Cyclometalation of 6-Phenyl-2,2′-Bipyridine and Iridium: Synthesis, Characterization, and Reactivity Studies

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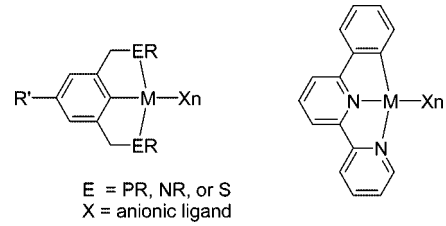
Heating the potential tridentate 6-(4-R-phenyl)-2,2′-bipyridine ligand **1a** (R = H), and derivatives **1b** (R = CMe_3) and **1c** (R = OH), with $IrCl_3$ hydrate in 2-methoxyethanol or acetone/H_2O gave the unexpected bidentate cyclometalated NC dinuclear complexes $[Ir(NC)Cl_2(C_5H_5N)]_2$ (**2a**−**cPy**), as the major product. Altering the ligand/metal ratio from 1:1 to 2:1 produced a mixture of bis-cyclometalated complexes, Ir(NNC)(NC)Cl (**3a,b**), with tridentate and bidentate binding modes. Using discrete Ir^I synthons, such as $Ir(dmso)_3Cl$ or $[Ir(cyclooctene)_2Cl]_2$, gave a complicated mixture of products. However, when $[Ir(C_2H_4)_2Cl]_2$ was used, then the desired tridentate cyclometalated Ir(NNC) complex $Ir(NNC)Et(C_2H_4)Cl$ (**4**) was synthesized cleanly. The dinuclear complex **2a-Py** was converted to the corresponding mononuclear dichloride complexes $Ir(NC)(NN)Cl_2$ (**5a**) upon refluxing with 4,4′-di-*tert*-butylbipyridine in *N*,*N*-dimethylacetamide (DMA). Treatment of **5a** with $ZnMe_2$ gives $Ir(NC)(NN^{tBu})MeCl$ (**6a**). Abstraction of the chloride with AgOTF yields $Ir(NC)(NN^{tBu})MeOTf$ (**7a**). Complex **7a** undergoes stoichiometric CH activation with arenes and shows catalytic activity for the H/D exchange between benzene and (trifluoro)acetic acids.

Introduction

The use of transition metal-mediated CH bond activation (CHA) remains a promising paradigm to ultimately achieve heteroatom functionalization of hydrocarbons.[1,2] The most efficient catalysts that utilize CHA are based on electrophilic, redox-active, metals such as Pd^{II}, Pt^{II}, Hg^{II}, and $Au^{I/III}$ and require strong acid solvents (due to water and methanol poisoning).[3] Our group is interested in developing new CHA systems that are thermally stable and do not show Lewis base inhibition. Therefore we are exploring the use of less electrophilic metal complexes[4] based on complexes with electron-donating ligands and metals to the left of platinum.

Several iridium complexes, such as Bergman's $Cp^*Ir(PMe_3)$ complexes, efficiently catalyze H/D exchange between arenes and water.[5] Our group has also previously shown that the O-donor $(acac)_2IrMePy$ complex[6] is protic and thermally stable and capable of CHA and functionalization. Given the success of these systems, we were encouraged to investigate other bidentate and tridentate ligands. Preliminary quantum mechanical rapid prototyping (QMRP) using density functional theory (DFT) of several ligand geometries and compositions attached to iridium showed the pincer ligand motif to be promising for CHA[7] (Scheme 1), with the NNC ligand motif[8] being the most promising.[9] The popularity of pincer ligand motifs is due to their stability and reactivity for organic transformations, such

Scheme 1



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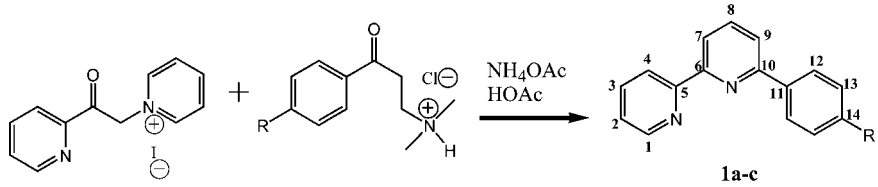
Scheme 2. Ligand Synthesis and NMR Label



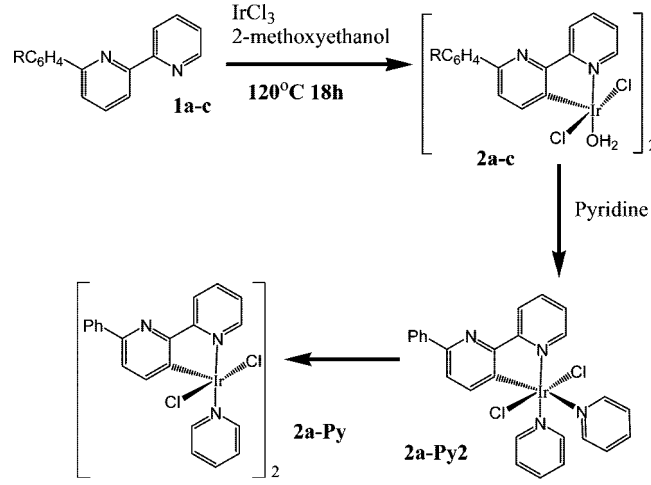
R= H (**1a**), CMe_3 (**1b**), OH (**1c**)

as Heck and Suzuki couplings, alkane dehydrogenation, catalytic alkane metathesis, hydrogen transfer dehydrogenation, hydroamination, and Kharsch addition.[10]

Prior to our initial communication,[11] Constable et al. showed that 6-phenyl-2,2′-bipyridine (NNC-H) binds in a tridentate NNC fashion to give Pd(NNC)Cl, Pt(NNC)Cl, and Rh(NNC)Cl_2L.[12] Also, Jahng et al. showed that the corresponding annulated 3,2′-polymethylene-6-(2″-pyridyl)-2-phenylpyridines undergoes cycloplatination.[13] In our initial communication, we reported that the pincer complex (NNC)Pt^{II}TFA (NNC = κ^3-6-phenyl-4,4′-di-*tert*-butyl-2,2′-bipyridine, TFA = trifluoroacetate) was sufficiently thermally and protic stable to catalyze the CH activation of benzene in trifluoroacetic acid-d_1 (DTFA).[11] It is known that 2-phenylpyridine undergoes cyclometalation when refluxed with $IrCl_3$ in 2-ethoxyethanol/H_2O to produce the corresponding cyclometalated dinuclear $[(NC)_2IrCl_2]_2$ complexes.[14] Given the precedence that 6-phenyl-2,2′-bipyridine forms pincer complexes with Pd, Pt, and Rh, and several examples of iridium-binding bipyridines and terpyridines to form the corresponding coordination compounds,[15] we envisioned that the corresponding iridium NNC pincer complex, (NNC)$Ir^{III}Cl_2$, could also be made in a similar fashion.

Here we report a cyclometalation study of para-substituted 6-phenyl-2,2′-bipyridine with iridium. Depending on ligand/metal ratios, solvent conditions, and the iridium synthon, several cyclometalated species, including dinuclear cyclometalated (NC)Ir complexes $[(NC)IrCl_2Py]_2$ (**2a**−**cPy**), mixed Ir(NNC)-(NC)Cl complexes (**3a,b**), and the Ir(NNC) complex (NNC)Ir$(C_2H_4)(C_2H_5)$Cl (**4**), were formed. Since the $(acac)_2$IrMePy complex was active for benzene CH activation and functionalization, we converted the dinuclear complex **2a-Py** to the mononuclear bis-bidentate methyl complex (NC)(NN^{tBu})-IrMeOTf (**7a**), which is also capable of benzene CH activation and functionalization.[16] Complex **7a** undergoes stoichiometric oxy-functionalization to generate methyl acetate (MeOAc) or methyl trifluoroacetate (MeTFA) when treated with $PhI(OAc)_2$ or $PhI(TFA)_2$. The methyl complex **7a** is capable of stoichiometric and catalytic benzene CH activation, and new details about the CH activation reaction are reported.

Scheme 3



Results and Discussion

1. Ligand Synthesis and Characterization. 6-Phenyl-2,2′-bipyridines can be readily synthesized by several different routes, such as the Kroehnke synthesis[17] or by nucleophilic substitution with lithiated arenes.[18] This allows easy derivatization of the NNC ligand and tuning of the electronic and steric properties of the ligand and resultant complexes. *tert*-Butyl (CMe_3-NNC, **1b**) and hydroxy (HO-NNC, **1c**) groups were introduced into the para position of the phenyl ring to increase the solubility of the metal complexes in nonpolar and polar solvents. Ligands **1a**−**c** were synthesized by heating *N*-[2-(2-pyridyl)-2-oxoethyl]pyridinium iodide with the appropriate para-substituted 3-(dimethylamino-1-phenyl-1-propanone hydrochloride and ammonium acetate in acetic acid (Scheme 2). **1b** was obtained in 60.8% yield and **1c** in 60.5% yield. The ligands were fully characterized by NMR, mass spectrometry, elemental analysis, and X-ray crystallography. The ^{1}H NMR of **1b** (R = CMe_3) in $CDCl_3$ and **1c** (R = OH) in dmso-d_6 showed nine aromatics peaks, which is expected for an unsymmetrical substituted bipyridine. The structures were also confirmed by X-ray structure analysis (see Supporting Information). Suitable crystals of **1b** and **1c** were obtained from a CH_2Cl_2/hexane solution (**1b**) and MeOH/hexane solution (**1c**) at −25 °C.

2. Cyclometalation Studies. A red precipitate formed upon heating the NNC ligand **1a** with $IrCl_3$ in 2-methoxyethanol (Scheme 3). This product is the undesired bidentate NC cyclometalated dinuclear complex $[Ir(NC)Cl_2L]_2$ (**2a**, L = H_2O), where cyclometalation occurs at the 3-position of the central pyridine ring. The proposed structure is supported by 1D and 2D NMR, mass spectrometry, and X-ray structure analysis. Upon dissolving in pyridine, the corresponding mononuclear

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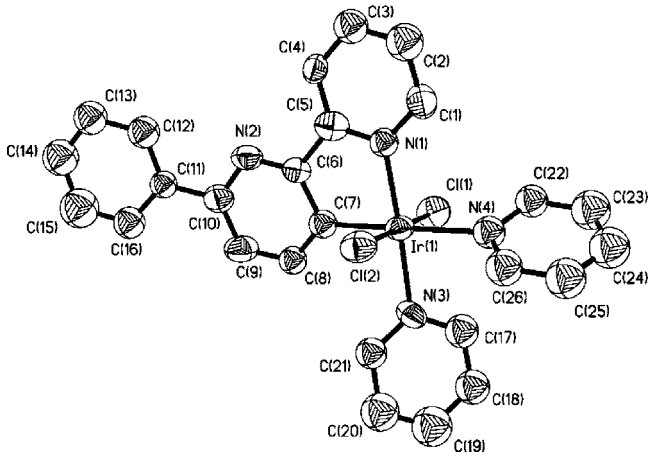

Figure 1. Thermal ellipsoid plot of $Ir(NC)(C_5H_5N)_2Cl_2$ complex **2a-Py$_2$**. Thermal ellipsoids are at 50% probability; hydrogens were omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir(1)−C(7) 2.012(13), Ir(1)−N(1) 2.048(10), Ir(1)−N(3) 2.081(10), Ir(1)−N(4) 2.203(8), Ir(1)−Cl(2) 2.352(4), Ir(1)−Cl(1) 2.350(4); C(7)−Ir(1)−N(1) 81.1(6), C(7)−Ir(1)−N(3) 96.15), N(1)−Ir(1)−N(3) 176.6(5), C(7)−Ir(1)−N(4) 178.9(5), N(1)−Ir(1)−N(4) 98.8(5), N(3)−Ir(1)−N(4) 84.0(4), N(3)−Ir(1)−Cl(2) 90.3(3), N(4)−Ir(1)−Cl(2) 90.2(3), N(1)−Ir(1)−Cl(1) 92.5(3), Cl(2)−Ir(1)−Cl(1) 178.67(13).

pyridyl complex, $Ir(NC)Cl_2(C_5H_5N)_2$ (**2a-Py$_2$**), is formed. This complex is initially quite soluble in chloroform and dichloromethane; however, the pyridine trans to the metalated ring is labile and slowly over time the corresponding dinuclear complex $[Ir(NC)Cl_2(C_5H_5N)]_2$ (**2a-Py**) forms and precipitates from the solution. The substituted ligands **1b** and **1c** also form the corresponding bidentate, cyclometalated dinuclear complexes $[Ir(CMe_3\text{-}NC)Cl_2(C_5H_5N)]_2$ (**2b-Py**) and $[Ir(HO\text{-}NC)Cl_2\text{-}(C_5H_5N)]_2$ (**2c-Py**) when refluxed in 2-methoxyethanol.

3. Synthesis of Dinuclear Cyclometalated Iridium Complexes 2a−c-Py (R = H (a), CMe_3 (b), OH (c)). The ^{1}H NMR of **2a-Py** in DMSO-d_6 shows nine aromatic resonances for the ligand (total of 12 including the pyridine ring) that integrate to 11 protons, which is expected for the proposed bidentate NC binding mode. If the ligand were to bind in a tridentate NNC binding mode, 11 resonances would be expected. The doublet of doublets (H-12) at 8.20 ppm and the triplet (H-13) at 7.52 ppm that both integrate for two protons further support that cyclometalation has not occurred at the phenyl ring. The gCOSY experiment (see Supporting Information) shows three spin systems consisting of a "two", "four", "three" pattern, with the doublet at 8.51 (H-8) with a cross-peak with the doublet at 7.70 (H-9) ppm, supporting that cyclometalation occurred on the 3-position of the central pyridine ring. In the free ligand **1a**, the carbon at the 3-position (C-7) appears at 119.48 ppm and the meta carbon (C-12) of the phenyl ring appears at 127.13 ppm. Upon cyclometalation, the signals at 119.48 ppm disappeared and a new resonance for the ipso carbon appears at 143.32 ppm, while the C-12 (125.94 ppm) remains, further supporting the proposed structure.

More evidence for the proposed binding mode can be seen in the crystal structure of **2a-Py$_2$** (Figure 1). Yellow crystals of **2a-Py$_2$** were grown by slow evaporation from a concentrated pyridine solution. Large crystals of **2a-Py$_2$** were not available, and data collection was performed over a period of 15 h. The resulting data were of decent quality, but the structure was refined with difficulty. Several atoms were refined using SIMU and DELU constraints, while others (N4, C17, C18, C19) were left isotropic. One pyridine ring was severely disordered and was constrained using appropriate DFIX commands. The remaining rings were only slightly disordered and were left alone. Figure 1 shows that metalation occurred at the 3-position of the central pyridine ring with the two chloride ligands arranged in a trans fashion and two pyridines cis to each other. Table 1 gives the crystallographic data and parameters.

Given the literature precedence for iridium-binding bipyridines and terpyridines to form the corresponding NN and NNN coordination compounds, as well as forming the cyclometalated product with 2-phenylpyridine, formation of the tridentate NNC product was expected.[15] The formation of these Ir(NC) type complexes (Scheme 4) are relatively uncommon. However, there are some reported exceptions in which the pyridyl ring rotates and cyclometalation occurs instead of nitrogen binding. The one example of an Ir(NNC) complex was formed when one of the quinoline arms of a terpyridine rotated and cyclometalation occurred on the back side.[19] There has also been a reported case in which one of the pyridyl rings of bipyridine rotated and formed the corresponding NC cyclometalated iridium complex.[14a,20]

When the ligand to metal ratio was changed from 1:1 to 2:1, the desired tridentate NNC coordination mode was observed. However, these complexes also have a bidentate NC cyclometalated ligand (Scheme 5). These new complexes are likely formed when the second equivalent of ligand cleaves the dinuclear Ir(NC) complex to form the monomeric intermediate, $Ir(NC)(NN)Cl_2$ (an example of such a complex is discussed later), which then undergoes CH activation of the phenyl ring to produce the mixed tridentate−bidentate cyclometalated iridium complex. These complexes are not expected to be efficient CH activation catalysts since they are coordinatively saturated. With the *tert*-butyl ligand **1b**, several mixed tridentate−bidentate cyclometalated iridium complexes, $Ir(CMe_3\text{-}NNC)(CMe_3\text{-}NC)Cl$ (**3b**), were observed. There are two possible conformers for each pair of diastereomers. Two complexes were cleanly isolated and characterized by ^{1}H and ^{13}C NMR, mass spectrometry, and elemental analysis, after passing the mixture through silica gel with dichloromethane. Unfortunately, at least two other minor species could not be cleanly separated and characterized. **1a** also forms the bis-cyclometalated Ir(NNC)-(NC)Cl products, on the basis of mass spectrometry. However, these products could not be separated and isolated.

The ^{1}H NMR of the first isomer in $CDCl_3$ is consistent with a bis-cyclometalated species. A total of 18 aromatic resonances that integrate to 20 protons were observed. The two doublets at 8.24 and 7.57 ppm for the aryl ring both integrate to two protons and are consistent with one of the ligands binding in a bidentate NC fashion. The doublet, doublet of doublets, and doublet at 7.49 (^3J = 8.2 Hz), 6.87 (^3J = 8.2 Hz, ^4J = 1.9 Hz), and 6.65 (^4J = 2.0 Hz) ppm support that metalation has occurred on the phenyl ring and that one of the ligands is binding in a tridentate NNC fashion. Further evidence for the proposed $Ir(CMe_3\text{-}NNC)(CMe_3\text{-}NC)Cl$ complex is the "four", "four", "three", "three", "two", "two" spin systems observed in the gCOSY experiment (see Supporting Information). Formation of the second isomer is also supported by ^{1}H and ^{13}C NMR.

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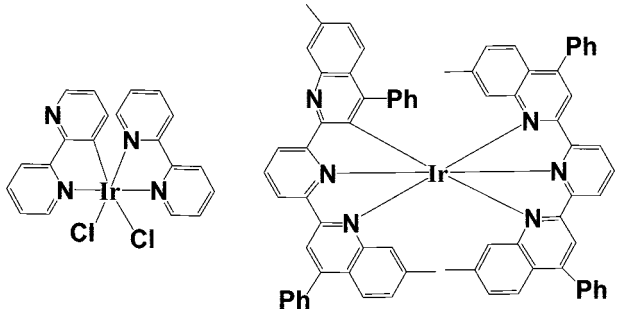
Table 1. Crystallographic Data and Parameters

	2a-Py$_2$	5a(NN-trans)	5a(NC-trans)	6a
formula	$C_{26}H_{21}Cl_2IrN_4$	$C_{34}H_{35}Cl_2IrN_4O_{0.5}$	$C_{34}H_{35}Cl_2IrN_4$	$C_{35}H_{38}ClIrN_4$
fw	652.57	770.76	762.76	742.34
T, K	298	133(2)	148(2)	153(2)
cryst syst	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a, Å	12.182(5)	12.0798(13)	7.119(4)	13.873(10)
b, Å	12.030(5)	13.2601(14)	14.764(9)	27.93(2)
c, Å	17.428(7)	13.3101(14)	16.725(10)	11.008(8)
α, deg	90	101.207(2)	78.679(8)	90
β, deg	109.190(7)	104.310(2)	79.307(10)	109.862(13)
γ, deg	90	110.491(2)	88.769(9)	90
V, Å^3	2412.2(17)	1840.2(3)	1693.6(17)	4011(5)
Z, D_{calc}, g/cm^3	4, 1.797	2, 1.391	2, 1.496	4, 1.229
μ, mm^{-1}	5.778	3.800	4.127	3.419
θ range, deg	1.77 to 27.64	1.66 to 26.37	1.26 to 27.70	1.46 to 25.68
GOF	1.036	1.099	1.023	1.226
R_1, R_w [$I > 2\sigma(I)$]	0.0599, 0.0896	0.0568, 0.1739	0.0673, 0.1744	0.0898, 0.2216

Scheme 4



Other solvents were also investigated. When a 5:1 acetone/H_2O mixture was used, the corresponding dinuclear complexes **2a**−**c-Py** were formed as the major product. However, when a THF/H_2O (5:1) mixture was used, a complex mixture of products was observed depending on the ligand. With **1a** (R = H) the cyclometalated dinuclear complex **2a-Py** was the major product. However, in the case of ligand **1b** (R = CMe_3), **2b-Py** and several other products were observed. One of the products was isolated and determined to be one of the isomers of the mixed tridentate/bidentate complex **3b** previously mentioned.

In all these cases cyclometalation occurred primarily at the central pyridine ring instead of the phenyl ring, suggesting that the reaction may occur via an electrophilic mechanism; cyclometalation is occurring at the most electron-rich ring.[21] In an attempt to disfavor this reaction, we tried several Ir^{I} synthons, as cyclometalation with Ir^{I} could be expected to proceed by an oxidative addition mechanism and favor cyclometalation of the phenyl ring. When **1a,b** was heated with Ir(dmso)$_3$Cl, a complicated mixture of products formed, and the products could not be cleanly separated. However, ^{1}H NMR analysis of the reaction mixture showed two triplets between 7.3 and 7.0 ppm, which suggested that some Ir(NNC)H(Cl) complex was formed. Iridium(I) cyclooctene dimer ([Ir(COE)$_2$Cl]$_2$) gave a complex mixture of products with **1a,b** after stirring at ambient temperature in CH_2Cl_2. In the reaction with [Ir(COE)$_2$Cl]$_2$ and **1b**, the undesired mixed tridentate/bidentate complex **3b** was the main product, based on ^{1}H NMR analysis. A minor side product (<5%) was observed and separated by column chromatography, and was assigned as an Ir(NNC) complex on the basis of ^{1}H NMR. However, when an Ir^{I} synthon with a very labile ligand is used, the desired Ir(NNC) product was obtained cleanly as the major product. When ethylene is bubbled through a solution of [Ir(ethylene)$_2$Cl]$_2$ in CH_2Cl_2 at −50 °C, a mononuclear Ir(ethylene)$_4$Cl species is generated in situ.[22] To this solution was added 1 equiv of ligand **1a**, and the solution was stirred at ambient temperature for 16 h (Scheme 6). ^{1}H NMR analysis of the reaction mixture indicates that the desired monoligated tridentate NNC binding mode was obtained and that the Ir(NNC)Cl(ethylene)ethyl complex (**4**) is now formed as the major product. Complex **4** was isolated as an orange air-stable solid after passing through alumina and was characterized by NMR, mass spectrometry, and elemental analysis. The ^{1}H NMR of **4** in $CDCl_3$ shows all expected 11 aromatic resonances (11 H's), which is consistent with the proposed tridentate NNC binding mode. The ethylene was observed as a singlet at 4.03 ppm, and the CH_2 group of the Ir-CH_2CH_3 is diastereotopic, appearing at 0.47 and 0.21 ppm. Further evidence for the proposed NNC binding mode is the "four", "three", "four" spin systems observed in the gCOSY experiment (see Supporting Information). Consistent with the proposed structure, 16 aromatic carbons were observed in the ^{13}C NMR. The reactivity of these monocyclometalated IrNNC complexes are reported elsewhere.[23]

4. Synthesis and Characterization of Mononuclear Cyclometalated Complexes. (a) Synthesis and Characterization of Ir(NC)(NN^{tBu})Cl$_2$ (5a,b). Given the previous success with our bis-bidentate (acac)$_2$IrRL system for CH activation and functionalization, we investigated whether the stable dinuclear (NC)Ir complexes could be converted to mononuclear bis-bidentate complexes by treatment with bidentate ligands. This would allow access to a vacant cis coordination site for possible C−H activation reactions. Upon refluxing **2a-Py** with 4,4′-di-*tert*-butylbipyridine (NN^{tBu}) in DMA (Scheme 7), the corresponding mononuclear bis-bidentate iridium dichloride complex Ir(NC)(NN^{t-Bu})Cl$_2$, **5a**, was obtained in good yields (70.8%) as a mixture of two *cis*-dichloride isomers. There are three possible isomers, one trans and two cis. The two cis isomers, **5a(NC-trans)** and **5a(NN-trans)**, were isolated after passing through silica gel with dichloromethane. The ratio of the two isomers varied from 2:1 to 1:1. **5a** is soluble in halogenated solvents and is slightly soluble in aromatic solvents such as benzene and toluene. These complexes were fully characterized by NMR, elemental analysis, mass spectrometry, and X-ray crystallography.

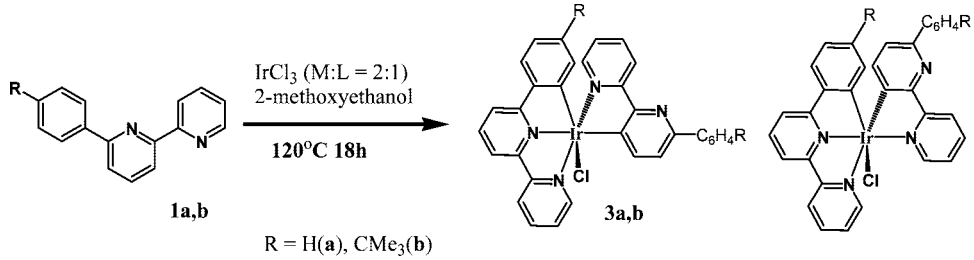
The conformation of the two isomers was confirmed by X-ray crystal analysis. Suitable crystals for X-ray analysis of **5a(NN-**

(21) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403.

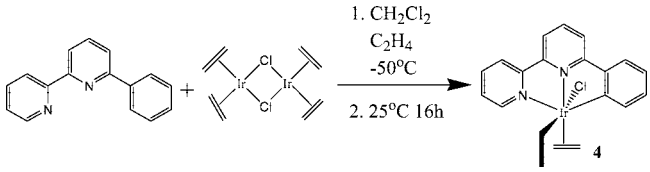
(22) Onderdelinden, A. L.; van der Ent, A. *Inorg. Chim. Acta* **1972**, *6*, 420.

(23) Young, K. J. H.; Oxgaard, J.; Ess, D. H.; Stewart, T.; Goddard, W. A., III.; Periana, R. A. *Chem. Commun* **2009**, DOI: 10.1039/b823303a.

Scheme 5. Mixed Binding Mode for Bis-cyclometalated Iridium Complexes



Scheme 6. Synthesis of Mononuclear Tridentate (NNC)IrEt(C_2H_4)Cl Complex 4



trans)[24] and **5a(NC-trans)** were grown by slow vapor diffusion of hexanes into a CH_2Cl_2 solution. Table 1 gives crystallographic data and conditions, and Figures 2 and 3 are molecular diagram views. Both iridium centers adopt a slightly distorted octahedral geometry with the two chlorides cis to each other. In the case of **5a(NN-trans)**, one of the *tert*-butyl groups was disordered and was solved by dual occupancy. As expected, the chloride (Cl-2) trans to the strong σ-donor C-bound pyridyl ring is elongated 2.480 (2) Å compared to the chloride (Cl-1) trans to the nitrogen, 2.363 (2) Å.

(b) Synthesis and Characterization of Methyl Complexes. The previous success using $Zn(Me)_2$ as an alkylating reagent for generating the reactive $(acac)_2IrRL$ complex[7] prompted us to use this reagent to replace the chloride ligands with a reactive alkyl group. The corresponding monomethyl complex **6a** was successfully synthesized by heating either isomer of the dichloride (**5a**) with $Zn(Me)_2$ in either toluene or THF at 120 °C in a sealed tube (Scheme 7). The solution turned black, and upon quenching with methanol and passing through silica, the monomethylated product was obtained as a red powder in good yields (70% yield). It is important that the reaction is carried out at these high temperatures since at lower temperatures only low conversions were observed. The methyl complex **6a** is readily soluble in a wide range of organic solvents, such as dichloromethane, THF, benzene, and methanol, and has been fully characterized by NMR, mass spectrometry, and X-ray crystallography.

The ^1H NMR spectra of **6a** in $CDCl_3$ shows a new peak at 0.66 ppm (3H's), which has been assigned to the iridium-bound methyl group. The ^{13}C NMR spectrum also supports the proposed structure and the Ir-CH_3 resonance was observed at −16.0 ppm. Formation of the methyl complex is further supported by X-ray crystallography. Red needles were grown by slow evaporation from a concentrated benzene solution. Large crystals of **6a** were also not available, which necessitated a data collection time of 15 h. However, the resulting data were of relatively poor diffraction quality, causing higher than normal *R* values. An appropriate weighting scheme was used to lower R_w to a reasonable value. A *tert*-butyl group was severely disordered, and appropriate SADI commands were used to constrain the geometry. Atoms C12, C13, and C14 of the *tert*-butyl group were not refined anisotropically. Although the crystal weakly diffracted, the molecular diagram (Figure 4) does suggest that the methyl complex was formed and that the methyl group is cis to the chloride and trans to one of the pyridines of the bipyridine ligand. Crystallographic data and parameters can be found in Table 1. In order to generate a more reactive catalytic precursor, the remaining chloride was replaced with the more labile triflate anion by halide abstraction using silver triflate.[17]

5. Reactivity Studies

(a) Reaction of Ir(NN^{tBu})(NC)MeOTf with Acids. To determine if these complexes are sufficiently protic and thermally stable, we treated these complexes with acetic, trifluoroacetic, and sulfuric acids. While the complex remains intact, the methyl group is very reactive and undergoes protonalysis with loss of methane; when D_2SO_4 was used, CH_3D was observed. Attesting to the thermal stability of this ligand motif, **7a** can be heated in neat H_2SO_4 at 200 °C for 20 h; the complex remains intact, and no loss of NC or NN ligand was observed. However mass spectral analysis indicated that the ligand undergoes sulfonation. Only methane loss was observed.

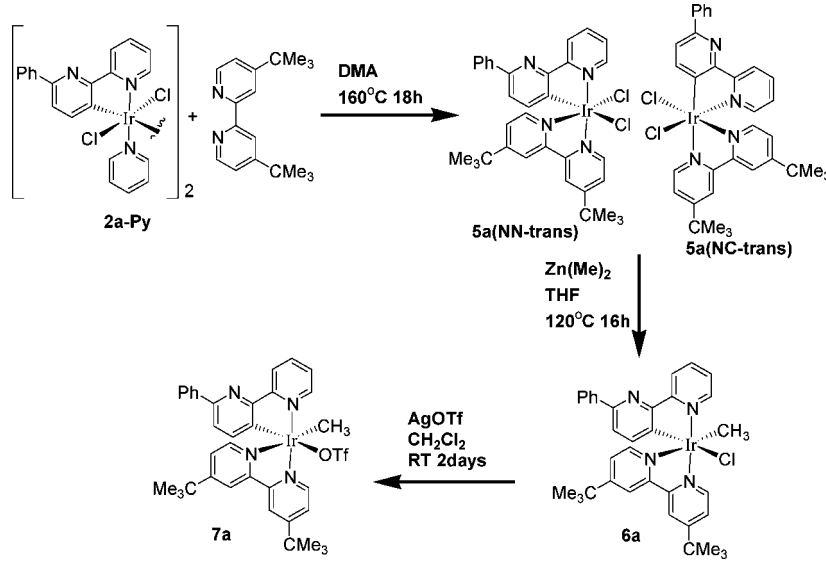
When 2−3 equiv of trifluoroacetic acid was used, protonolysis occurs over the course of a few hours (<2 h); however it is instantaneous when dissolved in neat or concentrated trifluoroacetic acid solutions. When trifluoroacetic acid-d_1 was used, only CH_3D was observed. After workup and isolation, the product of this reaction was determined to be a bis-trifluoroacetate complex based on ^1H, ^{13}C, and ^{19}F NMR. In the ^{19}F NMR, two trifluoroacetate groups were observed at −75.70 and −75.82 ppm since the trifluoroacetate groups are inequivalent. However, when **7a** is dissolved in acetic acid, the mono-acetate complex, Ir(NN)(NC)OAcOTf, was observed as the major product with small amounts of the diacetate complex, Ir(NN)(NC)$(OAc)_2$. ^1H and ^{19}F NMR confirms the formation of the monoacetate complex. Both complexes were characterized by NMR, mass spectrometry, and elemental analysis.

(b) Stoichiometric and Catalytic CH Activation Studies. Since these bis-bidentate complexes are protic and thermally stable in strong acids, we investigated the activation of methane by testing for H/D exchange between methane and sulfuric acid-d_2 or trifluoroacetic acid-d_1. Unfortunately all reactions with methane at temperatures up to 208 °C showed no incorporation of deuterium into methane after 21 h. Even though the complex was stable under these conditions, no loss of ligand was observed (see Supporting Information).

The more reactive substrate benzene was then tested. Upon heating **7a** in neat benzene at 170 °C, the stoichiometric C−H activation product Ir(NN)(NC)(C_6H_5)OTF, **8a**, was formed in quantitative yields as a crystalline yellow solid along with liberation of methane (Scheme 8). The formation of the phenyl complex was confirmed by ^1H and ^{13}C NMR as well as

(24) Crystals of **5a(NN-trans)** were grown in air from undried solvents. This may have caused water molecules to appear in the crystal lattice, and indeed large, lone residual peaks were observed. The largest of these peaks was refined as a water molecule.

Scheme 7. Synthesis of Mononuclear Bis-bidentate Complexes



elemental analysis. The disappearance of the methyl peak and the appearance of several broad peaks between 7.1 and 6.8 ppm support the formation of the phenyl complex. Production of methane was also confirmed by GC/MS. After treatment of **8a** with pyridine the phenyl peaks became well resolved. The formation of the phenyl complex was further verified by X-ray crystallography.[17] Consistent with the stoichiometry in Scheme 8, when the reaction is performed in neat C_6D_6, Ir(NN)-(NC)(C_6D_5)OTF complex (**8a-*d*$_5$**) as well as CH_3D is formed.

The preference for arene activation versus benzylic C−H bond activation was determined by heating **7a** in neat toluene (Scheme 8) at 170 °C for 4 h. Only the para and meta tolyl CH activation products were observed in a 1:1.7 ratio. Upon addition of pyridine to the reaction mixture and removal of volatiles under vacuum, the pyridine adduct [Ir(NN^{tBu})(NC)(C_6H_4-(CH_3))(C_5H_5N)]OTF (**9a-Py**) was obtained in good yields after passing through silica gel. The two isomers could not be separated. ^{1}H NMR analysis of the isolated product showed several new aromatic resonances between 7.0 and 6.6 ppm as well as two singlets for the methyl group of toluene, which is consistent with the proposed arene activation product. ^{13}C NMR also showed two methyl peaks (confirmed by DEPT) at 21.7 and 20.8 ppm also supporting arene activation. When a more sterically congested arene such as mesitylene was used, benzylic CH activation is observed. Upon heating **7a** in neat mesitylene, the stoichiometric CH activation product Ir(NN^{tBu})-(NC)($CH_2C_6H_3(CH_3)_2$)OTF is formed (Scheme 8). Addition of pyridine to the reaction mixture followed by removal of volatiles

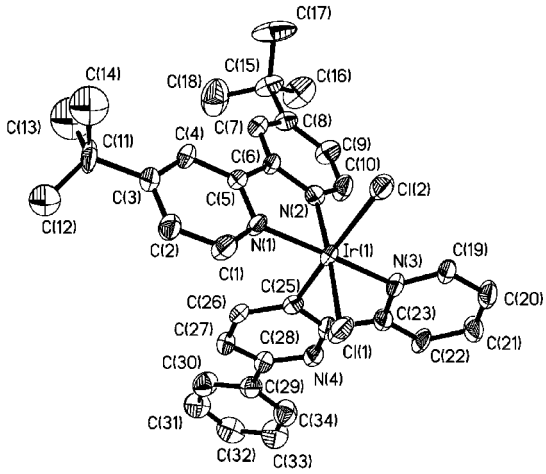


Figure 2. Thermal ellipsoid plot of Ir(NC)(NN^{tBu})Cl_2 complex **5a(NN-trans)**. Thermal ellipsoids are at 50% probability; hydrogens and water molecule were omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir(1)−C(25) 1.998(9), Ir(1)−N(2) 2.014(7), Ir(1)−N(1) 2.017(7), Ir(1)−N(3) 2.060(7), Ir(1)−Cl(1) 2.363(2), Ir(1)−Cl(2) 2.480(2); C(25)−Ir(1)−N(2) 88.7(3), C(25)−Ir(1)−N(1) 93.9(3), N(2)−Ir(1)−N(1) 79.6(3), C(25)−Ir(1)−N(3) 80.5(3), N(2)−Ir(1)−N(3) 96.1(3), N(1)−Ir(1)−N(3) 173.1(3), C(25)−Ir(1)−Cl(1) 90.9(3), N(2)−Ir(1)−Cl(1) 176.1(2), N(1)−Ir(1)−Cl(1) 96.6(2), N(3)−Ir(1)−Cl(1) 87.7(2), C(25)−Ir(1)−Cl(2) 175.8(3), N(2)−Ir(1)−Cl(2) 88.8(2), N(1)−Ir(1)−Cl(2) 88.9(2), N(3)−Ir(1)−Cl(2) 96.4(2), Cl(1)−Ir(1)−Cl(2) 91.81(9).

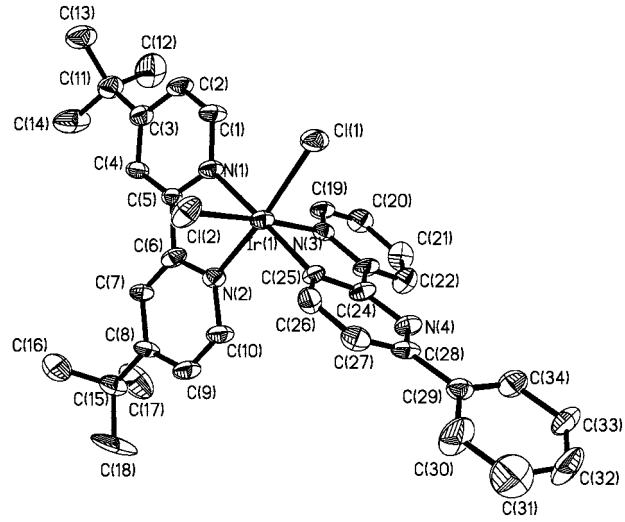


Figure 3. Thermal ellipsoid plot of Ir(NC)(NN^{tBu})Cl_2 complex **5a(NC-trans)**. Thermal ellipsoids are at 50% probability; hydrogens were omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir(1)−C(25) 1.990(9), Ir(1)−N(2) 2.016(8), Ir(1)−N(3) 2.023(8), Ir(1)−N(1) 2.103(8), Ir(1)−Cl(2) 2.334(3), Ir(1)−Cl(1) 2.353(3); C(25)−Ir(1)−N(2) 98.6(4), C(25)−Ir(1)−N(3) 80.6(4), N(2)−Ir(1)−N(3) 90.6(3), C(25)−Ir(1)−N(1) 175.9(4), N(2)−Ir(1)−N(1) 78.2(3), N(3)−Ir(1)−N(1) 96.9(3), C(25)−Ir(1)−Cl(2) 96.2(3), N(2)−Ir(1)−Cl(2) 87.7(2), N(3)−Ir(1)−Cl(2) 176.1(2), N(1)−Ir(1)−Cl(2) 86.2(3), C(25)−Ir(1)−Cl(1) 88.2(3), N(2)−Ir(1)−Cl(1) 173.3(2), N(3)−Ir(1)−Cl(1)90.7(2),N(1)−Ir(1)−Cl(1)95.1(2),Cl(2)−Ir(1)−Cl(1) 91.44(12).

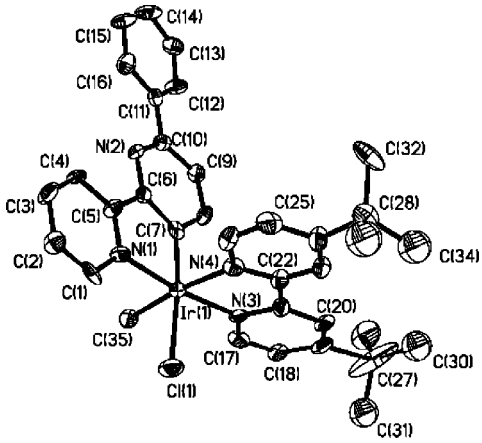
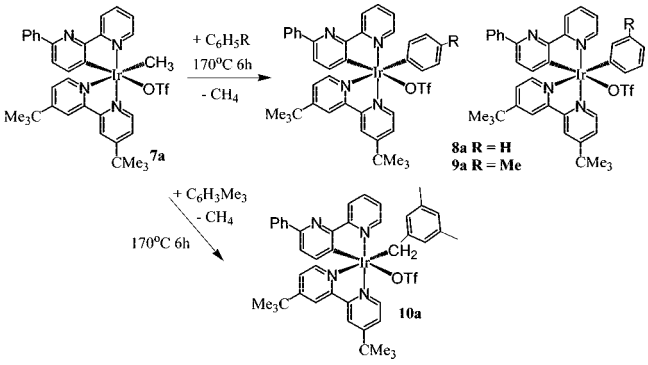


Figure 4. Thermal ellipsoid plot of Ir(NC)(NN^{tBu})ClCH$_3$ complex **6a**. Thermal ellipsoids are at 30% probability; hydrogens were omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir(1)−C(25) 1.94(2), Ir(1)−N(3) 2.053(17), Ir(1)−N(2) 2.064(16), Ir(1)−N(1) 2.132(15), Ir(1)−C(35) 2.163(17), Ir(1)−Cl(1) 2.469(6); C(25)−Ir(1)−N(3) 78.8(7), C(25)−Ir(1)−N(2) 96.3(7), N(3)−Ir(1)−N(2) 172.2(6), C25)-Ir(1)−N(1) 95.6(6), N(3)−Ir(1)−N(1) 95.8(7), N(2)−Ir(1)−N(1) 78.5(6), C(25)−Ir(1)−C(35) 88.5(7), N(3)−Ir(1)−C(35) 89.4(7), N(2)−Ir(1)−C(35) 96.7(7), N(1)−Ir(1)−C(35) 174.0(6), C(25)−Ir(1)−Cl(1) 174.3(6), N(3)−Ir(1)−Cl(1) 95.8(5), N(2)−Ir(1)−Cl(1)89.2(5),N(1)−Ir(1)−Cl(1)86.9(5),C(35)−Ir(1)−Cl(1) 89.5(6).

Scheme 8. Stoichiometric Benzene, Toluene, and Mesitylene Activation



under vacuum led to the isolation of the pyridine adduct [Ir(NN)(NC)(CH$_2$C$_6$H$_3$(CH$_3$)$_2$)(C$_5$H$_5$N)]OTF (**10a-Py**) in good yields after passing the mixture through silica gel. Formation of the benzylic activation product is supported by the appearance of two new doublets at 3.36 and 3.08, which integrate to one proton each, corresponding to the diastereotopic Ir-CH$_2$-R group in the ^{1}H NMR. The remaining methyl group (6H) at 1.78 ppm and aryl resonance signals at 6.22 (1H) and 5.66 (2H) ppm also support benzylic activation.

Since we established that **7a** is capable of performing stoichiometric arene C−H activation, we investigated whether the system is also able to promote catalytic C−H activation by examining the H/D exchange reaction between benzene and toluene-d_8. Interestingly, H/D exchange studies between benzene and toluene-d_8 at temperatures as high as 200 °C showed no observable deuterium incorporation into the benzene. When the reaction was repeated in a 1:1 benzene-h_6/toluene-h_8 mixture, analysis of the reaction mixture after treatment with pyridine showed that both the benzene and toluene CH activation products were formed in roughly a 1:1 ratio. Consistent with the stoichiometric toluene results, the tolyl products were observed as a mixture of para and meta isomers in a 1:1.8 ratio. The fact that no catalytic HD exchange is observed between tol-d_8 and C$_6$H$_6$ suggests the barrier for arene CH activation from the phenyl or tolyl complex is too high. Consistent with this observation, when **8a** was heated in benzene-d_6 at 170 °C for 12 h, **8a-*d*$_5$** was not observed and **8a** was recovered.

Significantly, the methyl triflate complex **7a** catalyzes H/D exchange between acids (acetic and trifluoroacetic acids) and benzene. When a 3.50 mM solution of **7a** in a 1:1 mixture of C$_6$H$_6$/acetic acid-d_4 was heated at 170 °C for 4 h, 11.2% of the benzene (208 turnovers, TOF = 0.014 s^{-1}) was converted into a mixture of deuterated isotopologues, which consisted mainly of C$_6$H$_5$D$_1$. Control reactions were performed to verify that the H/D exchange observed was metal mediated. In the absence of catalyst no H/D exchange between benzene and acetic acid-d_4 was observed. Catalytic activity slowly drops over time, presumably due to catalyst deactivation from formation of either the diacetate (Ir(NN)(NC)(OAc)$_2$) or acetate-bridged dinuclear complex. Consistent with the diacetate complex being an inactive species, no significant incorporation of deuterium (<1%) into benzene was observed with Ir(NN)(NC)(OAc)$_2$ at 170 °C after 4 h.

Analysis of the reaction products after H/D exchange was difficult since deuteration of the ligand had occurred. To address this, **7a** was heated in a 1:1 C$_6$H$_6$/CH$_3$CO$_2$H solution at 170 °C for 15 h. After removal of volatiles and treatment with pyridine, ^{1}H NMR analysis (see Supporting Information) showed three acetate complexes, two of which are proposed to be [Ir(NN)(NC)(OAc)(Py)]OTf (four possible complexes, Figure 5), and the third species is one of the Ir(NN)(NC)(OAc)$_2$ isomers (Figure 5). Both complexes have similar chemical shifts to independently synthesized mono- and bis-acetate complexes. There was no evidence of an Ir-phenyl species; however, this is expected since such species would not be stable in acid solvents. Consequently, when the phenyl product **8a** is dissolved in acetic acid-d_4, formation of benzene-d_1 (94.4% C$_6$H$_5$D$_1$, 4.3% C$_6$H$_6$, 0.64% C$_6$H$_4$D$_2$) is observed.

Scheme 9 shows the likely mechanism for H/D scrambling. An active five-coordinate species is generated upon triflate dissociation from intermediate **I**, which then binds (intermediate **II**) and cleaves the C−H bond of benzene to the putative iridium phenyl species (intermediate **III**). The iridium phenyl then undergoes protonalysis with DOAc to give benzene-d_1 and restart the cycle. On the basis of the observation that benzene-d_1 is the main product when **8a** is treated with acetic acid-d_4, and that H/D exchange follows a Schultz−Flory distribution (reaction mechanism where each encounter between a benzene molecule and the catalyst leads to a single H/D exchange), CH activation is most likely the rate-limiting step. If coordination is rate determining, then multiple deuterium incorporation into benzene would be expected for the stoichiometric reaction. As expected, when an H/D exchange reaction was performed with isolated Ir(NN)(NC)(OAc)OTf (**I**), the same turnover frequency (**I** = 0.015 s^{-1} versus **7a** = 0.014 s^{-1}) as **7a** was observed. Consistent with the proposed mechanism, and that CH activation occurs through a metal-mediated process, when Ir(NN)(NC)(OAc)OTf is heated in neat benzene at 160 °C for 1 h in the presence of a sterically hindered base such as ethyldiisopropylamine (1 equiv), the stoichiometric benzene activation product is formed in 76% yield based on ^{1}H NMR analysis (quantified by added mesitylene as a standard). The starting material was the only other species observed.

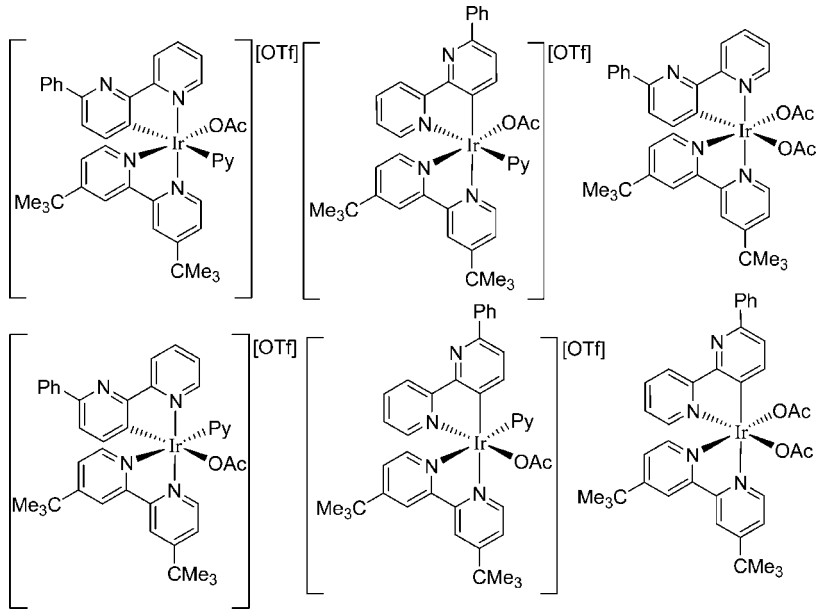
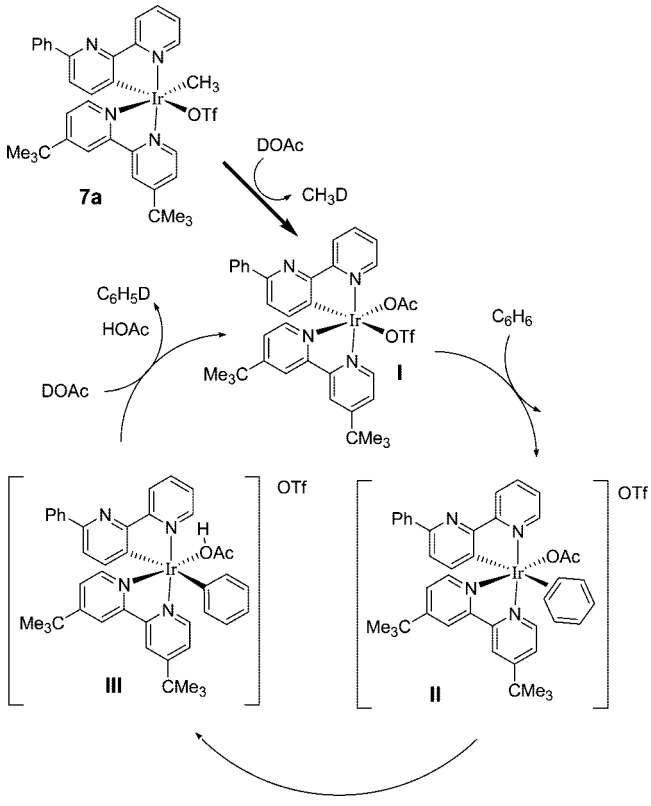


Figure 5. Possible isomers for the mono- and bis-acetate (NN^{tBu})(NC)Ir complexes.

Scheme 9. Possible Catalytic Cycle



Another possible mechanism is that the acidity of the bound acid increases, thus acting like a superacid that carries out the H/D exchange by protonating benzene. However, inconsistent with such a mechanism is the observation that H/D exchange in a stronger acid such as trifluoroacetic acid did not accelerate the rate of H/D exchange. Thus when a 2.16 mM solution of **7a** in 1:1 C_6H_6/trifluoroacetic acid-d_1 was heated at 170 °C, H/D for 5.5 h, 1.13% of the benzene (29 turnovers) was converted into a mixture of deuterated isotopologues, which consisted mainly of $C_6H_5D_1$. Benzene and trifluoroacetic acid-d_1 will undergo background H/D exchange at these temperatures, so a control was performed under identical conditions and these values were subtracted from the catalytic runs to obtain corrected values.

Experimental Section

General Considerations. Unless otherwise noted all reactions were performed using standard Schlenk techniques (argon) or in a Vacuum Atmosphere glovebox (nitrogen). $IrCl_3$ (Pressure Chemical) and $Zn(Me)_2$ (Aldrich) were used as is. All solvents were reagent grade or better. Anhydrous 2-methoxyethanol and anhydrous DMA (Sureseal bottle, Aldrich) were use as is. THF was dried over sodium/benzophenone ketyl and distilled over argon. Dichloromethane (stabilizer removed with sulfuric acid) was dried over P_2O_5 and distilled over argon. Acetic and trifluoroacetic acid were purchased from Aldrich, degassed by freeze−pump−thaw methods, and stored under argon. Deionized water was used as is. *N*-[2-Pyridyl)-2-oxoethyl]pyridinium iodide[15d] and 6-phenyl-2,2′-bipyridine[12] were prepared following literature procedures. The Mannich salts 4′-*tert*-butyl-3-(dimethylamino)-1-phenyl-1-propanone hydrochloride and 4′-hydroxy-3-(dimethylamino)-1-phenyl-1-propanone hydrochloride were prepared following standard procedures.[25] GC/MS analysis was performed on a Shimadzu GC-MS QP5000 (ver. 2) equipped with a cross-linked methyl silicone gum capillary column (DB5). ^1H (400 MHz), ^{13}C (100 MHz), and ^{19}F (376.5 MHz) NMR were collected on a Varian 400 Mercury plus spectrometer. Chemical shifts were referenced using residual protiated solvent. Fluorine chemical shifts were referenced to $CFCl_3$. All coupling constants are reported in Hz. Chemical shifts were assigned on the basis of gCOSY, NOEDIF, gHSQC, and gHMBC or cigar experiments. Mass spectrometry was performed at UCSB, UCLA, and UCR mass spectrometry laboratories. Elemental analyses were performed by Desert Analytical Laboratory, Inc., AZ. X-ray crystallography data were collected on a Bruker SMART APEX CCD diffractometer.

X-ray Structure Data Determination. Diffraction data were collected with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) on a Bruker SMART APEX CCD diffractometer. The cell parameters were obtained from the least-squares refinement of the spots (collected 60 frames) using the SMART program. A hemisphere of data was collected up to a resolution of 0.75 Å, and

(25) *Org. Synth.* **1943**, *23*, 30.

the intensity data were processed using the Saint Plus program. Absorption corrections were applied by using SADABS.[26] All calculations for the structure determination were carried out using the SHELXTL package (version 5.1).[27] Initial atomic positions were located by direct methods or by the Patterson method using XS, and the structure was refined by least-squares methods on F^2 using SHELX. Calculated hydrogen positions were input and refined in a riding manner along with the attached carbons.

Synthesis of 6-(4′′-R-phenyl)-2,2′-bipyridine (1b R = CMe$_3$, 1c R = OH). *N*-[2-(2-Pyridyl)-2-oxoethyl]pyridinium iodide (3.08 g, 9.45 mmol), ammonium acetate (20.54 g, 28.2 equiv), and acetic acid (19 mL) were heated at 115 °C until everything dissolved (∼10 min). Then the appropriate 4′-subsituted-3-(dimethylamino)-propiophenone hydrochloride (2.60 g, 9.64 mmol) was added, and the solution was refluxed for 6 h. The dark red-brown solution was reduced under vacuum, diluted with water, and neutralized with $NaHCO_3$. The solution was filtered, and the resulting red-brown residue was extracted with CH_2Cl_2 (**1b**) or acetone (**1c**). The extract was dried over $MgSO_4$, then purified by passing through silica gel with CH_2Cl_2 (**1b**) or acetone (**1c**), yielding an off-white solid.

Data for 1b. Yield: 1.69 g (60.8%). Mp = 74−76 °C. R_f(silica, CH_2Cl_2) = 0.24. Anal. Calcd for $C_{20}H_{20}N_2$: C 83.30; H 6.99; N 9.71. Found: C 83.51; H 7.28; N 9.59. HREI-MS $(M)^+$: calcd for $C_{20}H_{20}N_2$, 288.1626; found, 288.1621. ^{1}H NMR ($CDCl_3$): δ 8.71(dd, 1H, ^3J = 4.8, ^4J = 1.7, H-1), 8.65(dd, 1H, ^3J = 7.9, ^4J = 2.0, H-4), 8.37(dd, 1H, ^3J = 7.8, ^4J = 1.0, H-7), 8.11(d, 2H, ^3J = 8.7, H-12), 7.88(t, 1H, ^3J = 7.8, H-8), 7.85(dt, 1H, ^3J = 7.8, 7.6, ^4J = 1.8, H-3), 7.76(dd, 1H, ^3J = 7.8, ^4J = 1.0, H-9), 7.56(d, 2H, ^3J = 8.7, H-13), 7.32(dd, 1H, ^3J = 7.5, 4.7, ^4J = 1.2, H-2), 1.41(s, 9H, C(Me)$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 156.62(C-5), 155.79(C-6), 152.30(C-11), 150.15(C-14), 149.18(C-1), 137.74(C-8), 136.95(C-3), 136.81(C-11), 126.84(C-12), 125.83(C-13), 123.83(C-2), 121.45(C-4), 120.25(C-9), 119.13(C-7), 34.86(*C*Me$_3$), 31.49(C*Me*$_3$).

Data for 1c. Yield: 465.5 mg (60.5%). Mp = 209−213 °C. HREI-MS $(M)^+$: Anal. Calcd for $C_{16}H_{12}N_2O$, 248.0950. Found: 248.0946. Anal. Calcd for $C_{16}H_{12}N_2O$: C 77.40; H 4.87; N 11.28. Found: C 77.20; H 4.63; N 11.28. ^{1}H NMR (dmso-d_6): δ 9.81(s, 1H, OH), 8.70(dd, 1H, ^3J = 4.8, ^4J = 1.8, H-1), 8.57(dt, 1H, ^3J = 8.0, ^4J = 1.1, H-4), 8.25(dd, 1H, ^3J = 7.5, ^4J = 1.1, H-7), 8.10(d, 2H, ^3J = 8.9, H-12), 7.98(dt, 1H, ^3J = 7.8, 7.6, ^4J = 1.9, H-3), 7.95(t, 1H, ^3J = 7.8, 7.5, H-8), 7.90(dd, 1H, ^3J = 7.9, ^4J = 1.2, H-9), 7.46(dd, 1H, ^3J = 7.5, 4.8, ^4J = 1.2, H-2), 6.92(d, 2H, ^3J = 8.9, H-13). ^{13}C{^{1}H} NMR (dmso-d_6): δ 158.75(C-14), 155.59(C-5), 155.50(C-10), 154.69(C-6), 149.25(C-1), 138.17(C-8), 137.32(C-3), 129.38(C-11), 128.09(C-12), 124.19(C-2), 120.59(C-4), 119.29-(C-9), 117.94(C-7), 115.59(C-13).

Synthesis of [Ir(NC)Cl$_2$(C$_5$H$_5$N)]$_2$, 2a-Py. $IrCl_3 \cdot H_2O$ (4.06 g, 0.0116 mols), ligand **1a** (2.71 g, 0.0128 mols), and 2-methoxyethanol (50 mL) were heated at 130 °C in a Schlenk bomb[28] for 60 h. The red suspension was filtered and washed with H_2O (3 × 30 mL), MeOH (3 × 20 mL), and then ether (3 × 20 mL). The resulting red powder was extracted with pyridine, filtered over Celite, concentrated under vacuum, and then precipitated with ether. The precipitate was filtered and washed with ether. The product was then redissolved in CH_2Cl_2 and allowed to sit in the freezer (−25 °C), from which $[Ir(NC)Cl_2(C_5H_5N)]_2$ (4.49 g) fell out of solution. Suitable crystals of **2a-Py$_2$** were obtained by slow evaporation from a concentrated pyridine solution. The product obtained is of significant purity for the next step. MALDI-MS: 1111.0 (dimer − Cl)$^+$, 1077 (dimer − 2Cl)$^+$, 617.1 (monomer + Py − Cl)$^+$, 574.1 (monomer + H)$^+$. Anal. Calcd for $C_{21}H_{16}Cl_2IrN_3 \cdot 0.5C_5H_5N$: C, 46.56; H, 3.01; N, 7.92. Found: C, 46.47; H, 2.86; N, 7.93. ^{1}H NMR (dmso-d_6): δ 9.84(dd, 1H, ^3J = 5.9, ^4J = 1.6, H-1), 8.81(dd, 2H, ^3J = 6.3, ^4J = 1.6, o-Py), 8.51(d, 1H, ^3J = 8.2, H-8), 8.35(dd, 1H, ^3J = 7.9, ^4J = 1.6, H-4), 8.32(t, 1H, ^3J = 7.8, ^4J = 1.6, p-Py), 8.20(d, 2H, ^3J = 7.9, ^4J = 1.4, H-12), 7.84(t, 2H, ^3J = 7.9, 6.3, m-Py), 7.83(dt, 1H, ^3J = 7.8, 7.7, ^4J = 1.5, H-3), 7.70(d, 1H, ^3J = 8.1, H-9), 7.52(t, 2H, ^3J = 7.8, 7.5, H-13), 7.41(t, 1H, ^3J = 7.4, H-14), 7.37(dt, 1H, ^3J = 7.6, 5.9, ^4J = 1.7, H-2). ^{13}C{^{1}H} NMR (dmso-d_6): δ 166.07(C-5), 162.10(C-6), 152.94(C-1), 149.88(C-10), 144.61(o-Py), 143.32(C-7), 143.29(C-8), 143.02(p-Py), 139.55(C-11), 137.98(C-3), 128.68(C-13), 127.98(C-14), 126.14(m-Py), 125.94(C-12), 123.56(C-2), 120.20(C-4), 119.76(C-9).

Synthesis of [Ir(NC^{tBu})Cl$_2$(C$_5$H$_5$N)]$_2$, 2b-Py. $IrCl_3 \cdot H_2O$ (173.4 mg, 0.55 mmol), **1b** (158 mg, 0.55 mmol), and 2-methoxyethanol (12 mL) were heated at 130 °C in a Schlenk bomb for 16 h. The suspension was reduced to ∼1 mL, diluted with H_2O (10 mL), and then filtered. The solid was washed with H_2O and then CH_2Cl_2. The residue was then extracted with pyridine, filtered over Celite, concentrated under vacuum, and then precipitated with ether. Yield: 186 mg of crude material of suitable purity for the next step. Relatively pure material can be obtained by passing through alumina with a dichloromethane/MeOH gradient. FAB -MS: 630.2 $(M + H)^+$. ^{1}H NMR (dmso-d_6): δ 9.83(dd, 1H, ^3J = 5.9, ^4J = 1.5, H-1), 8.58(dd, 2H, ^3J = 5.7, ^4J = 1.7 o-Py), 8.48(d, 1H, ^3J = 7.9, H-8), 8.28(dd, 1H, ^3J = 7.9, ^4J = 1.8, H-4), 8.11(d, 2H, ^3J = 8.6, H-12), 7.84(dt, 1H, ^3J = 7.9, 7.4, ^4J = 1.5, H-3), 7.79(tt, 1H, ^3J = 7.6, ^4J = 1.7, p-Py), 7.65(d, 1H, ^3J = 8.0, H-9), 7.54(d, 2H, ^3J = 8.6, H-13), 7.41−7.34(m, 3H, m-Py, H-2), 1.36(s, 9H, CMe$_3$). ^{13}C{^{1}H} NMR (dmso-d_6): δ 166.30(C-5), 162.09(C-6), 152.92(C-1), 150.35(C-10), 150.07(C-14), 149.62(o-Py), 143.12(C-8), 142.73(C-7), 137.92(C-3), 136.99(p-Py), 136.14(C-11), 125.68(C-12), 125.42(C-13), 123.90(m-Py), 123.41(C-2), 120.04(C-4), 119.54(C-9), 34.35(*C*Me$_3$), 31.16(C*Me*$_3$).

Synthesis of [Ir(NC^{OH})Cl$_2$(C$_5$H$_5$N)]$_2$, 2c-Py. $IrCl_3 \cdot H_2O$ (65.1 mg, 0.21 mmol), **1c** (51.0 mg, 0.21 mmol), and 2-methoxyethanol (3 mL) were heated at 130 °C in a Schlenk bomb for 3 h. The solvent was removed under reduced pressure, and the resulting residue was washed with ether. The residue was extracted with pyridine, filtered over Celite, concentrated (1.5 mL), and then added dropwise to a 10:2 ether/methanol solution (24 mL). The precipitate was filtered and washed with more ether. Yield: 73.1 mg of **2c-Py**. HRFAB-MS $(M + H)^+$: calcd for $C_{21}H_{17}N_3OCl_2{}^{193}Ir$, 590.0378; found, 590.0379. ^{1}H NMR (dmso-d_6): δ 9.83(d, 1H, ^3J = 5.8, H-1), 8.82(dd, 2H, ^3J = 6.6, ^4J = 1.6, o-Py), 8.48(d, 1H, ^3J = 7.8, H-8), 8.35(tt, 1H, ^3J = 8.0, 6.6, ^4J = 1.7, p-Py), 8.31(dd, 1H, ^3J = 7.5, H-4), 8.02(d, 2H, ^3J = 8.8, H-12), 7.90−7.79(m, 3H, m-Py, H-3), 7.60(d, 1H, ^3J = 8.0, H-9), 7.36(dt, 1H, ^3J = 7.5, 5.8, ^4J = 1.7, H-2), 6.90(d, 2H, ^3J = 8.8, H-13). ^{13}C{^{1}H} NMR[29] (dmso-d_6): δ 166.45(C-5), 161.74(C-6), 157.60(C-14), 152.90(C-1), 150.24(C-10), 149.62(o-Py), 143.02(C-8), 141.52(C-7), 137.82(C-3), 136.14(p-Py), 130.68(C-11), 127.17(C-12), 123.92(m-Py), 123.27(C-2), 120.00(C-4), 118.79(C-9),115.39(C-13).

Synthesis of Ir(NNC^{tBu})(NC^{tBu})Cl, 3b. $IrCl_3 \cdot H_2O$ (109.8 mg, 0.35 mmol), **1b** (200 mg, 0.69 mmol), and 2-methoxyethanol (10 mL) were heated at 130 °C in a Schlenk bomb for 19 h. The solvent was removed under reduced pressure. The red residue was then passed through silica gel with CH_2Cl_2. Yield: 80.6 mg of isomer 1 and 14.2 mg of isomer 2. Data for isomer 1: HRESI-MS $(M + H)^+$: calcd for $C_{40}H_{39}ClIrN_4$, 801.2469; found, 801.2444. ^{1}H NMR ($CDCl_3$): δ 9.05(d, 1H, ^3J = 7.83, H-8), 8.35(d, 1H, ^3J = 7.43, H-4), 8.24(d, 2H, ^3J = 8.61, H-12), 8.06(d, 1H, ^3J = 5.48, H-15), 8.04(d, 1H, ^3J = 8.22, H-18), 7.89(d, 1H, ^3J = 7.83, H-23), 7.87(d, 1H, ^3J = 7.83, H-21), 7.79(d, 1H, ^3J = 7.83, H-9), 7.71(t, 1H, ^3J = 8.0, H-22), 7.68(dt, 1H, ^3J = 8.2, 7.8, ^4J = 1.57, H-17), 7.57(d, 2H, ^3J = 8.61, H-13), 7.49(d, 1H, ^3J = 8.22, H-26), 7.44(dt, 1H,

(26) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.

(27) Sheldrick, G. M. *SHELXTL*, version 5.1; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997.

(28) Thick glass walled ampule sealed with a resealable high-vac PTFE valve.

(29) ^{13}C NMR shifts were assigned on the basis of the free ligand and complexes **2a,b-Py**.

^3J = 8.61, 8.22, ^4J = 1.57, H-3), 7.30(d, 1H, ^3J = 5.48, H-1), 7.14(dd, 1H, ^3J = 7.6, 5.4, ^4J = 1.0, H-16), 6.87(dd, 1H, ^3J = 8.2, ^4J = 1.9, H-27), 6.65(d, 1H, ^4J = 2.0, H-29), 6.64(dt, 1H, ^3J = 7.5, 5.8, ^4J = 1.6, H-2), 1.42(s, 9H, CMe_3), 1.03(s, 9H, CMe_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 168.30(C-5), 165.60(C-19), 161.82(C-6), 158.83(C-20), 156.03(C-10), 154.27(C-24), 153.73(C-28), 152.79(C-15), 150.86(C-14), 149.84(C7) 148.40(C-1), 145.18(C30), 143.56(C-8), 143.06(C25), 138.36(C-11), 138.20(C-22), 137.88(C-17), 136.08(C-3), 134.41(C-29), 126.84(C-16), 125.97(C-12), 125.89(C-13), 125.00(C-26), 123.21(C-2), 123.14(C-18), 121.86(C-9), 121.11(C-4), 119.46(C-27), 118.54(C-23), 117.50(C-21), 34.86(*C*Me$_3$), 34.78(*C*Me$_3$), 31.59(C*Me*$_3$), 31.29(C*Me*$_3$).

Data for isomer 2: ^1H NMR ($CDCl_3$): δ 10.2(dd, 1H, ^3J = 5.7, ^4J = 1.6, H-1), 8.55(dd, 1H, ^3J = 8.0, ^4J = 1.6, H-4), 8.03(d, 1H, ^3J = 8.1, H-18), 7.98(m, 2H, H-3,15), 7.85(d, 2H, ^3J = 8.6, H-12), 7.81−7.73(m, 3H, H-17,21,22), 7.68(t, 1H, H-23), 7.49(dt, 1H, ^3J = 7.3, 5.8, ^4J = 1.6, H-2), 7.47(d, 1H, ^3J = 8.2, H-26), 7.39(d, 2H, ^3J = 8.6, H-13), 7.22(m, 1H, H-16), 6.98(d, 1H, ^3J = 8.0, H-8), 6.91(dd, 1H, ^3J = 8.2, ^4J = 1.9, H-27), 6.53(dd, 1H, ^3J = 8.2, ^4J = 1.9, H-9), 6.27(d, 1H, ^4J = 1.9, H-29), 1.31(s, 9H, CMe_3), 1.03(s, 9H, CMe_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 167.96(Py), 165.11(Py), 161.48(Py), 157.83(Py), 155.35(Py), 153.94(Ph), 150.98(Py), 150.95(Ph), 150.34(Py), 149.92(Py), 148.68(Py), 142.06(Ph), 141.06(Py), 138.71(Ph), 137.80(Ph), 137.48(Py), 137.30(Py), 136.76(Ph), 129.00(Py), 127.04(Py), 125.84(Ph), 125.73(Ph), 125.03(Ph), 124.04(Py), 122.95(Py), 121.24(Py), 121.09(Py), 119.37(Ph), 118.11(Py), 117.05(Py), 34.77(*C*Me$_3$), 34.71(*C*Me$_3$), 31.48(C*Me*$_3$), 31.27(C*Me*$_3$).

Synthesis of Ir(NNC)EtCl(C_2H_4), 4a. In a Schlenk bomb, $[Ir(C_2H_4)_2Cl]_2$ (868 mg, 0.969 mmol) was dissolved in CH_2Cl_2 (35 mL) and then chilled to −50 °C, and ethylene was bubbled through. In a second flask 6-phenyl-2,2′-bipyridine (450 mg, 1.94 mmol) was dissolved in CH_2Cl_2 (10 mL) and then transferred (by cannula) to the iridium solution. The flask was then washed with CH_2Cl_2 (5 mL) and then transferred over. The solution was then stirred at −50 °C for 5 min and then slowly allowed to warm to ambient temperature, after which it was allowed to stir for 16 h. The solvent was removed under vacuum, and the resulting residue was washed with ether and then passed through a silica gel plug (∼1.5 in. × 3 in.) with ether to remove a red-orange band (impurity), then ethyl acetate to remove the product. The product was then reprecipitated from CH_2Cl_2/pentane. Yield: 626.5 mg (62.7%). HRESI-MS $[2M - Cl]^+$ obsd 997.2178 calcd 997.220 (−2.2 ppm). Anal. Calcd for $C_{20}H_{20}ClIrN_2$: C, 46.55; H, 3.91; N, 5.43. Found: C, 45.32; H, 3.89; N, 5.12. ^1H NMR ($CDCl_3$): δ 9.36(d, 1H, ^3J = 5.7, H-1), 8.14(d, 1H, ^3J = 8.0, H-4), 8.02(dt, 1H, ^3J = 8.0, ^4J = 1.4, H-3), 7.94(dd, 1H, ^3J = 7.7, ^4J = 1.7, H-7), 7.85(dd, 1H, ^3J = 8.0, ^4J = 1.7, H-9), 7.81(t, 1H, ^3J = 7.8, H-8), 7.73(dd, 1H, ^3J = 8.9, ^4J = 0.9, H-15), 7.65(dd, 1H, ^3J = 7.9, ^4J = 1.7, H-12), 7.60(dt, 1H, ^3J = 7.2, 5.7, ^4J = 1.6, H-2), 7.29(dt, 1H, ^3J = 8.0, 7.3, ^4J = 1.6, H-14), 7.14(d, 1H, ^3J = 7.6, ^4J = 1.0, H-13), 4.03(s, 4H, C_2H_4), 0.48(m, 1H, $-CH_2$-CH_3), 0.22(m, 1H, $-CH_2$-CH_3), −0.29(t, 3H, $-CH_2$-CH_3), $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 164.27(C-16), 158.76(C-5), 153.74(C-6), 151.94(C-1), 145.14(C-10), 144.77(C-11), 139.17(C-3), 138.53(C-8), 135.25(C-15), 132.00(C-14), 127.80(C-13), 125.49(C-2), 123.74(C-12), 123.20(C-4), 119.52(C-9), 118.88(C-7), 67.08(C_2H_4), 14.70($-CH_2CH_3$), −7.13(CH_2CH_3).

Synthesis of Ir(NC)(NN^{tBu})Cl$_2$, 5a. 2a-Py (500 mg, 0.87 mmol) and 4,4′-di-*tert*-butyldipyridyl (257.4 mg, 0.96 mmol) were heated in DMA (10 mL) at 160 °C for 20 h. The solution was filtered through Celite, and the solvent was removed under vacuum. The red residue was extracted with CH_2Cl_2 and passed through silica (15−40 μm) with CH_2Cl_2, yielding 174.4 mg of **5a(NN-trans)** and 148.0 mg of **5a(NC-trans)**.

Data for **5a(NN-trans):** Anal. Calcd for $C_{34}H_{35}Cl_2IrN_4$: C, 53.54; H, 4.62; N, 7.34; Cl, 9.30. Found: C, 53.45; H, 4.91; N, 7.16; Cl, 9.59. MALDI-MS (DHB matrix): 845 $(M - 2Cl + DHB)^+$, 801 $(M + K)^+$, 727 $(M - Cl)^+$. ^1H NMR ($CDCl_3$): δ 10.01(dd, 1H, ^3J = 5.8, ^4J = 1.5, H-1), 9.97(d, 1H, ^3J = 6.3, H-24), 8.69(bs, 1H, H-4), 8.05(d, 1H, ^4J = 2.0, H-21), 7.98−7.92(m, 3H, H-3, H-12), 7.93(d, 1H, ^4J = 2.0, H-18), 7.71(dd, 1H, ^3J = 6.3, ^4J= 2.0, H-23), 7.51(d, 1H, ^3J = 6.3, H-15), 7.50(dt, 1H, ^3J = 7.4, 5.8, H-2), 7.43(t, 2H, ^3J = 7.4, 7.2, H-13′), 7.36(t, 1H, ^3J = 7.2, ^4J = 1.4, H-14), 7.21(d, 1H, ^3J = 8.0, H-8), 7.13(dd, 1H, ^3J = 6.3, ^4J = 2.0, H-16), 6.68(d, 1H, ^3J = 8.0, H-9), 1.54(s, 9H, CMe_3), 1.32(s, 9H, CMe_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 165.36, 162.96, 162.74, 162.15, 157.91, 157.79, 151.82, 151.66, 151.61, 149.42, 140.07, 139.70, 138.75, 137.17, 128.77, 128.32, 126.32, 124.85, 124.80, 124.71, 121.76, 121.23, 119.83, 119.58, 35.75(*C*Me$_3$), 35.52(*C*Me$_3$), 30.76, (C*Me*$_3$) 30.44(C*Me*$_3$).

Data for **5a(NC-trans)**: MALDI-MS (DHB matrix): 845 $(M - 2Cl + DHB)^+$, 801 $(M + K)^+$, 785 $(M + Na)^+$, 763 $(M + H)^+$, 727 $(M - Cl)^+$. ^1H NMR ($CDCl_3$): δ 9.96(d, 1H, ^3J = 5.8, H24), 8.92(d, 1H, ^3J = 8.0, H8), 8.50(dd, 1H, ^3J = 8.0, ^4J = 1.5, H-1), 8.23(dd, 2H, ^3J = 8.2, ^4J = 1.3, H-12), 8.20(d, 1H, ^4J = 1.8, H21), 8.02(d, 1H, ^4J = 2.0, H18), 7.98(d, 1H, ^3J = 6.3, H15), 7.90(dd, 1H, ^3J = 5.8, ^4J = 1.9, H23), 7.80(d, 1H, ^3J = 8.0, H9),7.64(dt, 1H, ^3J = 7.8, 7.6, ^4J = 1.6, H2), 7.55(m, 3H, H4,13), 7.45(t, 1H, ^3J = 7.4, H14), 7.10(d, 1H, ^3J = 6.3, ^4J = 2.1, H16), 6.95(dt, 1H, ^3J = 7.4, 5.8, ^4J = 1.6, H3), 1.58(s, 9H, CMe_3), 1.35(s, 9H, CMe_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 167.58, 163.37, 162.83, 162.07, 158.56, 155.91, 153.76, 151.99, 149.59, 149.33, 143.18, 140.41, 137.94, 128.81, 128.18, 126.61, 125.19, 124.43, 124.02, 122.26, 121.92, 119.98, 119.51, 35.86(*C*Me$_3$), 35.42(*C*Me$_3$), 30.85(C*Me*$_3$), 30.50(C*Me*$_3$).

Synthesis of Ir(NC)(NN^{tBu})CH$_3$Cl (6a). The dichloride **5a** (148.0 mg, 0.19 mmol) and $Zn(Me)_2$ 2 M in toluene (200 uL, 0.40 mmol) were heated in THF (8 mL) at 110 °C. The black solution was quenched with methanol. The solvent was removed under vacuum, and the red residue was extracted with CH_2Cl_2 and filtered through Celite. It was then purified by passing through silica with CH_2Cl_2 followed by ether. Yield: 101.8 mg (70.7% of **6a**). MALDI-MS (DHB matrix): 845.4 $(M - Cl + DHB + H)^+$, 743.3 $(M + H)^+$, 727.3 $(M - CH_3)^+$, 707.4 $(M - Cl)^+$. Anal. Calcd for $C_{35}H_{38}ClIrN_4 \cdot 0.25C_6H_6$: C, 57.54; H, 5.23; N, 7.35; Cl, 4.65. Found: C, 57.89; H, 5.54; N, 7.25; Cl, 4.41. ^1H NMR ($CDCl_3$): δ 9.89(dd, 1H, ^3J = 5.7, ^4J = 1.6, H-1), 9.26(d, 1H, ^3J = 6.1, H-24), 8.47(dd, 1H, ^3J = 7.9, ^4J = 1.6, H-4), 8.11(d, 1H, ^4J = 1.9, H-21), 8.05(dd, 2H, ^3J = 8.0, ^4J = 1.6, H-12), 8.02(d, 1H, ^4J = 1.9, H-18), 7.86(dt, 1H, ^3J = 7.6, ^4J = 1.6, H-3), 7.75(d, 1H, ^3J = 5.7, H-15), 7.59(dd, 1H, ^3J = 6.1, ^4J = 2.0, H-23), 7.43(t, 2H, ^3J = 7.6, 7.4, H-13), 7.33−7.38(m, 2H, H-2,14), 7.21(dd, 1H, ^3J = 5.7, ^4J = 1.9, H-16), 7.15(d, 1H, ^3J = 8.0, H-8), 6.69(d, 1H, ^3J = 8.0, H-9), 1.54(s, 9H, CMe_3), 1.35(s, 9H, CMe_3), 0.66(s, 3H, Ir-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 165.58, 162.79, 161.04, 160.92, 159.20, 155.35, 154.06, 150.99, 150.41, 148.82, 148.06, 145.67, 140.39, 139.07, 136.58, 128.78, 127.76, 125.90, 124.45, 124.40, 124.05, 120.93, 119.75, 119.20, 35.47(*C*Me$_3$), 35.37(*C*Me$_3$), 30.71(C*Me*$_3$), 30.52(C*Me*$_3$), −16.09(Ir-Me).

Synthesis of Ir(NC)(NN^{tBu})CH$_3$OTf (7a). Silver triflate (385.3 mg, 1.50 mmol) and **6a** (1.01 g, 1.36 mmol) were stirred in the dark for 2 days in CH_2Cl_2 (25 mL). The yellow-orange suspension was filtered over Celite and washed with CH_2Cl_2. The solvent was removed under reduced pressure. The orange-red residue was then redissolved in CH_2Cl_2 and passed through a silica gel plug, and the product (orange band) was removed with ether. The solvent was removed under reduced pressure, and the product was recrystallized from CH_2Cl_2/ether at −35 °C. Yield: 966.4 mg (82.8% isolated yield). Anal. Calcd for $C_{36}H_{38}F_3IrN_4O_3S$: C, 50.51; H, 4.47; N, 6.55; F, 6.66. Found: C, 50.20; H, 4.75; N, 6.31; F, 6.39. ESI-MS: 857.2 $(M + H)^+$, 841.2 $(M - CH_3)^+$, 748.3 $(M - OTf + NCCH_3)^+$, 707.3 $(M - OTf)^+$. ^1H NMR (CD_2Cl_2): δ 9.21(d, 1H, ^3J = 6.2, H-24), 9.07(d, 1H, ^3J = 5.8, H-1), 8.43(d, 1H, ^3J = 8.1, H-4), 8.17(d, 1H, ^4J = 2.1, H-21), 8.09(d, 1H, ^4J = 1.9, H-18),

7.99(d, 2H, ^3J = 8.3, ^4J = 1.4, H-12), 7.93(dt, 1H, ^3J = 7.8, 7.7, ^4J = 1.5, H-3), 7.73(d, 1H, ^3J = 5.9, H-15), 7.65(dd, 1H, ^3J = 6.2, ^4J = 2.2, H-23), 7.48(dt, 1H, ^3J = 7.3, 5.8, ^4J = 1.5, H-2), 7.40(t, 2H, ^3J = 8.4,7.8, H-13), 7.33(dt, 1H, ^3J = 7.4, ^4J =1.5, H-14), 7.29(dd, 1H, ^3J = 5.9, ^4J = 1.8, H-16), 7.07(d, 1H, ^3J = 8.1, H-8), 6.46(d, 1H, ^3J = 8.1, H-9), 1.54(s, 9H, CMe_3). 1.35(s, 9H, CMe_3), 0.58(s, 3H, Ir-Me). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 164.88, 163.28, 162.84, 162.78, 160.27, 156.38, 151.23, 149.62, 149.23, 148.61, 140.39, 139.61, 137.75, 135.24, 129.15, 128.37, 126.20, 125.15, 124.90, 124.69, 121.53, 120.89, 120.75, 119.72, 35.99(*C*Me$_3$), 35.89(*C*Me$_3$), 30.75(C*Me*$_3$), 30.56(C*Me*$_3$), −14.56(Ir-Me). ^{19}F NMR ($CDCl_3$): δ −79.0.

Synthesis of Ir(NC)(NN^{tBu})(C$_6$H$_5$)OTf (8a). In a Schlenk bomb complex **7a** (100 mg, 0.12 mmol) was heated at 170 °C in benzene (30 mL) for 6.5 h. The solvent was then removed under reduced pressure. The resulting yellow microcrystalline solid was redissolved in a minimal amount of CH_2Cl_2 and reprecipitated with pentane, yielding 103.9 mg (96.9%) of **8a**. Anal. Calcd for **8a**: C, 53.64; H, 4.39; N, 6.10,; F, 6.21. Found: C, 53.30; H, 4.31; N, 6.03; F 6.33. ^1H NMR ($CDCl_3$): δ 9.18 (d, 1H, ^3J = 5.9, H-1), 8.89 (d, 1H, ^3J = 6.1, NN^{tBu}), 8.40 (d, 1H, ^3J = 8.1, H-4), 8.13 (d, 1H, ^4J = 2.0, NN^{tBu}), 8.07 (d, 1H, ^4J = 1.8, NN^{tBu}), 8.04 (d, 2H, ^3J = 7.3, H-12), 7.82(dt, 1H, ^3J = 7.8, ^4J = 1.4, H-3), 7.61 (d, 1H, ^3J = 5.9, NN^{tBu}), 7.46−7.32(m, 5H, H-2, 13, 14, NN^{tBu}), 7.27(dd, 1H, ^3J = 5.9, ^4J = 1.8, NN^{tBu}), 7.17 (d, 1H, ^3J = 8.2, H-8), 7.11−6.60(bs, Ph), 6.86(bt, 1H, ^3J = 7.0, Ph), 6.53(d, 1H, ^3J = 8.1, H-9), 1.50(s, 9H, CMe_3), 1.35(s, 9H, CMe_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 161.17, 162.55, 161.90, 159.06, 156.14, 152.80, 149.82, 149.08, 148.17, 139.41, 138.97, 137.60, 137.51, 135.45, 128.64, 128.28, 128.03, 126.45, 125.72, 124.56, 124.25, 124.18, 122.39, 121.14, 120.86(q, CF_3, J = 318.6), 120.66, 119.31, 118.88, 35.43(*C*Me$_3$), 35.36(*C*Me$_3$), 30.38(C*Me*$_3$), 30.26(C*Me*$_3$). ^{19}F NMR ($CDCl_3$): δ −78.97.

Synthesis of [Ir(NC)(NN^{tBu})(C$_6$H$_5$)(C$_6$H$_5$N)]OTf (8a-py). In a Schlenk bomb **8a** (20 mg, 0.0218 mmol) was dissolved in 1:1 pyridine/CH_2Cl_2 (4 mL). The yellow solution was stirred for 30 min. Then the solvent was removed under reduce pressure. Suitable crystals for X-ray diffraction were grown overnight in a NMR tube from a concentrated solution in $CDCl_3$. ^1H NMR ($CDCl_3$): δ 9.16(d, 1H, ^3J = 6.3, H-15 or 24), 8.59(d, 1H, ^3J = 5.6, H-1), 8.50(d, 2H, ^3J = 5.4, *o*-Py), 8.41(dd, 1H, ^3J = 8.0, ^4J = 1.2, H-4), 8.16(d, 1H, ^4J = 2.0, NN^{tBu}), 8.10(d, 1H, ^4J = 1.9, NN^{tBu}), 7.99(d, 2H, ^3J = 7.3, H-12), 7.90(dt, 1H, ^3J = 7.8, H-3), 7.90(d, 1H, ^3J = 5.9, NN^{tBu}), 7.86(dt, 1H, ^3J = 7.7 ^4J = 1.4 *p*-Py), 7.60(dd, 1H, ^3J = 6.1, ^4J = 2.2, NN^{tBu}) 7.53−7.58(m, 2H, NN^{tBu}, H-2), 7.46(t, 2H, ^3J = 6.7, *m*-py), 7.40(t, 2H, ^3J = 7.7, 7.1, H-13), 7.33(dt, 1H, ^3J = 7.3, ^4J = 2.3, 1.4, H-14), 7.28(d, 1H, ^3J = 7.9, H-8), 7.06(bs, 2H, Ph), 6.88(bm, 3H, Ph), 6.69(d, 1H, ^3J = 7.9, H-9), 1.49(s, 9H, CMe_3), 1.35(s, 9H, CMe_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 165.61, 163.78, 163.72, 162.14, 158.52, 154.38, 151.93, 151.21, 151.17, 149.18, 149.00, 142.50, 139.57, 138.79, 138.58, 137.10, 128.87, 128.47, 127.14, 126.88, 126.10, 125.90, 125.03, 122.81, 122.17, 121.40, 120.94, 120.54, 35.92, 35.86, 30.58, 30.45. ^{19}F NMR ($CDCl_3$): δ −78.53.

Synthesis of [Ir(NC)(NN^{tBu})(tolyl)(C$_6$H$_5$N)]OTf (9a-py). A Schlenk bomb containing 80.1 mg of **7a** (0.0936 mmol) in 15 mL of toluene was heated at 170 °C for 4 h. After cooling, ∼3 mL of pyridine was added. The yellow solution was stirred for 30 min. Then the solvent was removed under reduced pressure. The resulting yellow solid was redissolved in CH_2Cl_2 and reprecipitated with pentane, yielding the stoichiometric CH activation product as a yellow powder in quantitative yields (94.2 mg). MALDI-MS: 845 (M − tolyl − Py − OTf + matrix)$^+$, 783 (M − Py − OTf)$^+$, found 783.2958, calc 783.3033. ^1H NMR ($CDCl_3$): δ 9.19(d, 1H, ^3J = 6.0, NN^{tBu}), 8.60(d, 1H, ^3J = 6.0, H-1 for meta isomer), 8.58(d, 1H, ^3J = 6.0, H-1 for para isomer), 8.51(d, 2H, ^3J = 5.5, *o*-Py), 8.41(dd, 1H, ^3J = 7.9, ^4J = 0.6, H-4), 8.14(d, 1H, ^4J = 1.9, NN^{tBu}), 8.08(d, 1H, ^4J = 1.9, NN^{tBu}), 7.99(dd, 2H, ^3J = 7.1, H-12), 7.88−7.94(m, 2H, H-3, NN^{tBu}), 7.85(t, 1H, ^3J = 7.8, *p*-Py), 7.52−7.60(m, 3H, H-2, NN^{tBu}),7.56(t, 2H ^3J = 7, *m*-Py), 7.40(dt, 2H ^3J = 7.8, 7.0, ^4J = 1.5, H13), 7.33(dt, 1H, ^3J = 7.8, H14), 7.31(d, 1H, ^3J = 7.9, H-8), 6.93(bd, 0.7H, ^3J = 7.8, tolyl), 6.85(bd, 2H, *o*,*p*-tolyl for meta isomer), 6.77(t, 1H, ^3J = 7.7, 7.3, *m*-tolyl for meta isomer), 6.66−6.73(m, 3H, *o*-tolyl for para isomer, *o*-tolyl for meta isomer, H-9), 2.17(s, 1H, *p*-tolyl-CH_3), 2.09(s, 2H, *m*-tolyl-CH_3), 1.49(s, 9H, CMe_3), 1.35(s, 9H, CMe_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 166.15, 164.36, 164.33, 164.27, 162.20, 162.17, 158.36, 155.30, 155.27, 152.02, 152.01, 151.76, 151.50, 151.48, 149.33, 149.29, 148.64, 148.58, 142.99, 140.76, 140.72, 139.94, 139.62, 139.11, 139.06, 138.57, 137.17, 136.51, 135.82, 132.66, 132.30, 129.13, 128.74, 128.50, 127.49, 127.18, 127.08, 127.03, 127.00, 126.56, 126.40, 125.99, 125.93, 125.83, 125.78, 124.09, 122.45, 122.43, 121.78, 121.45, 121.57(q, J = 320, OTf), 121.01,, 36.12, 36.10, 30.57, 30.47, 21.67, 20.83. ^{19}F NMR ($CDCl_3$): δ −78.5.

Reaction of 7a with Mesitylene. A Schlenk bomb containing 81.7 mg of **7a** (0.0936 mmol) in 15 mL of mesitylene was heated at 170 °C for 16 h. After cooling, ∼3 mL of pyridine was added. The yellow solution was stirred for 30 min. Then the solvent was removed under reduced pressure. The resulting yellow solid was redissolved in CH_2Cl_2 and reprecipitated with pentane, yielding the stoichiometric CH activation product [Ir(NC)-(NN^{tBu})(mesityl)(C$_6$H$_5$N)]OTf (**10a-Py**) as a yellow powder (90% conversion by NMR). MALDI-MS (2,5-DHB matrix): 811 (M − Py − OTf)$^+$, 845 (M − mesityl − Py − OTf + matrix)$^+$. ^1H NMR ($CDCl_3$): δ 9.18(d, 1H, ^3J = 6.1, H-1), 8.65(d, 2H, *o*-Py), 8.20(dd, 1H, ^3J = 8.0, ^4J = 2, H-4), 8.19(d, 1H, NN^{tBu}), 8.07(d, 1H, NN^{tBu}), 8.00(d, 2H, H-12), 7.94(dt, 1H, ^3J = 7.6, H-3), 7.92 (d, 1H, NN^{tBu}), 7.77(dd, 1H, NN^{tBu}), 7.70(m, 2H, NN^{tBu}), 7.59(t, 2H, *m*-Py), 7.42 (m, 4H, H-2, NN^{tBu}), 7.35 (dt, 1H, H-14), 7.19(d, 1H, H-8), 7.11 (dt, 1H, Py), 6.53 (d, 1H, H-9), 6.24(s, 1H, mesityl), 5.65(s, 2H, mesityl), 3.30(d, 1H ^3J = 9.2, −CH_2-ArMe$_2$), 3.03(d, 1H ^3J = 9.2, −CH_2-ArMe$_2$), 1.79(s, 6H, −CH_2-ArMe$_2$), 1.43 (s, 9H, CMe_3), 1.30 (s, 9H, CMe_3). ^{19}F NMR ($CDCl_3$): δ −78.59.

Reaction of 7a with Acetic Acid. In a 30 mL screw cap vial **7a** (214 mg, 0.29 mmol) was dissolved in acetic acid (10 mL) and stirred for 2 h. The solution was then diluted with water (20 mL) and extracted with CH_2Cl_2 (2 × 10 mL). The extracts were then washed with water and dried with $MgSO_4$. The solvent was removed under vacuum, and the resulting orange residue was sonicated with ether, then precipitated with pentane. The product was obtained as a yellow-orange powder after redissolving and precipitating with pentane. Yield: 127 mg of Ir(NN)(NC)OAcOTf (48.9%). ^1H NMR analysis of the supernatant showed some of the diacteate complex Ir(NN)(NC)(OAc)$_2$.

Data for Ir(NN)(NC)OAcOTf: Anal. Calcd for $C_{37}H_{38}F_3IrN_4O_5S \cdot H_2O$: C, 48.41; H, 4.39; N, 6.10. Found: C, 48.36; H, 4.13; N, 6.06. HRESI-MS: (M − OTf)$^+$ calc for $C_{36}H_{38}IrN_4O_2$ 751.2624, found 751.2625 (0.1 ppm). ^1H NMR ($CDCl_3$): δ 9.27(d, 1H, ^3J = 5.4, H-1), 8.84(d, 1H, ^3J = 6.1, NN^{tBu}), 8.58(dd, 1H, ^3J = 8.0, ^4J = 0.9, H-4), 8.23(d, 1H, ^4J = 1.9, NN^{tBu}-H), 8.07(d, 1H, ^4J = 1.9, NN^{tBu}), 7.99−8.04(m, 3H, H-3, *o*-Ph), 7.77(dd, 1H, ^3J = 6.1, ^4J = 1.9, NN^{tBu}), 7.59(dt, 1H, ^3J = 7.5, 5.8, ^4J = 1.5, H-2), 7.44(t, 2H, ^3J = 7.7, 7.1, *m*-Ph), 7.40(d, 1H, ^3J = 6.2, NN^{tBu}), 7.37(t, 1H, ^3J = 7.1, *p*-Ph), 7.23(d, 1H, ^3J = 8.1, H-8), 7.18(dd, 1H, ^3J = 6.2, ^4J = 2.1, NN^{tBu}), 6.54(d, 1H, ^3J = 8.0, H-9), 1.86(s, 3H, OAc), 1.57(s, 3H, CMe_3), 1.35(s, 3H, CMe_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 184.35(OAc), 165.11, 164.91, 164.06, 163.03, 158.42, 158.27, 152.55, 150.96, 150,45, 149.16, 140.79, 139.87, 139.21, 130.47, 128.92, 128.77, 126.35, 125.07, 124.95, 122.00, 121.97, 121.24, 121.20, 120.91, 120.42(q, J_{C-F} = 321.7, OTF), 118.82, 36.11, 35.74, 30.64, 30.33, 24.54(OAc). ^{19}F NMR ($CDCl_3$): δ −78.91.

Data for Ir(NN)(NC)(OAc)$_2$: HRESI-MS: (M − OAc)$^+$ calc for $C_{36}H_{38}IrN_4O_2$ 751.2624, found 751.2613 (1.5 ppm). ^1H NMR ($CDCl_3$): δ 9.42(d, 1H, ^3J = 6.2, NN^{tBu}-H), 9.37(d, 1H, ^3J = 5.9,

H-1), 8.51(dd, 1H, ^3J = 8.1, H-4), 8.02(d, 1H, ^4J = 2.0, NN^{tBu}-H), 7.99(d, 2H, ^3J = 8.0, *o*-Ph), 7.91(dt, 1H, ^3J = 7.8, H-3), 7.84(d, ^4J = 1.9, NN^{tBu}-H), 7.71(dd, 1H, ^3J = 6.0, ^4J = 2.0, NN^{tBu}-H), 7.46(dt, 1H, ^3J = 7.4, 5.9, ^4J = 1.8, H-2), 7.39(t, 2H, ^3J = 7.4, m-Ph), 7.36(d, 1H, ^3J = 5.9, NN^{tBu}-H), 7.30(t, 1H, ^3J = 7.1, *p*-Ph), 7.13(dd, 1H, ^3J = 8.0, H-8), 6.98(d, 1H, ^3J = 6.0, ^4J = 2.0, NN^{tBu}-H), 6.53(d, 1H, ^3J = 8.0, H-9), 1.93(s, 3H, OAc), 1.89(s, 3H, OAc), 1.53(s, 3H, CMe_3), 1.29(s, 3H, CMe_3).

Reaction of 7a with Trifluoroacetic Acid. In a 30 mL screw cap vial **7a** (183 mg, 0.25 mmol) was dissolved in trifluoroacetic acid (10 mL) and stirred for 2 h. The solution was reduced by half, then diluted with water (20 mL) and extracted with CH_2Cl_2 (2 × 10 mL). The extracts were then washed with water and dried with $MgSO_4$. The solvent was removed under vacuum, and the resulting yellow-orange residue was sonicated with ether, then precipitated with pentane. The product was obtained as a yellow powder after redissolving and precipitating with pentane. Yield: 172.7 mg of Ir(NN)(NC)$(TFA)_2$ (76.3%). Anal. Calcd for $C_{38}H_{35}F_6IrN_4O_4$: C, 49.72; H, 3.84; N, 6.10. Found: C, 49.36; H, 3.68; N, 5.95. HRESI-MS: calc for $C_{36}H_{35}F_3IrN_4O_2$ 805.2342, found 805.2326 (1.9 ppm). ^{1}H NMR ($CDCl_3$): δ 9.41(d, 1H, ^3J = 5.6, H-1), 9.36(d, 1H, ^3J = 6.1, H-24), 8.55(d, 1H, ^3J = 8.0, H-4), 8.06(d, 1H, ^4J = 2.0, H-21), 8.01−7.96(m, 3H, H-3,12), 7.89(d, 1H, ^4J = 2.0, H-18), 7.82(dd, 1H, ^3J = 6.1, ^4J = 2.1, H-22), 7.56(t, 1H, ^3J = 7.4, 5.7, ^4J = 1.6, H-2), 7.41(t, 2H, ^3J = 7.8, 7.3, H-13), 7.33(t, 1H, ^3J = 7.4, H-14), 7.31(d, 1H, ^3J = 6.3, H-15), 7.17(d, 1H, ^3J = 8.0, H-8), 7.09(dd, 1H, ^3J = 6.3, ^4J = 2.0, H-16), 6.41(d, 1H, ^3J = 8.0, H-9), 1.56(s, 9H, CMe_3), 1.31(s, 9H, CMe_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.77, 163.74, 163.71, 163.23(q, J = 36.1, O*C*(O)CF_3), 162.98(q, J = 37.0, O*C*(O)CF_3), 162.77, 159.53, 158.12, 151.87, 150.00, 149.89, 149.36, 140.42, 139.45, 139.39, 131.11, 128.81, 128.52, 126.32, 124.66, 124.40, 124.34, 121.59, 120.55, 119.48, 119.17, 113.98(q, J = 36.1, OC(O)*CF_3*), 116.05(q, J = 36.1, OC(O)*CF_3*), 35.90, 35.54, 30.76, 30.44. ^{19}F NMR ($CDCl_3$): δ −75.66, −75.79.

Reaction of Ir(NN)(NC)OAcOTf with Benzene and Base. In a 10 mL Schlenk bomb Ir(NN)(NC)OAcOTf (33.1 mg, 0.0368 mmol) and Hunig's base (6.4 uL) were heated in benzene (5 mL) at 160 °C for 1 h. After cooling to ambient temperature, 2 mL of pyridine was added. The product was then obtained as a yellow power by adding the solution dropwise to pentane (∼30 mL). The suspension was centrifuged and decanted, and 5 uL of mesitylene and 1 mL of $CDCl_3$ were added. The solution was then analyzed by ^{1}H NMR, which showed two species, **8-Py** (76%) and Ir(NN)(NC)OAcOTf (24%).

H/D Exchange Studies. Catalytic H−D exchange reactions were quantified by monitoring the increase of deuterium into C_6H_6 by GC/MS analyses. This was achieved by deconvolution of the mass fragmentation pattern obtained from the MS analysis, using a program developed with Microsoft EXCEL.[11] An important assumption used in the program is that there are no isotope effects on the fragmentation pattern of the benzenes due to replacement of H with D. Fortunately, because of the relative stability of the parent ion toward fragmentation, it can be used reliably to quantify the exchange reactions. The mass range from 78 to 84 (for benzene) was examined for each reaction and compared to a control reaction where no metal catalyst was added. The program was calibrated with known mixtures of benzene isotopoloques. The results obtained from this method are reliable to within 5%.

H−D Exchange Experiments. In a typical experiment, a homogeneous solution of **7a** (5−10 mg) in a benzene/deuterium source solvent mixture (toluene-d_8, acetic acid-d_4, or trifluoroacetic acid-d_1) (2 mL, 1:1 volume ratio) was heated at 170 °C in a Schlenk bomb. The liquid phase was then analyzed by GC/MS to determine the extent of H/D exchange. TON was calculated as moles of product/moles of catalyst. Benzene and trifluoroacetic acid-d_1 showed background H/D exchange, so a control was also performed. The control values were subtracted from the catalytic values to obtain corrected values.

Conclusions

In the attempt to synthesize discrete monoligated tridentate iridium NNC complexes several new bindentate iridium NC complexes, $[Ir(R\text{-}NC)Cl_2(C_5H_5N)]_2$ (**2a**−**c-Py**), and mixed tridentate, bidentate iridium complexes, Ir(NNC)(NC)Cl (**3a,b**), have been synthesized. However, when an Ir^I precursor such as $[Ir(ethylene)_2Cl]_2$ was used, the desired mononuclear tridentate Ir(NNC)Cl(ethyl)(ethylene) complex (**4**) was formed cleanly. On the basis of the previously successful cis-, bis-bidentate motif, we were able to convert the bidentate NC dinuclear complexes (**2a,b-Py**) into a thermally and protic stable cis-, bis-bidentate complex, Ir(NN^{tBu})(NC)MeOTf (**7a**), which is stable in acids and arene solvents at 200 °C. While these complexes do not activate methane, they cleanly activate arene substrates such as benzene, toluene, and mesitylene, as well as undergo catalytic H/D exchange with benzene in the presence of acids (acetic and trifluoroacetic acid).

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Supporting Information Available: Crystallographic data and parameters (cif) as well as spectroscopic details are available, free of charge, via the Internet at http://pubs.acs.org.

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