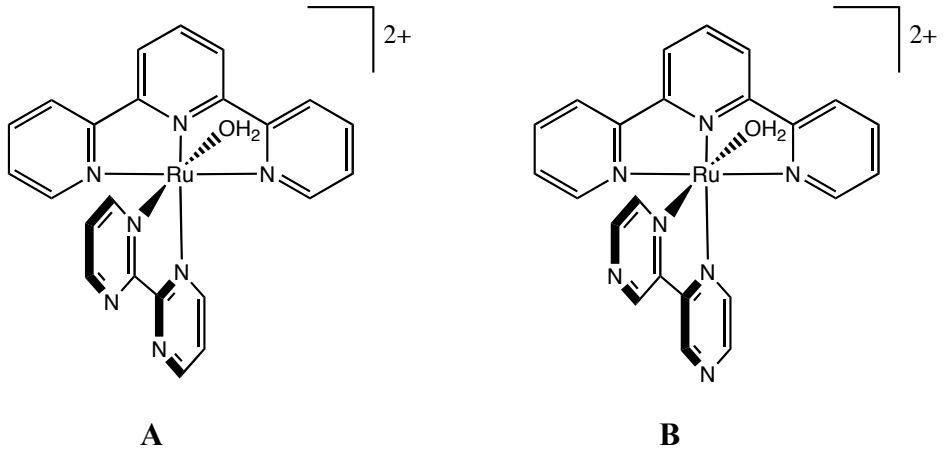


Figure 9.0: Mononuclear Ru(II) catalysts generated by Thummel *et al*.[16]

In 2008 Meyer *et al* reported that the mononuclear complexes, $[Ru(tpy)(bpm)(OH_2)]^{2+}$ and $[Ru(typ)(bpz)(OH_2)]^{2+}$, oxidize water by a well defined mechanism involving Ru(V) intermediates.[17]



A **B**

Figure 10.0: Mononuclear Ru(II) catalysts, (**A**) $[Ru(tpy)(bpm)(OH_2)]^{2+}$ and (**B**) $[Ru(typ)(bpz)(OH_2)]^{2+}$ synthesized by Meyer *et al*.[17]

Continued development of mononuclear water oxidation catalysts is desirable. Mononuclear catalysts support sturdier ligand frameworks, are more robust and leave more than one site open for catalysis. The Ru(II) system developed by Meyer *et al*[17] employs one open coordination site where as the mononuclear Ir(III) system developed by Bernhard *et al*[14] has two cis- coordination sites available for water oxidation. The mononuclear Ir(III) catalysts developed by Crabtree *et al*[15] exploit a single site for water oxidation. Since these systems differ in metal, oxidation state, charge, and ligand framework it is difficult to infer any conclusion on the activity of the catalyst and the number of open coordination sites. It is our intention to use a tridentate pincer ligand environment to systematically vary the number the open coordination sites in a d^6 Ir(III) catalyst. This would provide a basis for comparison between the activity of the catalyst and the number of open coordination sites. Since the mechanism of water oxidation continues to be disputed it is also our intention to isolate and explore potential intermediates. Few examples of terminal oxo-complexes of late high valent transition metals exist. Hill *et al* were successful in isolating Pt(IV)[18] and Pd(IV)[19] oxo-complexes using a π-accepting polytungstate ligand. In 2008 Milstein *et al* provided the first example of a d^6 metal-oxo complex bearing a pincer ligand.[20] Isolation of such a species would be an exciting opportunity to explore the reactivity of the metal-oxo bond.

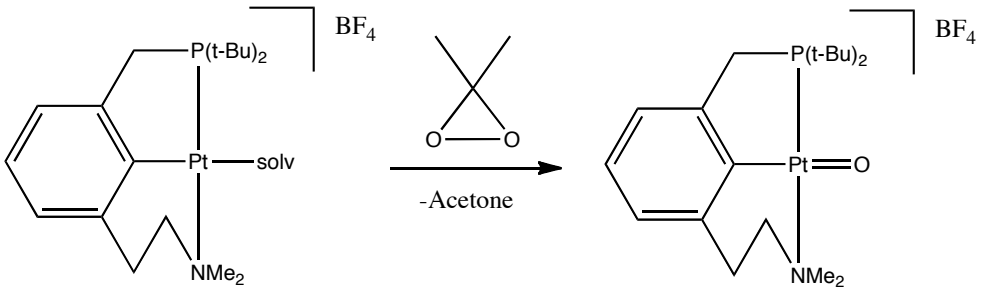


Figure 11.0: Terminal Pt(IV)-oxo complex synthesized by Milstein *et al*.[20]

Results and Discussion

Attempted metalation of C^N^C pincer ligands.

First developed by Moulton and Shaw, organometallic pincer complexes have grown in number and importance over the past thirty years.[21] The synthesis of pincer complexes is achieved through the coordination of two neutral donor atoms and the activation of a central carbon hydrogen bond. Pincer complexes have a robust ligand backbone that dictates a meridional coordination mode and promotes an octahedral geometry. The steric and electronic properties of pincer ligands can be fine tuned by modifying the donor atoms and the corresponding substituents. Pincer complexes catalyze a wide variety of reactions including the dehydrogenation of alkanes[22], Suzuki-Miyaura couplings[23], Heck reactions[24,25,26], hydrogen transfer reaction[27,28], aldol condensations[29] and asymmetric allylic alkylations.[30]

Pincer complexes of monoanionic N^C^N[31,32], P^C^P[33,34], S^C^S[35] or C^N^N[36] tridentate ligands are well known. Only a few *C,C*-trans bis-cyclometalation dianionic pincer complexes have been reported. Examples include Pt(II) and Pd(II) complexes with C^P^C[37] and C^N^C[38,39,40] ligands. Our goal is to generate cyclometalated Ir(III) complexes with 2,6-

diphenylpyridine. Previous work has established the synthesis of chloro-bridged Ir(III) dimers from the reaction of $IrCl_3 \cdot 3H_2O$ and various ligand frameworks.[41,42,43,44,45,46,47] Reaction of 2,6-diphenylpyridine with $IrCl_3 \cdot 3H_2O$ in a weakly coordinating solvent should offer access to a dinuclear Ir(III) complex with two bridging chlorides. Abstraction of the chloride bridges should open up the remaining two coordination sites for catalysis. A two site Ir(III) catalyst will be imitated using the pincer ligand and a neutral monodentate ligand. The parent pincer ligand and a neutral bidentate ligand should offer access to a single site catalyst.

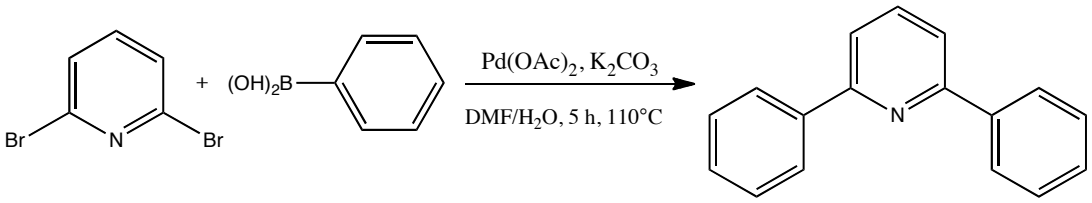
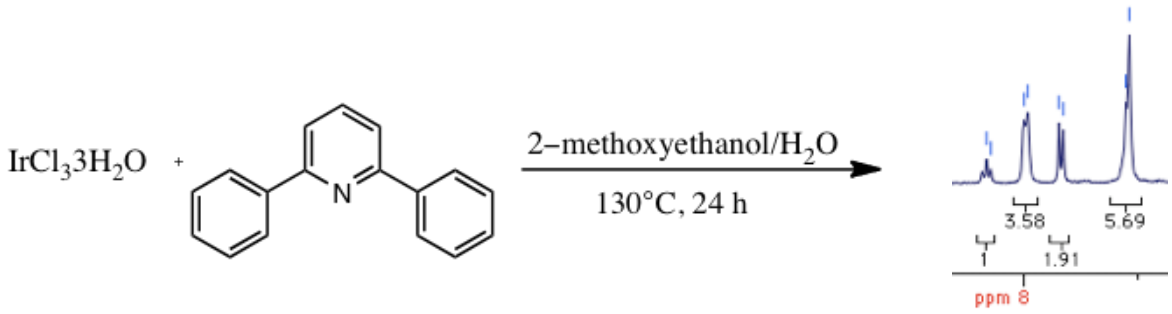


Figure 12.0: Reported synthesis of 2,6-diphenylpyridine.[48]

Commonly cyclometalation reactions employing $IrCl_3 \cdot 3H_2O$ as a starting material use polar high boiling solvents such as 2-methoxyethanol or 2-ethoxyethanol in combination with water. The C-H activation is monitored by ^1H NMR. 2,6-diphenylpyridine was synthesized via a Miyaura & Suzuki coupling.[48] No cyclometalated product was observed upon reaction of one equivalent of 2,6-diphenylpyridine with one equivalent of $IrCl_3 \cdot 3H_2O$ in refluxing 2-methoxyethanol/water.



Scheme 1.0: Attempted metalation of 2,6 – diphenylpyridine.

Instead a simple Lewis acid Lewis base adduct was observed upon evaporation of the solvent and extraction with acetone. The ^{1}H NMR of the product accounts for all thirteen protons of 2,6-diphenylpyridine but the chemical shifts differ from that of the starting material. The contrasting chemical shifts reflect coordination to the metal center through the postulated Ir(III)-N bond. Addition of excess triethylamine to one equivalent of $IrCl_3 \cdot 3H_2O$ and one equivalent of 2,6-diphenylpyridine in refluxing 2-methoxyethanol/water, to facilitate proton abstraction, was also unsuccessful. Addition of two equivalents of Ag(OTf), to extract a chloride from $IrCl_3 \cdot 3H_2O$ yielded only unreacted starting material. Using more forcing conditions, heating one equivalent of 2,6-diphenylpyridine with one equivalent of $IrCl_3 \cdot 3H_2O$ in ethylene glycol at 160^{o}C for 5 hours, returned only starting materials.

Williams *et al* reported similar problems with the preparation of a neutral octahedral Ir(III) complex bearing 1,3-di(2-pyridyl)-4,6-dimethylbenzene and 2,6-diphenylpyridine.[43] The use of forcing conditions was found to be unsuccessful. The *C,C*-trans bis-cyclometalation of 2,6-diphenylpyridine was finally achieved by heating $[Ir(1,3\text{-di}(2\text{-pyridyl})\text{-}4,6\text{-dimethylbenzene})Cl]_2$ with silver triflate in molten 2,6-diphenylpyridine at

110°C. From this work, a harsh solvent free procedure was adapted to force the cyclometalation of 2,6-diphenylpyridine. In an analogous fashion heating one equivalent of 2,6-diphenylpyridine (mp = 78°C) with one equivalent of $IrCl_3 \cdot 3H_2O$ at 130°C inside of a sealed schlenk tube resulted in no reaction. However, heating one equivalent of 2,6-diphenyl pyridine and one equivalent of $IrCl_3 \cdot 3H_2O$ in a 0.5 ml aliquot of water at 120°C for 72 hours in a sealed Schlenk tube resulted in the appearance of a new set of aryl resonances.

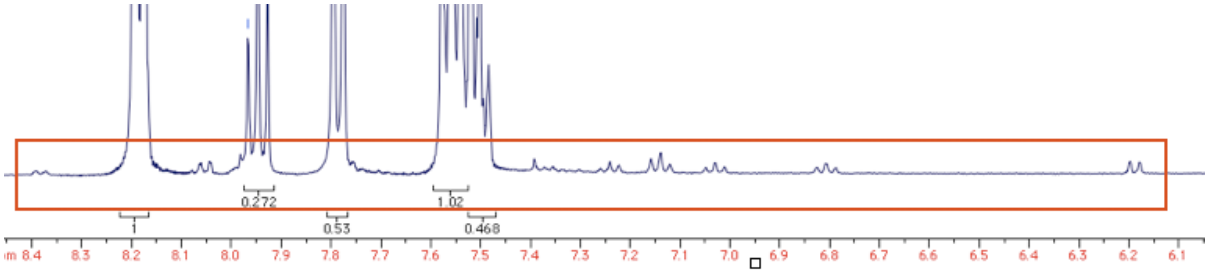


Figure 13.0: ^{1}H NMR of *C,C*-trans bis-cyclometalation of 2,6-diphenylpyridine.

Although the resulting ^{1}H NMR is dominated by starting material (~99%) the presence of a new set of peaks spanning 6.2 ppm – 8.4 ppm is the only indication of cyclometalation of 2,6-dipehnylpyridine using $IrCl_3 \cdot 3H_2O$ as a starting material. The new aryl resonances could not be assigned with certainty, and no conclusion to whether they result from C-H activation or a decomposition reaction could be gleaned. The uncertainty surrounding the results of this experiment did not justify continuing to pursue the cyclometalation of 2,6-dipheneylpyridine using $IrCl_3 \cdot 3H_2O$ as a starting material.

Although rarely reported for preparing *C,C*-trans bis-cyclometalation complexes, $[Ir(COD)Cl]_2$, $[Ir(COE)_2Cl]_2$ and $[Ir(C_2H_4)_2Cl]_2$ have been utilized in the activation of

monoanionic pincer ligands. Reacting μ-dichloro-bridged Ir(I) dimers with a monoanionic pincer ligand produces five coordinate Ir(III) hydrido-chlorides. Reaction of two equivalents of 2,6-diphenylpyridine with one equivalent of $[Ir(COD)Cl]_2$ in refluxing toluene produced no observable change in the ^1H NMR. Reaction of two equivalents of 2,6-diphenylpyridine with one equivalent of $[Ir(COE)_2Cl]_2$ in refluxing toluene also returned starting material. Additionally a mixture of one equivalent of $[Ir(C_2H_4)_2Cl]_2$ with two equivalents of 2,6-diphenylpyridine in $CDCl_3$ at room temperature resulted in decomposition of the Ir(I) starting material.

Several reports have detailed the difficulties surrounding the formation of *C,C*-trans bis-cyclometalated complexes. In 1992 Crabtree *et al* reported the reaction of 2,6-diarylpyridine ligands with $[Ir(COD)(PR_3)_2]X$ in the presence of H_2.[49] Instead of the expected double ortho metalation, the 2,6-diarylpyridine ligands cyclometalate once to form complexes with aryl M-C and agostic M-H bonds. In solution, the agostic and metalated phenyl groups interconvert rapidly at room temperature. It is peculiar that the second phenyl ring is close enough to the metal center to bond in an agostic fashion but does not oxidatively add.

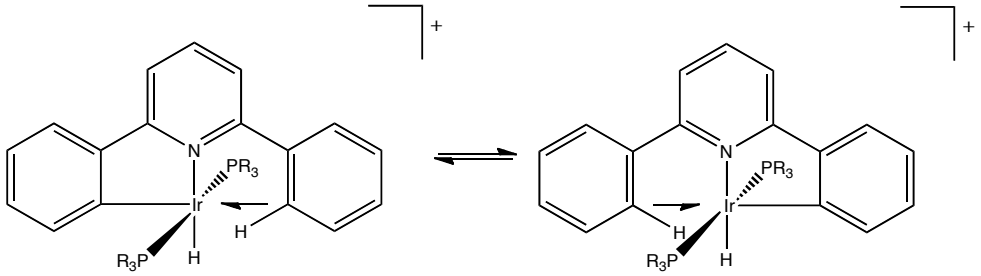


Figure 14.0: Reversible metalation of $[Ir(diphpyH)H\{P(p\text{-}C_6H_4CH_3)_3\}_2]SbF_6$.[49]

Two explanations have been presented to justify this observation: steric inhibition in the approach of the second phenyl ring and polycyclic ring strain.[50,51] Other examples of Pd and Pt cyclometalated complexes with C^N^C and N^C^C ligands undercut the argument that the approach of the second phenyl ring is sterically hindered. Secondly the crystal structure of [Pd(terpy)Cl]Cl shows no significant ring strain. It is not expected that 2,6-diphenylpyridine would produce any unfavorable ring strain. Reactions of $[Ir(COD)(PR_3)_2]X$ with H_2 and 7,8-benzoquinoline activate the aromatic C-H bond of 7,8-benzoquinoline to give a η^2-H_2 complex.[49] The iridium center is not basic enough to break the H-H bond of the coordinated H_2. Similarly it is not expected to break the C-H bond of the second phenyl ring of 2,6-diphenylpyridine.

In 2004 Williams *et al* reported luminescence of the cyclometalated Ir(III) complex [Ir(dpyx)(dppy)].[42] Photodissociation of a trans Ir-C bond of 2,6-diphenylpyridine is observed after prolonged irradiation.

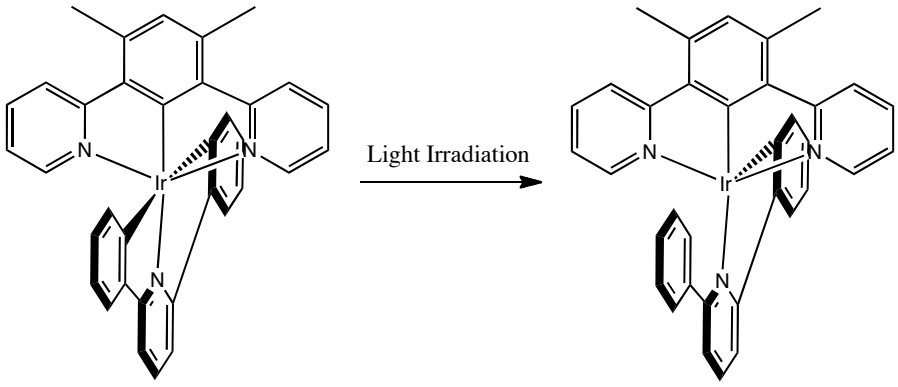


Figure 15.0: Photodissociation of [Ir(dpyx)(dppy)] as reported by Williams *et al*.[42]

A similar process is observed for *mer*-[Ir(ppy)$_3$] where one of the trans Ir-C bonds is cleaved upon irradiation of the excited state. [Ir(dpyx)(dppy)] is stable indefinitely in the solid state. The lability of the Ir-C bonds of 2,6-diphenylpryrine in solution is likely the reason that solution preparative routes have been unsuccessful in synthesizing C^N^C pincer complexes. The N^N^N structural analogue, [Ir(dppy)(tpy)]$^+$, shows no instability in solution. The presence of a third cyclometalating carbon within the coordination sphere of the metal may facilitate the decomposition process.

Presented with the evidence within these manuscripts it is not surprising that we have encountered difficulties generating a cyclometalated Ir(III) complex with 2,6-diphenylpyridine. By modifying the ligand backbone from a terdentate C^N^C ligand to a terdentate N^C^N ligand we should be able to exploit established synthetic procedures to generate cyclometalated Ir(III) water oxidation catalysts.

Synthesis of bis(imino)aryl pincer ligands.

Few reports have outlined the synthesis of bis(imino)ayrl metal complexes. Examples include Ni(II)[52], Cu(II)[53], Pt(II)[54], Mn(I)[55], Pd(II)[54], Sb(I)[56] and Bi(I)[56]. Until recently bis(imino) ayrl Ir(III) complexes proved elusive. Examples typically employ heterocyclic N-donor ligands such as benzimidazolyl[57,58], pyridyl[43] and oxazolyl[59]. A lack of reliable synthetic routes has prevented the study of non-heterocyclic bis(imino)aryl iridium complexes. Kinetically, the C-H activation of the 4- and 6- positions of the aryl backbone is preferred over the activation of the 2- position. C-H activation of the 4- and 6- positions of the aryl backbone results in the formation of bidentate C^N complexes instead of N^C^N terdentate complexes.

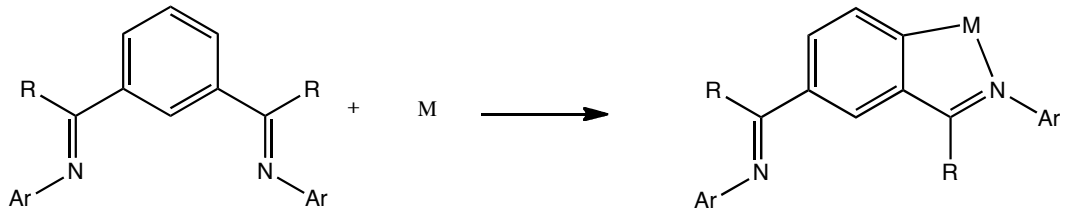
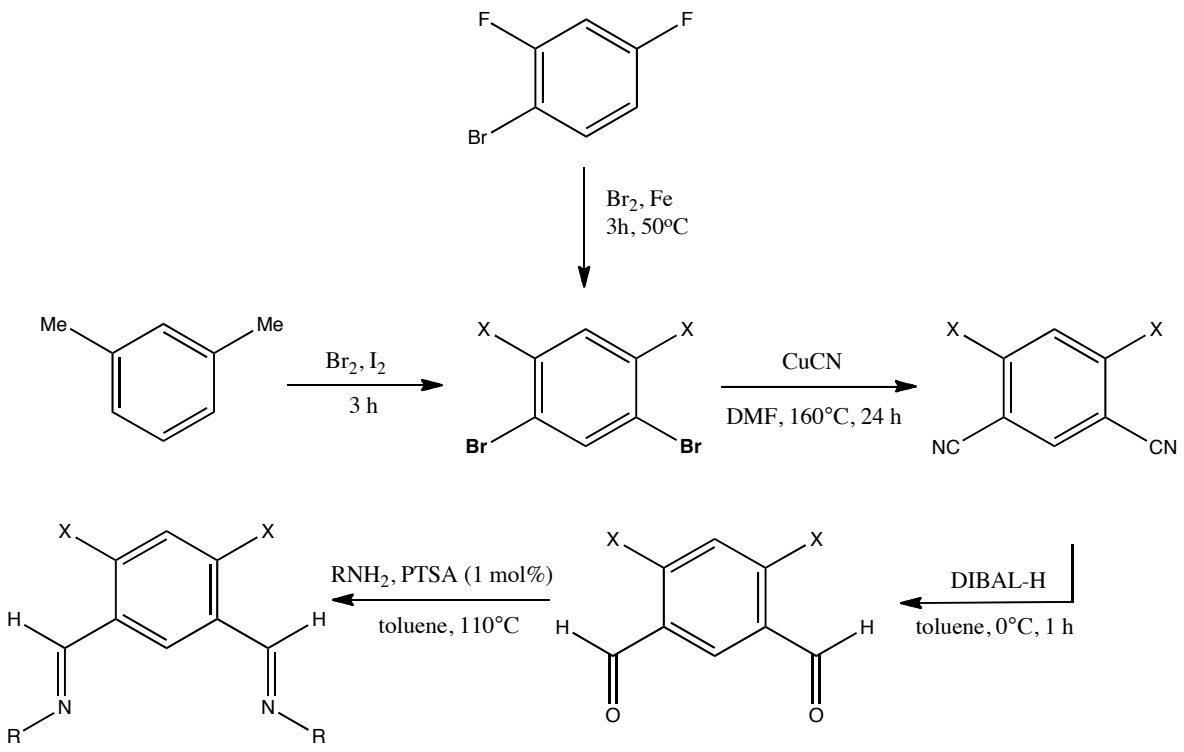


Figure 16: Bidentate chelation of bis(imino)aryl ligands.

In 2007 Arthur *et al* reported the first examples of Ir(III) N^C^N terdentate dihalide complexes containing bis(imino)aryl ligands.[32] Instead of oxidatively adding a central C-H bond, Arthur *et al* synthesized bis(imino)aryl iridium complexes through the oxidative addition of a central C-Br bond. Conversely in 2004 Williams *et al* reported that the introduction of blocking substituents in the 4- and 6- positions of the aryl backbone promotes the oxidative addition of the C-H bond in the 2- position.[43] Our study outlines the synthesis of a series of bis(imino)aryl ligands with methyl and fluoro substituents in the 4- and 6-positions of the aryl backbone.

Bromination of *m*-xylene using Br_2 as a brominating agent and I_2 as an activator generates dibromoxylene.[60] Reaction of dibromoxylene with an excess of CuCN in refluxing DMF followed by extraction into CH_2Cl_2 and purification on a silica column yields 4,6-dimethylisophthalonitrile.[61] Reduction of 4,6-dimethylisophthaladehyde with diisobutylaluminum hydride in toluene at 0^oC produces 4,6-dimethylisophthalaldehyde. Reaction of 4,6-dimethylisophthalaldehyde with two equivalents of anline and a catalytic amount of *p*-toluenesulfonic acid (1 mol%) in refluxing toluene followed by removal of the volatiles and precipitation with methanol produces the electron rich bis(imino)aryl ligands.[62]

(X = Me; R = -phenyl, -2,6-dimethylphenyl, -2,6-diisopropylphenyl, -3,5-ditertbutylphenyl, -4-tertbutylphenyl)



Scheme 2.0: N^^{X}C^{X}^N (X = Me, F) pincer ligand synthesis.

Similarly, bromination of 1-bromo-2,4-difluorobenze using Br_2 as a brominating agent and Fe as an activator yields 4,6-diflouroisophthalaldehyde.[63] Employing an identical series of reactions used to produce 4,6-dimethylisophthalonitrile and 4,6-dimethylisophthalaldehyde yields 4,6-difluoroisophthalonitrile and 4,6-difluoroisophthalaldehyde respectively. The desired electron poor bis(imino)aryl ligand (X = F; R = -2,6-diisopropylphenyl) were synthesized by condensing 4,6-difluoroisophthalaldehyde with the apt aniline and a catalytic amount of *p*-toluenesulfonic acid (1 mol%) in refluxing toluene.[64]

Metalation of bis(imino)aryl ligands

Williams *et al* synthesized μ-dichloro-bridged Ir(III) dimers by reacting $IrCl_3 \cdot 3H_2O$ with 1,3-di(2-pyridyl)-4,6-dimethylbenzene in 2-ethoxyethanol at 80°C for three days.[42]

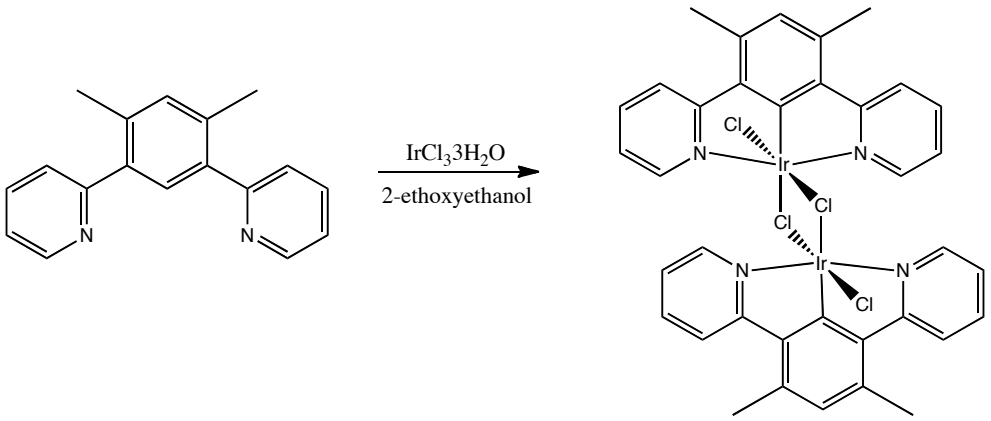
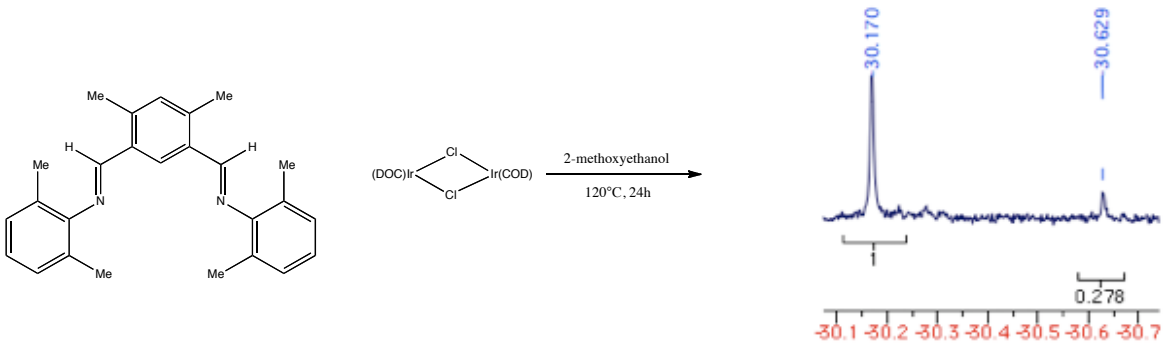


Figure 17.0: Reported synthesis of μ-dichloro-bridged Ir(III) dimers by Williams *et al*.[42]

The reaction of one equivalent of $[4,6\text{-}(CH_3)_2C_6H_2\text{-}1,3\text{-}(CHNC_6H_3\text{-}2,6\text{-}(CH_3)_2)_2]$ with one equivalent of $IrCl_3 \cdot 3H_2O$ in 2-methoxyethanol at 80°C for three days resulted in significant changes in the ^1H NMR spectrum. The proton in the 2- position of $[4,6\text{-}(CH_3)_2C_6H_2\text{-}1,3\text{-}(CHNC_6H_3\text{-}2,6\text{-}(CH_3)_2)_2]$ in no longer present in the ^1H NMR, a strong suggestion of cyclometalation. Likewise the signals of the imino protons and the proton in the 5- position have shifted. Similar results were observed for the reaction of one equivalent of $[4,6\text{-}(CH_3)_2C_6H_2\text{-}1,3\text{-}(CHNC_6H_3\text{-}2,6\text{-}(CH(CH_3)_2)_2)_2]$ with one equivalent of $IrCl_3 \cdot 3H_2O$ in 2-methoxyethanol at 80°C for three days. All efforts to purify the resulting products using column chromatography and recrystallization were unsuccessful. $IrCl_3 \cdot 3H_2O$ was abandoned

as a starting precursor. Instead $[Ir(COD)Cl]_2$, $[Ir(COE)_2Cl]$ and $[Ir(C_2H_4)_2Cl]_2$ were employed as Ir(I) starting materials.

$[Ir(COD)Cl]_2$, $[Ir(COE)_2Cl]_2$ and $[Ir(C_2H_4)_2Cl]_2$ are well known Ir(I) starting materials used to generate Ir(III) pincer complexes. Reacting one equivalent of $[Ir(COD)Cl]_2$ with two equivalents of $[4,6\text{-}(CH_3)_2C_6H_2\text{-}1,3\text{-}(CHNC_6H_3\text{-}2,6\text{-}(CH_3)_2)_2]$ in $CDCl_3$ at room temperature for 24 hours failed to metalate the ligand. Likewise reacting two equivalents of $[4,6\text{-}(CH_3)_2C_6H_2\text{-}1,3\text{-}(CHNC_6H_3\text{-}2,6\text{-}(CH_3)_2)_2]$ and one equivalent of $[Ir(COD)Cl]_2$ in refluxing toluene for 24 hours resulted in no reaction. Heating one equivalent of $[Ir(COD)Cl]_2$ and two equivalents of $[4,6\text{-}(CH_3)_2C_6H_2\text{-}1,3\text{-}(CHNC_6H_3\text{-}2,6\text{-}(CH_3)_2)_2]$ in 2-ethoxyethanol at 120°C for 24 hours generated an Ir(III) hydride as evidenced by ^1H NMR.



Scheme 3.0: Synthesis of Ir(III)N^C^N hydride.

The proton in the 2- position of $[4,6\text{-}(CH_3)_2C_6H_2\text{-}1,3\text{-}(CHNC_6H_3\text{-}2,6\text{-}(CH_3)_2)_2]$ at $\delta = 8.59$ ppm no longer integrates for a 2:1 ratio with the imino protons at $\delta = 8.55$ ppm. Since complete activation of the ligand would result in the full loss of the signal at $\delta = 8.59$ ppm, these results imply lingering starting material in the reaction mixture. The diminished

intensity of the signal at δ = 8.59 ppm along with the new signal at δ = –30.16 ppm strongly insinuates C-H activation at the 2- position of [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH_3)_2)_2$]. All efforts to purify the newly formed Ir(III) hydride using column chromatography were unsuccessful. Reacting one equivalent of $[Ir(COD)Cl]_2$ with two equivalents of [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$] yielded only unreacted starting materials. It is likely that the isopropyl groups of [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$] hinder C-H activation at the 2- position. In this case more reactive Ir(I) starting materials such as $[Ir(COE)_2Cl]_2$ and $[Ir(C_2H_4)_2Cl]_2$ may be more effective in generating Ir(III) hydrides.

Reacting one equivalent of $[Ir(COE)_2Cl]_2$ with two equivalents of [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_5)_2$] in toluene at 90°C overnight resulted in several prominent changes in the ^{1}H NMR. The signal for the proton in the 2- position of [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_5)_2$] is no longer present. This is a strong indication of C-H activation at the 2- position. The emergence of signals at δ = -20.88 ppm, δ = -21.13 ppm, δ = -27.19 ppm and δ = -29.85 ppm are indicative of a mixture of six coordinate (δ = -20.88 ppm and δ = -21.13 ppm) and five coordinate (δ = -27.19 ppm and δ = -29.85) Ir(III) hydrides. Ligands that lack steric bulk have no means to impede the formation of chloro- bridged dimers. Dimer formation between two five coordinate Ir(III) hydrides would explain the downfield shift from δ = ~30 ppm to δ = ~20 ppm. None of the hydrides in the ^{1}H NMR could be precisely assigned as all efforts to isolate them by means of column chromatography or recrystallization failed. Reacting one equivalent of $[Ir(COE)_2Cl]_2$ with two equivalents of the slightly bulkier ligand, [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH_3)_2)_2$], in toluene at 90°C for 24 hours generated two Ir(III) hydrides. The species at δ = -30.15 ppm is twice as prevalent than the species at δ = -

31.52 ppm. The proton in the 2- position of [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH_3)_2)_2$] at δ = 8.44 ppm is completely consumed. The ^{1}H NMR of the product also reveals three methyl signals at δ = 2.16 ppm, δ = 2.45 ppm and δ = 2.56 ppm. Ordinarily [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH_3)_2)_2$] has two methyl signals at δ = 2.09 ppm and δ = 2.52 ppm. The signal at δ = 2.09 ppm corresponds to the four methyl groups in the 2- and 6- positions of the aryl groups. In solution free rotation of the aryl groups equates the methyl signals in the ^{1}H NMR. The other signal at δ = 2.52 ppm of free [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH_3)_2)_2$] is a result of the methyl groups in the 4- and 6- positions of the backbone. The three methyl signals in the ^{1}H NMR of the product are a result of the desymmetrization of [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH_3)_2)_2$]. Hindered rotation about the C-N bond of the Ir(III) hydride locks the aryl groups in position. As a result the methyl groups are exposed to different molecular faces. The two methyl groups pointing “up” will be non-identical to the two methyl groups pointing “down”. Symmetry relates the two methyl groups pointing “up” and also relates the two methyl groups pointing “down”. This produces the two non-equivalent methyl signals in the ^{1}H NMR. Bubbling carbon monoxide through the reaction shifts the hydride signals downfield from δ = -30.15 ppm and δ = -31.52 ppm to δ = -21.73 ppm and δ = -22.15 ppm, respectively. The change of δ = ~9.0 ppm reflects the chemical shift difference between five coordinate and six coordinate Ir(III) hydrides. The ratio between the major and minor hydrides also changes after exposure to carbon monoxide. After bubbling carbon monoxide through the reaction the ratio between the two species changes to 5:1 (δ = -21.73 ppm: δ = -22.15 ppm). None of the resulting structures could be elucidated from the ^{1}H NMR, as all attempts to purify and isolate the Ir(III) hydrides failed.

Heating one equivalent $[Ir(COE)_2Cl]_2$ with two equivalents of $[4,6\text{-}(CH_3)_2C_6H_2\text{-}1,3\text{-}(CHNC_6H_3\text{-}2,6\text{-}(CH(CH_3)_2)_2)_2]$ in toluene at 85°C for 24 hours followed by removal of the solvent in *vacuo* yielded a red residue with two prominent hydride signals at δ = -30.40 ppm and δ = -32.02 ppm. The ratio between the two signals is measured as 1.7:1 (δ = -30.40 ppm: δ = -32.02 ppm). All attempts to purify the residue on a silica column led to decomposition. Following removal of the solvent, treatment of the residue with cold pentanes precipitated a red powder. The two prominent hydride signals at δ = -30.42 ppm and δ = -31.98 ppm are present in the ^1H NMR of the powder. The ratio between the two signals is now 4.5:1 (δ = -30.42 ppm: δ = -31.98 ppm). Recrystallization of the powder from dichloromethane and pentanes yielded red crystals. After washing the crystals with cold pentanes and drying in *vacuo*, the ^1H NMR once again revealed two hydride signals at δ = -30.49 ppm and δ = -31.96 ppm.

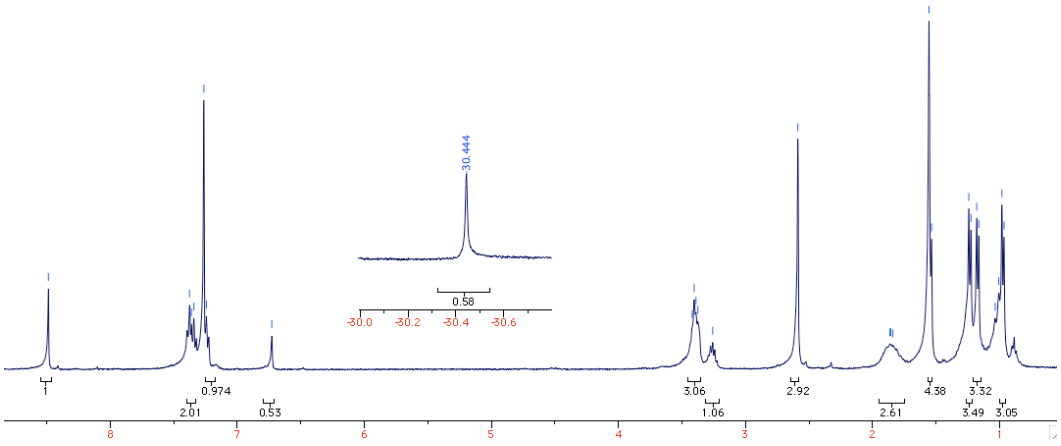
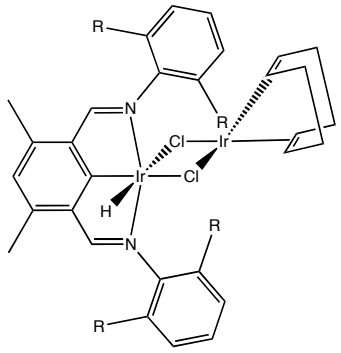


Figure 18: ^1H NMR spectrum of $[(4,6\text{-}(CH_3)_2C_6H\text{-}1,3\text{-}(CHNC_6H_3\text{-}2,6\text{-}(CH(CH_3)_2)_2)_2)IrH\text{-}\mu\text{-}Cl_2\text{-}Ir(C_8H_{12})]$

The species at δ = -30.49 ppm is now sixteen fold more prevalent than the species at δ = -31.96 ppm. The ^{1}H NMR of the red crystals revealed that the proton in the 2- position of [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$] at δ = 8.57 ppm is no longer present. The signal at δ = 7.14 ppm which is representative of the proton in the 5- position of [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$] is shifted upfield to δ = 6.76 ppm. Both transformations are suggestive of metalation at the 2-position. The product also possesses sterically rigid aryl groups. In solution the ^{1}H NMR of free [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$] has a doublet at δ = 1.17 ppm is representative of the eight methyl groups of the isopropyl substituents. The ^{1}H NMR of free [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$] also has a multiplet at δ = 2.99 ppm which integrates for 4 protons. The multiplet is illustrative of the four methine protons of the isopropyl substituents. Free rotation about the N-C bond between the imino nitrogen and the aryl substituents equates the isopropyl groups. The rigid positioning of the aryl groups in the product destroys the parity between the isopropyl groups. Instead of one multiplet at δ = 2.99 ppm for the methine protons, the ^{1}H NMR of the product contains two multiplets at δ = 3.30 ppm and δ = 3.43 ppm. The two multiplets are representative of the two nonequivalent "up" and "down" sets of methine protons. Equally the doublet at δ = 1.17 ppm in free [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$] is split into four signals. The "up" and "down" faces of the Ir(III) hydride directionally distinguish between the methyl groups of the isopropyl substituents. The methyl groups of each isopropyl substituent are also nonequivalent. Two ambiguous signals in the ^{1}H NMR of the product make it difficult to definitively assign the complete structure of the hydride. One signal is a broad multiplet at δ = 1.89 ppm and the second is a broad multiplet at δ = 3.40 ppm that overlaps with the methine signal at δ = 3.40

ppm. Although the crystals did not diffract well enough to accurately solve a solid-state structure, an adequate amount of data was retrieved to speculate the structure of the product. The best conjecture of the total structure of the Ir(III) hydride is an asymmetrical Ir(III)-Ir(I) chloro- bridged dimer. One half of the dimer consists of the expected terdentate ligand, [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$], a hydride and two bridging chlorides. The other half of the dimer consists of two bridging chlorides and two olefinic fragments bound in an η^2- fashion. The crystal data and the ^{1}H NMR both suggest that the olefinic fragments are part of a 1,5-cyclooctadiene bound in a bidentate fashion to the Ir(I) center. This is similar to one half of the $[Ir(COD)Cl]_2$ dimer.



R = $CH(CH_3)_2$

Figure 19: Proposed structure of [(4,6-$(CH_3)_2C_6H$-1,3-$(CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$)IrH-μ-Cl_2-Ir(C_8H_{12})]

Although the mechanism is unclear and unproved, the formation of 1,5-cyclooctadiene would suggest the consecutive dehydrogenation and hydrogenation of one molecule of cyclooctene. Brookhart *et al* along with Goldman *et al* have helped establish Ir(III) pincer complexes as alkane dehydrogenation catalysts.[65] Consequently with such

literature precedent it is not unreasonable to suggest a mechanism involving the dehydrogenation of cyclooctene. It is likely that after the dehydrogenation of one molecule of cyclooctene to form 1,5-cyclooctadiene that one molecule of cyclooctene is hydrogenated to form a molecule of octane. Cationic iridium diolefin complexes such as $[Ir(COD)L_2]PF_6$, $[Ir(COD)L(py)]PF_6$, have been instituted by Crabtree *et al* to be good alkene hydrogenation catalysts.[66] Postulation of the hydrogenation of cyclooctene by a terdentate ligated Ir(III) catalyst is not irrational.

The formation of mixed valent dimers, such as the proposed Ir(III)-Ir(I), are uncommon. Cotton *et al* successfully synthesized and characterized $[(COD)Ir(\mu\text{-form})_2Ir(OCOCF_3)_2(H_2O)]$ an Ir(III)-Ir(I) mixed valent dimer containing an Ir(III)-Ir(I) dative bond.[67] The clean addition $[4,6\text{-}(CH_3)_2C_6H_2\text{-}1,3\text{-}(CHNC_6H_3\text{-}2,6\text{-}(CH(CH_3)_2)_2)_2]$ to $[Ir(COE)_2Cl]_2$ to generate an Ir(III)-Ir(I) dimer is an encouraging result. Using the Ir(III)-Ir(I) dimer as a starting material, it is conceivable to oxidatively add a second equivalent of ligand to the Ir(I) fragment forming a symmetrical Ir(III)-Ir(III) chloro- bridged dimer. The Ir(III)-Ir(I) mixed valent dimer should also be a promising starting point to directly generate an Ir(III) hydrido chloride monomer. Abstraction of the bridging chlorides followed by trapping of the Ir(III) intermediate would yield a five coordinate Ir(III) species and an Ir(I) species that would be predisposed to decompose in solution. Starting with the mixed valent Ir(III)-Ir(I) and reacting it with one equivalent of $[4,6\text{-}(CH_3)_2C_6H_2\text{-}1,3\text{-}(CHNC_6H_3\text{-}2,6\text{-}(CH(CH_3)_2)_2)_2]$ in toluene at 80^oC for 24 hours resulted in no reaction. It is not surprising that $[4,6\text{-}(CH_3)_2C_6H_2\text{-}1,3\text{-}(CHNC_6H_3\text{-}2,6\text{-}(CH(CH_3)_2)_2)_2]$ does not displace the 1,5-cyclooctadiene fragment. The reaction of two equivalents of $[4,6\text{-}(CH_3)_2C_6H_2\text{-}1,3\text{-}(CHNC_6H_3\text{-}2,6\text{-}(CH(CH_3)_2)_2)_2]$ with one equivalent of $[Ir(COD)Cl]_2$ in toluene at 90^oC also

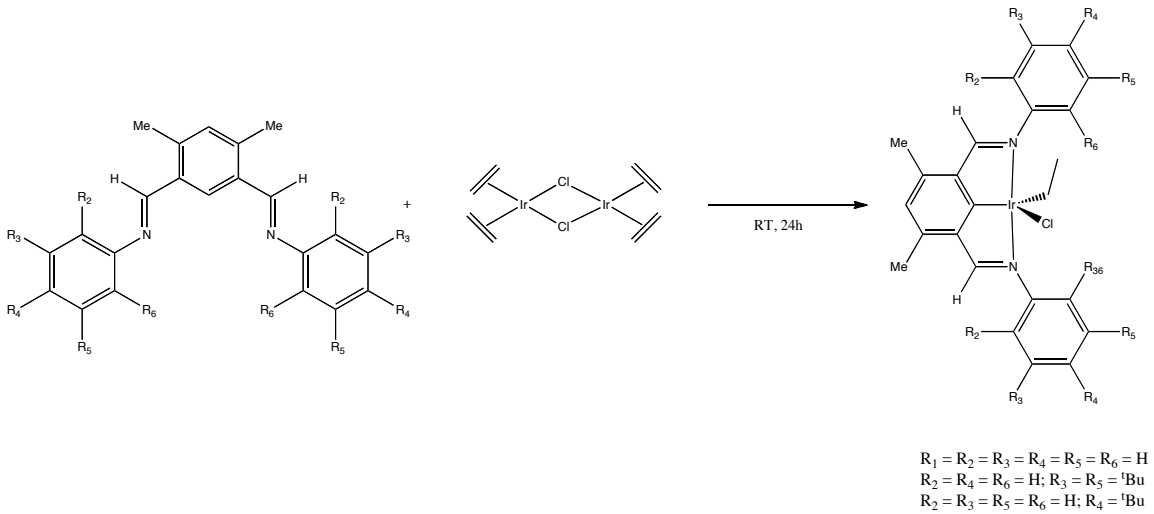
resulted in no reaction. A solution of the mixed valent Ir(III)-Ir(I) dimer and two equivalents of NaO^{t}Bu was treated with ethylene for 30 minutes at room temperature. The ^{1}H NMR in C_6D_6 revealed a new signal at δ = 4.58 ppm suggesting the coordination of ethylene to the metal center. The remaining peaks assigned to [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$] remain unchanged. The hydride signals have shifted from δ = -30.49 ppm and δ = -31.96 ppm to at δ = -25.98 ppm and δ = -29.75 ppm, respectively. The shift in the hydride signals is suggestive of a change in coordination environment of the metal. In general the persistence of a hydride signal is surprising. While [Na^+] is expected to abstract the chlorides, the residual [$^-$O^{t}Bu] is expected to deprotonate the Ir(III)-H and generate a four coordinate Ir(I) ethylene species. From the ^{1}H NMR it is difficult to conclude the precise structure of the complex. It is possible that the dimer decomposed to form the Ir(III) ethylene hydrido chloride or that ethylene was incorporated into the Ir(I) fragment with no further transformation. Further investigation into this reaction is needed to explicitly detail the product.

Reacting two equivalents of [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-3,5-$(C(CH_3)_3)_2)_2$] with one equivalent of $[Ir(COE)_2Cl]_2$ in toluene at 90^{o}C results in the formation of five new metal hydride signals at δ = -21.08 ppm, δ = -21.36 ppm, δ = -21.64 ppm, δ = -21.90 ppm and δ = -30.08 ppm. Both of the signals at δ = -21.36 ppm and δ = -21.64 ppm integrate equally and are one-third the intensity of the signal at δ = -30.08 ppm. The signals at δ = -21.08 ppm and δ = -21.90 ppm integrate equally and are one half the intensity of the signal at δ = -30.08 ppm. No other constructive information could be gleaned from the remainder of the ^{1}H NMR spectrum. Treatment of the product with carbon monoxide collapsed the five hydride signals into one signal at δ = -21.88 ppm. This change is indicative of the formation of a new six

coordinate hydride complex. Again no new information could be gleaned from the rest of the ^{1}H NMR. Repeating the reaction in toluene-d_8 at 90^{o}C produced two metal hydride signals at δ = -21.02 ppm and δ = -29.36 ppm that integrate 1.5:1 (δ = -21.02 ppm: δ = -29.36 ppm).

Reacting two equivalents of [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-4-$C(CH_3)_3)_2$] with one equivalent of $[Ir(COE)_2Cl]_2$ in toluene at 90^{o}C results in the formation of two new hydride signals at δ = -20.82 ppm and δ = -29.17 ppm. The two product hydrides integrate equally. The remainder of the ^{1}H NMR is too convoluted to glean any new information concerning the structure of the metal-hydride products. $[Ir(COE)_2Cl]_2$ was abandoned in favor of $[Ir(C_2H_4)_2Cl]_2$ as a starting material.

Reacting two equivalents of [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_5)_2$] with one equivalent of $[Ir(C_2H_4)_2Cl]_2$ in toluene-d_8 at room temperature generates a clean Ir(III) ethyl chloride complex. The proton in the 2- position of [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_5)_2$] at δ = 7.11 ppm is no longer present in the ^{1}H NMR of the product. Additionally the proton in the 5- position of [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_5)_2$] at δ = 8.61 ppm has shifted upfield to δ = 6.40 ppm. The ^{1}H NMR also reveals a new triplet at δ = 0.326 ppm that integrates for three protons and a new quartet at δ = 1.16 ppm that integrates for two protons. These signals are characteristic of an ethyl fragment.



Scheme 4.0: Synthesis of five coordinate Ir(III) ethyl chlorides.

Attempts to form the β-hydrogen elimination product, the Ir(III) ethylene hydride, were unsuccessful. In all cases AgOTf was added to a mixture of the Ir(III) ethylene hydride in C_6D_6 and stirred at room temperature for 24 hours. The peaks in ^{1}H NMR were too broad to differentiate between starting material and product.

Reacting two equivalents of [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH_3)_2)_2$] with one equivalent of $[Ir(C_2H_4)_2Cl]_2$ in toluene-d_8 at room temperature generates an Ir(III) ethyl chloride complex. The ^{1}H NMR reveals the disappearance of the proton in the 2- position of [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH_3)_2)_2$] and the upfield shift of the proton in the 5-position to δ = 6.38 ppm. The unique methyl signals in the ^{1}H NMR at δ = 2.11 ppm and δ = 2.13 ppm arise from the hindered rotation of the aryl groups. The ^{1}H NMR also reveals the triplet and quartet of the newly formed ethyl fragment. The quartet is positioned at δ = 1.55 ppm and integrates for two protons where as the triplet is situated at δ = -0.324 ppm and

integrates for three protons. The drastic upfield shift is the result of the increased shielding of the ethyl fragment by the methyl groups of [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH_3)_2)_2$].

Mixing one equivalent of [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$] with two and a half equivalents of $[Ir(C_2H_4)_2Cl]_2$ at room temperature produces a mixture of Ir(III) ethyl chlorides. An excess of $[Ir(C_2H_4)_2Cl]_2$ is required because [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$] is slower to react then less bulky bis(imino)aryl ligands. Typically $[Ir(C_2H_4)_2Cl]_2$ decomposes before complete consumption of the ligand. Using two and a half equivalents of $[Ir(C_2H_4)_2Cl]_2$ consumes all of [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$]. The proton in the 5- position is shifted up field to $\delta = 6.24$ ppm. A signal is also present at $\delta = 6.56$ ppm from a second product. The aryl groups of the product Ir(III) ethylene chloride are locked in place creating four distinct methyl groups ($\delta = 0.98$ ppm, $\delta = 1.19$ ppm, $\delta = 1.28$ ppm, $\delta = 1.63$ ppm) and 2 unique methine groups ($\delta = 2.65$ ppm, $\delta = 3.84$ ppm). 2-D NMR techniques as well as ^{1}H NMR and ^{13}C NMR were used to identify and assign the other signals of the product mixture. The methlyene group of the ethyl fragment appears as a doublet at $\delta = 1.43$ ppm. The triplet signal is positioned at $\delta = -0.23$ ppm.

Similarly reacting two equivalents of [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-3,5-$(CCH_3)_2)_2$] or two equivalents of [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-4-$(CCH_3)_2$] with one equivalent of $[Ir(C_2H_4)_2Cl]_2$ in toluene-d_8 at room temperature generates clean Ir(III) ethyl chloride complexes analogous to those previously mentioned.

Summary

A series of electron rich and electron poor bis(imino)aryl ligands have been prepared. Methyl groups and fluorine substituents were introduced in the 4- and 6- positions of the

backbone to hinder C-H activation of these positions. As a result activation of the 2- position was observed. Originally cyclometalation of the ligand was achieved from the reaction of two equivalents of [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$] with one equivalent of $[Ir(COE)_2Cl]_2$. Alternatively reaction of two equivalents of [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_5)_2$], [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-3,5-$(C(CH_3)_3)_2)_2$] or [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_4$-4-$(C(CH_3)_3)_2$] with one equivalent of $[Ir(C_2H_4)_2Cl]_2$ cleanly generated the respective Ir(III) ethyl chloride complexes. Using these complexes as starting materials, further investigation into the synthesis of water oxidation catalysts is underway. Exploration of the cyclometalation of [4,6-$(F)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$] is also intended.

Experimental

General Procedures. Unless otherwise stated all reactions were carried out under an atmosphere of dry nitrogen or argon using standard drybox and Schlenk techniques. Argon and nitrogen were purified by passage through columns of BASF R3-11 catalyst and 4 Å molecular sieves. All glassware was oven dried before use. Methylene chloride, toluene and pentanes were purified under an argon atmosphere by passage through a column of activated alumina.[68] Chloroform-d_1, methylene chloride-d_2, toluene-d_8 and benzene-d_6 were vacuum transferred from CaH_2 and degassed by several freeze-pump-thaw cycles. [1,3-$(Br)_2$-4,6-$(CH_3)_2C_6H_2$], [1,3-$(Br)_2$-4,6-$(F)_2C_6H_2$], [1,3-$(CN)_2$-4,6-$(F)_2C_6H_2$], [1,3-$(COH)_2$-4,6-$(F)_2C_6H_2$], $[Ir(COD)Cl]_2$[69] , $[Ir(COE)_2Cl]_2$[70] and $[Ir(C_2H_4)_2Cl]_2$[71] were synthesized according to published procedures. Carbon monoxide and ethylene were obtained from Matheson Gas Products, Inc. All other reagents were used as received from Sigma Aldrich, Fisher Scientific or J&J Materials Incorporated.

^{1}H NMR spectra were obtained on Bruker Avance 400 MHz or Bruker DRX 500 MHz spectrometers. ^{1}H NMR chemical shifts were referenced to the residual signals of the deuterated solvents.

[1,3-$(CN)_2$-4,6-$(CH_3)_2C_6H_2$]. 7.10 g (26.9 mmol) of [1,3-$(Br)_2$-4,6-$(CH_3)_2C_6H_2$] and 6.18 g (69.0 mmol) of CuCN were dissolved in 100 ml DMF and heated to 160^{o}C. After 24 h the solution was cooled to room temperature and 200 ml of CH_2Cl_2 and 50 ml of ice cold water were added. The aqueous layer was extracted with 2 x 50 ml of CH_2Cl_2. The organic layers were combined and washed with 8 x 50 ml of H_2O and subsequently dried with $MgSO_4$. After filtration, the solvent was removed in *vacuo*. The crude product was purified via column chromatography using a silica gel column and a mobile phase of 8:2 (methylene chloride:hexanes) to yield 0.96 g of [1,3-$(CN)_2$-4,6-$(CH_3)_2C_6H_2$]. ^{1}H NMR (δ, $CDCl_3$, 400 MHz, 298 K): 7.80 (1H, s, [1,3-$(CN)_2$-4,6-$(CH_3)_2C_6$*H_2*]); 7.23 (1H, s, [1,3-$(CN)_2$-4,6-$(CH_3)_2C_6$*H_2*]); 2.55 (6H, s, [1,3-$(CN)_2$-4,6-(CH_3)$_2C_6H_2$]).

[1,3-$(COH)_2$-4,6-$(CH_3)_2C_6H_2$]. A Schlenk flask containing 0.83 g (5.36 mmol) of [1,3-$(CN)_2$-4,6-$(CH_3)_2C_6H_2$] dissolved in 15 ml anhydrous toluene was cooled to 0^{o}C. 16.08 ml (16.08 mmol) of DIBAL-H (1 M in toluene) was added dropwise. The reaction was stirred for 1 h at 0^{o}C. 30 ml of $CHCl_3$ and 50 ml of 10 % HCl (13.5 ml of 12 M HCl in 36.5 ml of H_2O) were added. The reaction was slowly warmed to room temperature and stirred for 1 h. The aqueous layer was extracted with 2 x 20 ml of $CHCl_3$. The combined organic layers were washed with 2 x 50 ml H_2O and dried with $MgSO_4$. After filtration and removal of the solvent, the crude product was purified via column chromatography using a silica column

and a mobile phase of 9:1 (methylene chloride:hexanes) to yield 0.73 g (4.52 mmol, 84.3 %) of [1,3-$(COH)_2$-4,6-$(CH_3)_2C_6H_2$]. ^{1}H NMR (δ, $CDCl_3$, 400 MHz, 298 K): 10.28 (2H, s, [1,3-$(CO\mathit{H})_2$-4,6-$(CH_3)_2C_6H_2$]); 8.24 (1H, s, [1,3-$(COH)_2$-4,6-$(CH_3)_2C_6\mathit{H}_2$]); 7.21 (1H, s, [1,3-$(COH)_2$-4,6-$(CH_3)_2C_6\mathit{H}_2$]); 2.73 (6H, s, [1,3-$(COH)_2$-4,6-$(C\mathit{H}_3)_2C_6H_2$]).

[4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_5)_2$]. 0.48 ml (5.34 mmol) of $C_6H_5NH_2$ was added to a Schlenk flask containing 0.5 g (2.67 mmol) of [1,3-$(COH)_2$-4,6-$(CH_3)_2C_6H_2$], 0.015 g (0.08 mmol) of PTSA and 30 ml of anhydrous toluene. The reaction was refluxed for 24 h using a dean stark apparatus to remove residual water. The solution was cooled to room temperature after which the solvent was removed in *vacuo*. The resulting residue was treated with cold methanol to precipitate 0.70 g (2.00 mmol, 78.0 %) of [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_5)_2$] as a powder. ^{1}H NMR (δ, $CDCl_3$, 400 MHz, 298 K): 8.70 (2H, s, [4,6-$(CH_3)_2C_6H_2$-1,3-$(C\mathit{H}NC_6H_5)_2$]); 8.61 (1H, s, [4,6-$(CH_3)_2C_6\mathit{H}_2$-1,3-$(CHNC_6H_5)_2$]); 7.38 (4H, t, [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6\mathit{H}_5)_2$]); 7.19 (6H, m, [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6\mathit{H}_5)_2$]); 7.11 (1H, s, [4,6-$(CH_3)_2C_6\mathit{H}_2$-1,3-$(CHNC_6H_5)_2$]); 2.61 (6H, s, [4,6-$(C\mathit{H}_3)_2C_6H_2$-1,3-$(CHNC_6H_5)_2$]).

[4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH_3)_2)_2$]. 0.31 g (1.91 mmol) of [1,3-$(COH)_2$-4,6-$(CH_3)_2C_6H_2$] and 0.01 g (0.0573 mol) PTSA were dissolved in 30 ml of anhydrous toluene. 0.47 ml (3.82 mmol) of 2,6-$((CH_3)_2)_2C_6H_3NH_2$ was added. The reaction was refluxed for 24 h using a dean stark apparatus to remove residual water. After cooling the reaction to room temperature the solvent was removed in *vacuo*. Treatment of the residue with cold methanol precipitated an oil. Drying the oil in *vacuo* for 24 h yielded [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH_3)_2)_2$]. ^{1}H NMR (δ, $CDCl_3$, 400 MHz, 298 K): 8.44 (1H, s, [4,6-$(CH_3)_2C_6\mathit{H}_2$-1,3-

($CHNC_6H_3$-2,6-$(CH_3)_2)_2$]); 8.38 (2H, s, [4,6-$(CH_3)_2C_6H_2$-1,3-(C*H*NC_6H_3-2,6-$(CH_3)_2)_2$]); 7.09 (1H, s, [4,6-$(CH_3)_2C_6H_2$-1,3-($CHNC_6H_3$-2,6-$(CH_3)_2)_2$]); 7.04 (4H, d, [4,6-$(CH_3)_2C_6H_2$-1,3-($CHNC_6H_3$-2,6-$(CH_3)_2)_2$]); 6.84 (2H, t, [4,6-$(CH_3)_2C_6H_2$-1,3-($CHNC_6H_3$-2,6-$(CH_3)_2)_2$]); 2.52 (6H, s, [4,6-$(CH_3)_2C_6H_2$-1,3-($CHNC_6H_3$-2,6-$(CH_3)_2)_2$]); 2.09 (12H, s, [4,6-$(CH_3)_2C_6H_2$-1,3-($CHNC_6H_3$-2,6-$(CH_3)_2)_2$]).

[4,6-$(CH_3)_2C_6H_2$-1,3-($CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$]. 1.45 ml (7.72 mmol) of 2,6-$(CH(CH_3)_2)_2C_6H_3NH_2$ was added to a Schlenk flask containing 0.69 g (3.68 mmol) of [1,3-$(COH)_2$-4,6-$(CH_3)_2C_6H_2$] and 0.021 g (0.11 mmol) of PTSA. The reaction was refluxed for 24 h using a dean stark apparatus to remove residual water. After cooling the solution to room temperature the solvent was removed in *vacuo*. Treating the residue with cold methanol precipitated a powder. Recrystallization of the powder in cold methanol yielded [4,6-$(CH_3)_2C_6H_2$-1,3-($CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$]. ^{1}H NMR (δ, $CDCl_3$, 400 MHz, 298 K): 8.57 (1H, s, [4,6-$(CH_3)_2C_6H_2$-1,3-($CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$]); 8.48 (2H, s [4,6-$(CH_3)_2C_6H_2$-1,3-(C*H*NC_6H_3-2,6-$(CH(CH_3)_2)_2)_2$]); 7.15 (5H, m, [4,6-$(CH_3)_2C_6H_2$-1,3-($CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$]); 7.08 (2H, t, [4,6-$(CH_3)_2C_6H_2$-1,3-($CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$]); 2.99 (4H, m, [4,6-$(CH_3)_2C_6H_2$-1,3-($CHNC_6H_3$-2,6-(C*H*$(CH_3)_2)_2)_2$]); 2.60 (6H, s, [4,6-$(CH_3)_2C_6H_2$-1,3-($CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$]); 1.16 (24H, d, [4,6-$(CH_3)_2C_6H_2$-1,3-($CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$]).

[4,6-$(CH_3)_2C_6H_2$-1,3-($CHNC_6H_3$-3,5-$(C(CH_3)_3)_2)_2$]. A Schlenk flask was charged with 0.35 g (1.72 mmol) of 3,5-$(C(CH_3)_3)_2C_6H_3NH_2$, 0.16 g (0.85 mmol) of [1,3-$(COH)_2$-4,6-$(CH_3)_2C_6H_2$], 0.005 g (0.02 mmol) of PTSA and 30 ml dry toluene. The reaction was

refluxed for 24 h using a dean stark apparatus to remove residual water. After cooling the solution to room temperature the solvent was removed in *vacuo*. The resulting residue was treated with cold methanol to precipitate 0.22 g (0.4 mmol, 46 %) of [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-3,5-$(C(CH_3)_3)_2)_2$] as a powder. ^{1}H NMR (δ, $CDCl_3$, 400 MHz, 298 K): 8.71 (2H, s, [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-3,5-$(C(CH_3)_3)_2)_2$]); 8.54 (1H, s, [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-3,5-$(C(CH_3)_3)_2)_2$]); 7.28 (2H, s, [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-3,5-$(C(CH_3)_3)_2)_2$]); 7.10 (1H, s, [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-3,5-$(C(CH_3)_3)_2)_2$]); 7.01 (4H, s, [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-3,5-$(C(CH_3)_3)_2)_2$]); 2.61 (6H, s, [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-3,5-$(C(CH_3)_3)_2)_2$]); 1.33 (36H, s, [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-3,5-$(C(CH_3)_3)_2)_2$]).

[4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_4$-4-$(C(CH_3)_3)_2$]. A Schlenk flask was charged with 0.5 g (2.67 mmol) of [1,3-$(COH)_2$-4,6-$(CH_3)_2C_6H_2$] and 0.015 g (0.08 mmol) of PTSA and 30 ml dry toluene. 0.84 ml (5.34 mmol) of 4-$C(CH_3)_3C_6H_3NH_2$ was syringed into the reaction. The reaction was refluxed for 24 h using a dean stark apparatus to remove residual water. After cooling the solution to room temperature the solvent was removed in *vacuo*. The resulting residue was dried in *vacuo* for 24 h to yield 0.88 g (1.97 mmol, 73.8 %) of [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_4$-4-$(C(CH_3)_3)_2$] as a crystalline solid.^{1}H NMR (δ, $CDCl_3$, 400 MHz, 298 K): 8.72 (2H, s, [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_4$-4-$(C(CH_3)_3)_2$]); 8.58 (1H, s, [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_4$-4-$(C(CH_3)_3)_2$]); 7.39 (4H, d, [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_4$-4-$(C(CH_3)_3)_2$]); 7.15 (4H, d, [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_4$-4-$(C(CH_3)_3)_2$]); 7.08 (1H, s, [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_4$-4-$(C(CH_3)_3)_2$]); 2.59 (6H, s, [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_4$-4-$(C(CH_3)_3)_2$]); 1.32 (18H, s, [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_4$-4-$(C(CH_3)_3)_2$]).

[4,6-$(F)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$]. A Schlenk flask was charged with 0.3 g (1.5 mmol) of [1,3-$(COH)_2$-4,6-$(F)_2C_6H_2$], 0.009 g (0.045 mmol) of PTSA and 30 ml of anhydrous toluene. 0.54 g (3.0 mmol) of 2,6-$(CH(CH_3)_2)_2C_6H_3NH_2$ was syringed into the reaction. The reaction was refluxed for 24 h using a dean stark apparatus to remove residual water. After the reaction was cooled to room temperature the solvent was removed in vacuo. The residue was treated with cold methanol to precipitate [4,6-$(F)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$] as a powder. ^{1}H NMR (δ, $CDCl_3$, 400 MHz, 298K): 8.99 (1H, t, [4,6-$(F)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$]); 8.45 (2H, s, [4,6-$(F)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$]); 7.10 (6H, m, [4,6-$(F)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$]); 6.99 (1H, t, [4,6-$(F)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$]); 2.94 (4H, m, [4,6-$(F)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$]); 1.15 (24H, d, [4,6-$(F)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$]).

[(4,6-$(CH_3)_2C_6H$-1,3-$(CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$)IrH-μ-Cl_2-Ir(C_8H_{12})]. 0.10 g (0.22 mmol) of [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$] and 0.10 g of (0.11 mmol) $[Ir(COE)_2Cl]_2$ were dissolved in 3.0 ml anhydrous toluene in a Schlenk tube. The reaction was heated at 90^{o}C for 24 hours. After the solution was cooled to room temperature the solvent was removed in *vacuo*. Treatment of the residue with pentanes precipitated a red powder. After decantation of the remaining pentanes the powder was dried in *vacuo*. Recrystallization of the powder from slow diffusion of CH_2Cl_2 into pentanes to yielded [(4,6-$(CH_3)_2C_6H$-1,3-$(CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$)IrH-μ-Cl_2-Ir(C_8H_{12})] as red crystals. ^{1}H (δ, $CDCl_3$, 400 MHz, 298K): 8.48 (2H, s, [(4,6-$(CH_3)_2C_6H$-1,3-$(CHNC_6H_3$-2,6-

$(CH(CH_3)_2)_2)_2$)IrH-μ-Cl_2-Ir(C_8H_{12})]); 7.36 (4H, m, [(4,6-$(CH_3)_2C_6$H-1,3-($CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$)IrH-μ-Cl_2-Ir(C_8H_{12})]); 7.23 (2H, m, [(4,6-$(CH_3)_2C_6$H-1,3-($CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$)IrH-μ-Cl_2-Ir(C_8H_{12})]); 6.73 (1H, s, [(4,6-$(CH_3)_2C_6H$-1,3-($CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$)IrH-μ-Cl_2-Ir(C_8H_{12})]); 3.34 (6H, m [(4,6-$(CH_3)_2C_6$H-1,3-($CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$)IrH-μ-Cl_2-Ir(C_8H_{12})]); 3.26 (2H, m, [(4,6-$(CH_3)_2C_6$H-1,3-($CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$)IrH-μ-Cl_2-Ir(C_8H_{12})]); 2.58 (6H, s, [(4,6-$(CH_3)_2C_6$H-1,3-($CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$)IrH-μ-Cl_2-Ir(C_8H_{12})]); 1.84 (6H, bm, [(4,6-$(CH_3)_2C_6$H-1,3-($CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$)IrH-μ-Cl_2-Ir(C_8H_{12})]); 1.54 (6H, d, [(4,6-$(CH_3)_2C_6$H-1,3-($CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$)IrH-μ-Cl_2-Ir(C_8H_{12})]); 1.23 (6H, d, [(4,6-$(CH_3)_2C_6$H-1,3-($CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$)IrH-μ-Cl_2-Ir(C_8H_{12})]); 1.17 (6H, d, [(4,6-$(CH_3)_2C_6$H-1,3-($CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$)IrH-μ-Cl_2-Ir(C_8H_{12})]); 1.01 (6H, d, [(4,6-$(CH_3)_2C_6$H-1,3-($CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$)IrH-μ-Cl_2-Ir(C_8H_{12})]); -30.44 (1H, s, [(4,6-$(CH_3)_2C_6$H-1,3-($CHNC_6H_3$-2,6-$(CH(CH_3)_2)_2)_2$)Ir*H*-μ-Cl_2-Ir(C_8H_{12})]).

[(4,6-$(CH_3)_2C_6$H-1,3-($CHNC_6H_5)_2$)Ir(CH_2CH_3)Cl]. 0.015 g (0.026 mmol) of $[Ir(C_2H_4)_2Cl]_2$ and 0.004 g (0.013 mmol) of [4,6-$(CH_3)_2C_6H_2$-1,3-$(CHNC_6H_5)_2$] were dissolved in 0.5 ml of dry C_6D_6 in a J-Young tube. The reaction was stirred for 24 h at room temperature and filtered to yield [(4,6-$(CH_3)_2C_6$H-1,3-$(CHNC_6H_5)_2$)Ir(CH_2CH_3)Cl] without any further purification. ^{1}H NMR (δ, C_6D_6, 400 MHz, 298K): 8.31 (2H, s, [(4,6-$(CH_3)_2C_6$H-1,3-($CHNC_6H_5)_2$)Ir(CH_2CH_3)Cl]); 7.63 (4H, d, [(4,6-$(CH_3)_2C_6$H-1,3-($CHNC_6H_5)_2$)Ir(CH_2CH_3)Cl]); 7.21 (4H, t, [(4,6-$(CH_3)_2C_6$H-1,3-($CHNC_6H_5)_2$)Ir(CH_2CH_3)Cl]); 7.08 (2H, d, [(4,6-$(CH_3)_2C_6$H-1,3-($CHNC_6H_5)_2$)Ir(CH_2CH_3)Cl]); 6.40 (1H, s, [(4,6-$(CH_3)_2C_6H$-1,3-

($CHNC_6H_5)_2$)Ir(CH_2CH_3)Cl]); 2.13 (6H, s, [(4,6-(CH_3)$_2$$C_6$H-1,3-($CHNC_6H_5)_2$)Ir($CH_2CH_3$)Cl]); 1.17 (2H, q, [(4,6-(CH_3)$_2$$C_6$H-1,3-($CHNC_6H_5)_2$)Ir($CH_2CH_3$)Cl]); 0.327 (3H, t, [(4,6-(CH_3)$_2$$C_6$H-1,3-($CHNC_6H_5)_2$)Ir($CH_2CH_3$)Cl]).

[(4,6-(CH_3)$_2$$C_6$H-1,3-($CHNC_6H_3$-3,5-($C(CH_3)_3)_2)_2)Ir(CH_2CH_3)Cl]. 0.015 g (0.026 mmol) of [Ir(C_2H_4)$_2$Cl]$_2$ and 0.007 g (0.013 mmol) of [4,6-(CH_3)$_2$$C_6H_2$-1,3-($CHNC_6H_3$-3,5-($C(CH_3)_3)_2)_2$] were dissolved in 0.5 ml of dry $C_6D_5CD_3$ in a J-Young tube. The reaction was stirred for 24 h at room temperature to yield [(4,6-(CH_3)$_2$$C_6$H-1,3-($CHNC_6H_3$-3,5-($C(CH_3)_3)_2)_2$)Ir($CH_2CH_3$)Cl] without any further purification. ^{1}H NMR (δ, $C_6D_5CD_3$, 400 MHz, 298K): 8.72 (2H, s, [(4,6-(CH_3)$_2$$C_6$H-1,3-($CHNC_6H_3$-3,5-($C(CH_3)_3)_2)_2$)Ir($CH_2CH_3$)Cl]); 7.68 (4H, s, [(4,6-(CH_3)$_2$$C_6$H-1,3-($CHNC_6H_3$-3,5-($C(CH_3)_3)_2)_2$)Ir($CH_2CH_3$)Cl]); 7.62 (2H, s, [(4,6-(CH_3)$_2$$C_6$H-1,3-($CHNC_6H_3$-3,5-($C(CH_3)_3)_2)_2$)Ir($CH_2CH_3$)Cl]); 6.39 (1H, s, [(4,6-(CH_3)$_2$$C_6H$-1,3-($CHNC_6H_3$-3,5-($C(CH_3)_3)_2)_2$)Ir($CH_2CH_3$)Cl]); 2.17 (6H, s, [(4,6-(CH_3)$_2$$C_6$H-1,3-($CHNC_6H_3$-3,5-($C(CH_3)_3)_2)_2$)Ir($CH_2CH_3$)Cl]); 1.51 (36H, s, [(4,6-(CH_3)$_2$$C_6$H-1,3-($CHNC_6H_3$-3,5-($C(CH_3)_3)_2)_2$)Ir($CH_2CH_3$)Cl]); 1.14 (2H, q, [(4,6-(CH_3)$_2$$C_6$H-1,3-($CHNC_6H_3$-3,5-($C(CH_3)_3)_2)_2$)Ir($CH_2CH_3$)Cl]); 0.42 (3H, t, [(4,6-(CH_3)$_2$$C_6$H-1,3-($CHNC_6H_3$-3,5-($C(CH_3)_3)_2)_2$)Ir($CH_2CH_3$)Cl]).

[(4,6-(CH_3)$_2$$C_6$H-1,3-($CHNC_6H_4$-4-($C(CH_3)_3)_2)Ir(CH_2CH_3)Cl]. 0.030 g (0.052 mmol) of [Ir(C_2H_4)$_2$Cl]$_2$ and 0.023 g (0.052 mmol) of [4,6-(CH_3)$_2$$C_6H_2$-1,3-($CHNC_6H_4$-4-($C(CH_3)_3)_2$] were dissolved in 3.0 ml dry CH_2Cl_2. After stirring the reaction for 1 h at room temperature

the solvent was removed in *vacuo*. Treatment of the residue with cold pentanes precipitated a powder. Decantation of the pentanes followed by removal of the solvent in *vacuo* yielded [(4,6-$(CH_3)_2C_6H$-1,3-$(CHNC_6H_4$-4-$(C(CH_3)_3)_2)Ir(CH_2CH_3)Cl$] without any further purification. ^{1}H NMR (δ, $CDCl_3$, 400 MHz, 298K): 8.71 (2H, s, [(4,6-$(CH_3)_2C_6H$-1,3-$(CHNC_6H_4$-4-$(C(CH_3)_3)_2)Ir(CH_2CH_3)Cl$]); 7.47 (8H, s, [(4,6-$(CH_3)_2C_6H$-1,3-$(CHNC_6H_4$-4-$(C(CH_3)_3)_2)Ir(CH_2CH_3)Cl$]); 6.62 (1H, s, [(4,6-$(CH_3)_2C_6H$-1,3-$(CHNC_6H_4$-4-$(C(CH_3)_3)_2)Ir(CH_2CH_3)Cl$]); 2.56 (6H, s, [(4,6-$(CH_3)_2C_6H$-1,3-$(CHNC_6H_4$-4-$(C(CH_3)_3)_2)Ir(CH_2CH_3)Cl$]); 1.36 (18H, s, [(4,6-$(CH_3)_2C_6H$-1,3-$(CHNC_6H_4$-4-$(C(CH_3)_3)_2)Ir(CH_2CH_3)Cl$]); 0.83 (2H, b, [(4,6-$(CH_3)_2C_6H$-1,3-$(CHNC_6H_4$-4-$(C(CH_3)_3)_2)Ir(CH_2CH_3)Cl$]); -0.10 (3H, b, [(4,6-$(CH_3)_2C_6H$-1,3-$(CHNC_6H_4$-4-$(C(CH_3)_3)_2)Ir(CH_2CH_3)Cl$]).

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