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# Tautomerization of Pyridine and 2-Substituted Pyridines to Pyridylidene Ligands by the Iridium(I)−Diene Complex $Tp^{Me2}Ir(\eta^4\text{-}CH_2{=}C(Me)C(Me){=}CH_2)$

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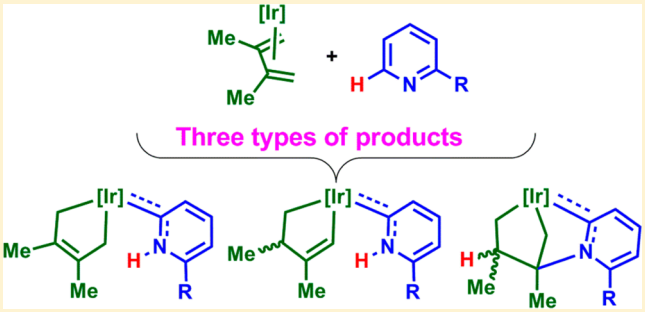
Supporting Information

**ABSTRACT:** The complex $Tp^{Me2}Ir(\eta^4\text{-}CH_2{=}C(Me)C(Me){=}CH_2)$ (**3**; $Tp^{Me2}$ = hydrotris(3,5-dimethylpyrazolyl)borate) reacts with pyridines $NC_5H_4$-2-R (R = H, Me, $SiMe_3$, F, OMe, $NMe_2$, C(=O)Me) in cyclohexane, with formation of Ir(III) products whose natures depend strongly on the reaction conditions and on the R substituent. The simplest case is for R = $NMe_2$, C(=O)Me, where $\kappa^2{:}\sigma^2$-but-2-enediyl N−H pyridylidenes, i.e. the result of the metal-promoted tautomerization of the pyridines, are the only species obtained from 60 to 150 °C. For R = Me, F the N-bonded adducts $Tp^{Me2}Ir(\kappa^2\text{-}CH_2C(Me){=}C(Me)CH_2)(NC_5H_4\text{-}2\text{-}R)$ are formed at 60 °C but, under harsher conditions (120−150 °C), the observed products are, exclusively and respectively, the N−H pyridylidene and a bicyclic carbene compound derived from the formal, trans-stereospecific transfer of the N−H hydrogen of the corresponding (not observed) pyridylidene onto one of the carbons of the C=C double bond of the but-2-enediyl moiety, the other experiencing C−N formation. For R = OMe, the N adduct formed at 60 °C transforms, at higher temperatures, into a mixture of the N−H pyridylidene and the bicyclic carbene, with no further evolution. More complex behavior is observed for the rest of the pyridines studied. Thus, when R = $SiMe_3$, in addition to the expected N−H pyridylidene, two isomeric N−H pyridylidenes containing a $\kappa^2{:}\sigma^2$-but-1-enediyl coligand are also formed under kinetic control (60 °C) but with both cleanly transforming into the former compound at higher temperatures. Finally, for R = H only the N adduct is formed under kinetic control at 25 °C but this species transforms almost completely into a mixture of the N−H pyridylidene and two epimeric, N−C bicyclic carbenes after prolonged heating at 150 °C. A detailed study of the temperature-dependent behavior of **3** in $C_6H_6$ has also been undertaken, revealing the interesting deuteration of its $=CH_2$ termini by $C_6D_6$.




## INTRODUCTION

In two recent papers we have reported on the synthesis and reactivity[1] of a series of Ir(III) NHC carbenes (pyridylidenes[2]) of formula $Tp^{Me2}Ir(C_6H_5)_2(C(CH)_3C(R)NH)$ (**1**; $Tp^{Me2}$ = hydrotris(3,5-dimethylpyrazolyl)borate; R = H, Me, Ph, etc.). With the exception of the parent compound (R = H), they were obtained by the reaction of the $Ir^{III}$ dinitrogen complex $Tp^{Me2}Ir(C_6H_5)_2(N_2)$ (**2**) with the corresponding 2-substituted pyridines ($C_6H_6$, 60 °C for bulky R, i.e. $SiMe_3$, $NMe_2$; 90 °C for R = Me; Scheme 1). Experimental and DFT calculation data were in accord with a $\sigma$ C−H bond metathesis mechanism[3] that involved, after dissociation of the $N_2$ ligand and formation of the 16e unsaturated species **A**, a concerted C−H activation of the pyridine and extrusion of $C_6H_6$. The resulting pyridyl−phenyl fragment **B** then reacted with an incoming benzene molecule to restore the lost phenyl ligand whith the activated hydrogen atom ending bonded to the pyridyl nitrogen. Therefore, a phenyl ligand of **A** was acting as a shuttle in the formal CH → N 1,2-H shift (i.e., tautomerization) of the pyridine.[4,5]

On the other hand, in 1997,[6] the synthesis of a series of $Tp^{Me2}Ir(\eta^4\text{-}CH_2{=}C(R)C(R){=}CH_2)$ diene Ir(I) complexes (R = H, H; H, Me; Me, Me) was reported and these species were later found[7,8] to react, in some cases reversibly, with both soft and hard Lewis bases (CO, $C_2H_4$, NCMe, $NC_5H_5$, etc.) with formation of $\kappa^2{:}\sigma^2$-but-2-enediyl−Ir(III) adducts. The 2,3-dimethylbutadiene complex **3** was the more reactive among them and, for the case of the hard ligands, it was suggested that the mechanism of this unusual transformation[8] is that depicted in Scheme 2, in which the 16e unsaturated species **C** was the active intermediate which formed reversibly from the diene

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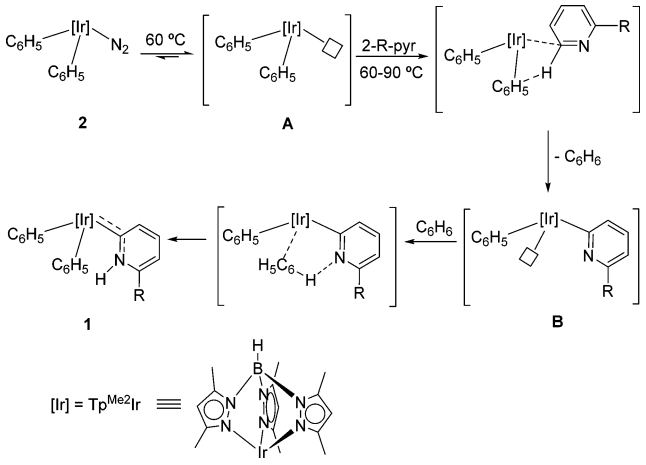
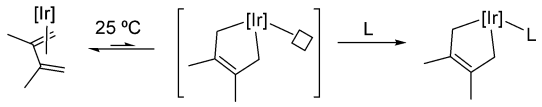
**Scheme 1. Tautomerization of 2-Substituted Pyridines by the Unsaturated 16e Fragment $[Tp^{Me2}Ir(C_6H_5)_2]$ (A)[1a]**




**Scheme 2. Proposed Mechanism for the Reaction of the Ir(I) Diene Complex 3 with Hard Lewis Bases[8]**




complex. Depending on L, the reaction took place at 25 °C or needed higher temperatures to complete the formation of adducts **4** at reasonable rates.

It was reasoned that complex **3** may also react with 2-substituted pyridines to give the corresponding pyridylidenes if one of the $RCH_2$ alkyl chains of **C** is able to act as a shuttle for the tautomerization: i.e., through an intramolecular version of the mechanism shown in Scheme 1. This has been found to be the case, and herein we report these studies which disclose enhanced reactivity because of the presence of a C=C double bond in **C** that is responsible for the formation of some interesting carbene metallabicyclic structures having a N−C bond. The reactivity of complex **3** with polypyridines such as bipy, phen, and terpy has been described in a recent publication.[9]

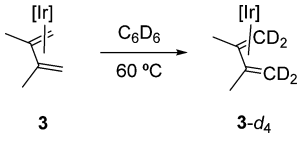
## RESULTS AND DISCUSSION

**Reaction of Complex 3 with $C_6H_6$.** As many of the reactions of complex **3** with 2-substituted pyridines were carried out in $C_6H_6$ and as a result benzene-derived products were obtained, it is convenient to start this section by discussing the reactivity of complex **3** with benzene.

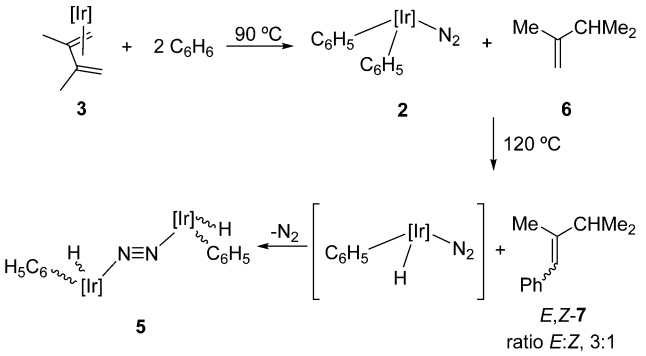
In the paper describing the synthesis of complex **3**, we reported[6] its reaction with $C_6H_6$ ($N_2$, 120 °C), which resulted in the isolation of the dinuclear hydride $[Tp^{Me2}Ir(H)(C_6H_5)]_2(N_2)$ (**5**), in an unspecified yield. Complex **5** was then thought to be the result of a simple $C_6H_6$ oxidative addition to the Ir(I) center with concomitant extrusion of the diene, with no effort being made to detect the latter product. Now it has been found that this is not the case, with a more complex process having been revealed by subjecting this reaction to a closer scrutiny. To begin with, it was observed that a $C_6D_6$ solution of **3** easily underwent deuteration at the $CH_2$ termini by heating to 60 °C (Scheme 3, $t_{1/2}$ ca. 45 min).

Further heating of **3** in $C_6H_6$ at 90 °C for ca. 1 h gave the dinitrogen complex $Tp^{Me2}Ir(C_6H_5)_2(N_2)$ (**2**) and the commercial olefin $Me_2CHC(Me)=CH_2$ (**6**). The latter was identified by $^1H$ and $^{13}C$ NMR spectroscopy after recovering it by collecting the volatiles of the reaction mixture (Scheme 4).

**Scheme 3. Deuteration of Complex 3 with Neat $C_6D_6$ (60 °C, $t_{1/2}$ ca. 45 min)**



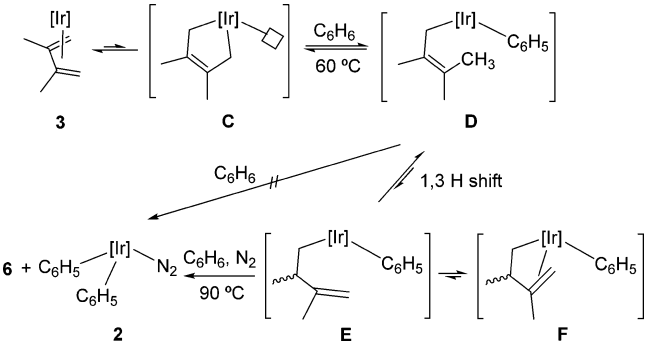

**Scheme 4. Chemical Transformations Observed When $C_6H_6$ Solutions of Complex 3 Are Heated at 90−120 °C**




Finally, as part of unpublished research on the reactivity of complex **2** with olefins other than ethylene[10] and propene,[1b] it was found that this species reacted with $Me_2CHC(Me)=CH_2$ at 120 °C with formation of the hydride **5**, as a mixture of stereoisomers (only an unassigned species was obtained by the crystallization reported in ref 4), and the unknown phenyl-substituted olefins *E*- and *Z*-**7**, with the former, less hindered, predominating (ratio 3:1), as the result of an interesting $C_6H_5 \leftrightarrow H$ exchange between the two reaction partners (Scheme 4).

With respect to the formation of the diphenyl species **2** and olefin **6**, at 90 °C, it may be explained by the mechanism depicted in Scheme 5 in which the $\eta^1$-allyl intermediate **D**,

**Scheme 5. Proposed Mechanism for the Formation of Complex 2 and the Olefin 6 by the Reaction of 3 with $C_6H_6$**




formed from **C** by a C−H bond activation of an entering $C_6H_6$, experiences a 1,3-H shift that gives the 16e $\gamma$-butenyl **E**, which then reacts with $C_6H_6$ to form the observed products. Obviously, this latter species must be in equilibrium with the more stable olefin-coordinated 18e compound **F**, but it is believed that this is an inactive species with respect to any C−H $\sigma$-CAM activation process, although a pyridyl counterpart (Ir−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pyridyl instead of Ir−phenyl) is thought to be responsible for C−N bond formation in some reactions to be described below. Probably the unsaturated species **D** and **E** are also in equilibrium, in accord with the thermodynamics of olefinic systems, with the former predominating. However, as there are no obvious steric reasons for a difference in the reactivities of **D** and **E** vs $C_6H_6$, we conclude that the latter species is reacting preferentially owing to its higher energy content: i.e., **E** is a "hotter" intermediate.

The deuteration of the $CH_2$ termini of **3** that takes place with $C_6D_6$ at 60 °C may be explained if the intermediates **C** and **D** are in equilibrium at this temperature. This explanation must also be reconciled with the fact that by monitoring the deuteration in neat $C_6D_6$ by $^1$H NMR and mass spectroscopy, only the **3**-$d_0$ and **3**-$d_4$ isotopomers were detected in the process: i.e., we are dealing with two, at first glance, isochronous neat $=CH_2 \rightarrow =CD_2$ transformations (only ca. 5% of CHD groups were detected by $^1$H NMR spectroscopy).[11] It is therefore concluded that species **C** must be a sufficiently long-lived intermediate to experience multiple interchange events with $C_6D_6$ before its decay back to species **3**. This conclusion is supported by a kinetic study of the deuteration process in $C_6D_{12}$−$C_6D_6$ mixtures, which clearly showed saturation behavior upon increasing the $C_6D_6$ molarity (Figure 1), with the two different methylene hydrogens (i.e., those occupying the endo and exo positions) both having the same rate of incorporation, within experimental error.

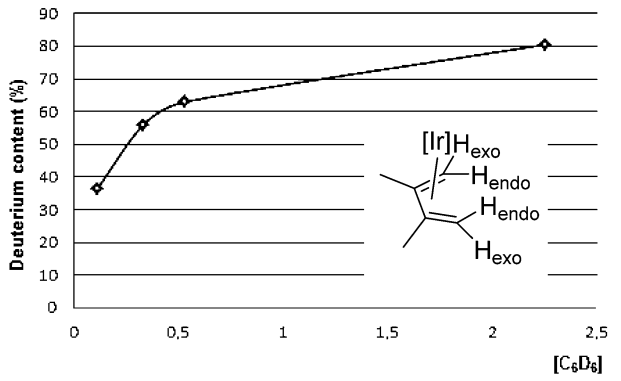



**Figure 1.** Deuterium content (%) of the exo (or endo) positions of the $=CH_2$ termini of complex **3** as a function of $[C_6D_6]$ ($C_6D_{12}$−$C_6D_6$, 60 °C, 0.5 h).

Figure 2 shows the time evolution of the $^1$H NMR signal corresponding to the exo hydrogens of the $=CH_2$ termini, at the lowest $C_6D_6$ concentration tested (0.11 M; (a) after 0.5 h, (b) after 1.5 h). As four different signals are observed and as up to eight different isotopomers could be drawn from **3**-$d_0$ to **3**-$d_3$, it is proposed that, apart from the expected geminal deuterium isotope effects on the corresponding exo hydrogens, only the presence of deuterium in a specific position of the other $=CH_2$ terminus gives rise to an additional upfield shift. In the assignment of the different signals to the structures represented in the drawing (**I**−**IV**) we have arbitrarily considered that it is the deuteration at the other exo hydrogen that is responsible for this chemical shift effect.

Interestingly, the deuteration process in neat $C_6D_6$ is completely suppressed by the presence of a few equivalents of pyridine, and thus complex **3** reacts with 5 equiv of $C_5H_5N$ in $C_6D_6$ to form the known N adduct **4a** (0.5 M, 25 °C, $t_{1/2}$ =

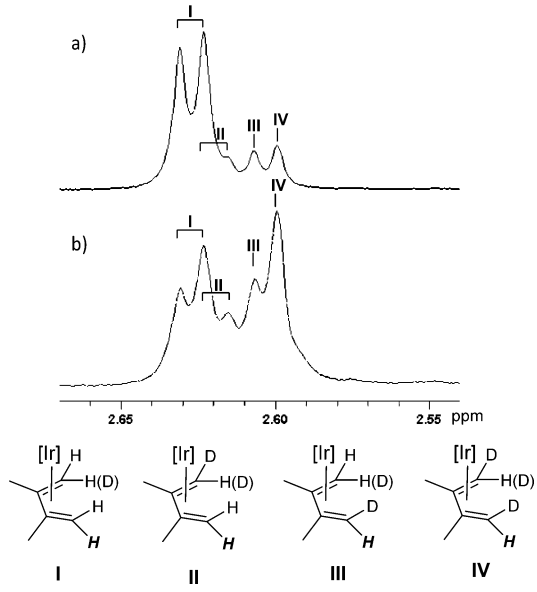
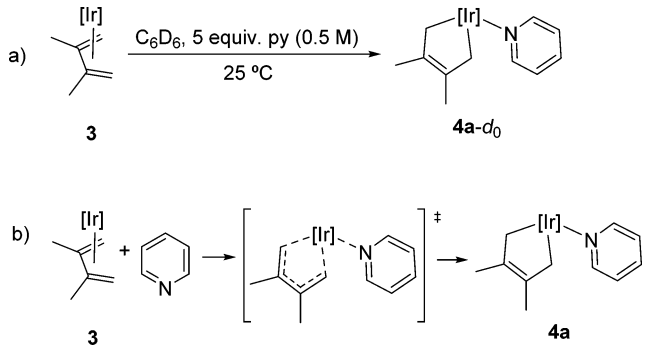



**Figure 2.** $^1$H NMR resonances of the exo hydrogens (***H***) of the $=CH_2$ termini of complex **3** in a $C_6D_{12}$−$C_6D_6$ mixture (0.11 M in $C_6D_6$) as a function of heating time (60 °C): (a) 0.5 h; (b) 1.5 h.

80 min), but with almost no deuterium incorporation (Scheme 6a). This may be due to the fact that this Lewis base reacts

**Scheme 6. (a) Reaction of Complex 3 with an Excess of Pyridine in $C_6D_6$ (25 °C) and (b) New Mechanistic Proposal for This Reaction**




more quickly than $C_6D_6$ with the intermediate **C**, in accord with the mechanism depicted in Scheme 2. However, we note that the rate of the reaction of complex **3** with pyridine fails, in this solvent, to show any sign of entering a saturation regime up to 2.8 M and this strongly contrasts with the behavior of the much less nucleophilic $C_6D_6$. Therefore, we have to conclude that pyridine does not form the N adduct **4a** by trapping intermediate **C** but instead by an alternative associative mechanism, in which it directly attacks complex **3** (Scheme 6b), and this may be also the case for other good nucleophiles such as acetonitrile and hydroxylamine.[12]

**Reactivity of Complex 3 with 2-Methylpyridine.** Complex **3** reacted with an excess of 2-picoline in $C_6H_{12}$ at 60 °C with formation of the adduct **4b** (Scheme 7), which has been characterized completely by NMR spectroscopy. The Ir−$CH_2$ functionalities are responsible for two somewhat broad doublets ($^2J_{HH}$ = 14.0 Hz) at 3.24 and 2.55 ppm in the $^1$H NMR spectrum and for a $^{13}$C resonance at 13.2 ppm with $^1J_{CH}$ = 120 Hz.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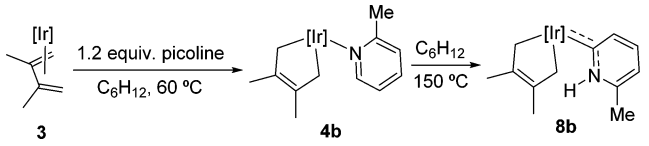
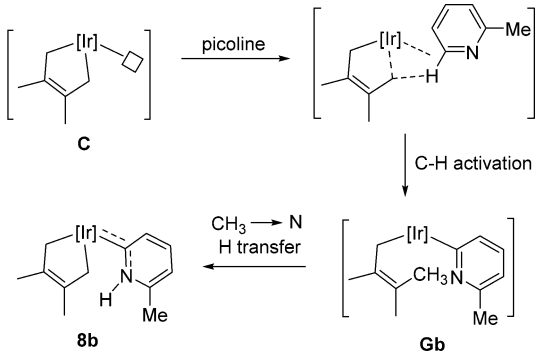
**Scheme 7. Reaction of Complex 3 with 2-Picoline at Different Temperatures ($C_6H_{12}$, 60−150 °C)**




Interestingly, **4b** transformed in $C_6H_{12}$ into the pyridylidene **8b** but this reaction required, for completion, heating to 150 °C for more than 24 h (Scheme 7): i.e., conditions much harsher than those needed for the analogous tautomerization of the diphenyl N adduct $Tp^{Me2}Ir(C_6H_5)_2$(Me-2-$NC_5H_4$), which was completed in a few hours at 90 °C.[1a] This difference in reactivity may be due, at least partially, to the inertness of the Ir−N bond of **4b** toward dissociation, as it only reluctantly exchanged with neat pyridine to give **4a** ($t_{1/2}$ ca. 48 h at 90 °C). Carbene formation in this $[Tp^{Me2}Ir(C_6H_5)_2]$ system is an intermolecular process through a $\sigma$-C−H intermediate of a 2-substituted pyridine and a 16e Ir substrate (Scheme 1). The Ir−pyridylidene functionality in **8b** is characterized by a $^{13}C\{^1H\}$ NMR resonance at 184.5 ppm corresponding to the iridium-bound carbon.

Only the rotamers depicted in the schemes for **4b** and **8b** are present in $CDCl_3$ solutions according to the NOESY spectra, and the same is true for all adducts **4** and pyridylidenes **8** of 2-substituted pyridines described in this paper (for the case of the parent **8a**, see below). A plausible mechanism for pyridylidene formation starting from **C** is shown in Scheme 8, where it reacts

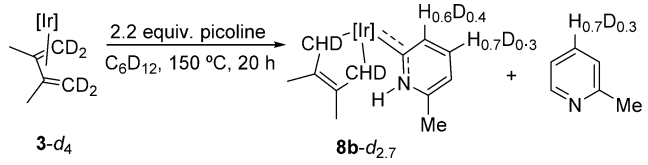
**Scheme 8. Proposed Mechanism for the Formation of the Pyridylidene 8b**




with 2-picoline via a C−H $\sigma$-CAM process to give the pyridyl intermediate **Gb**, related to the phenyl intermediate **D** of Scheme 5, having a $\eta^1$-allyl chain. Then, one of the hydrogens of the newly created methyl is back-transferred to the nitrogen atom to give the final product. Therefore, one of the Ir−$CH_2$ termini in **C** plays the same role as a phenyl ligand of **1** (Scheme 1), but the overall process is intramolecular.

As was the case in the $[Tp^{Me2}Ir(C_6H_5)_2]$ system,[1a] nonproductive C−H activation of the 2-picoline takes place before formation of complex **8b**. Thus, if complex **3**-$d_4$ was reacted with 2.2 equiv of 2-picoline in $C_6D_{12}$ (150 °C, 20 h), both the pyridylidene ligand of **8b** and the remaining free 2-picoline were partially deuterated in the positions depicted in Scheme 9. From the amount of deuterium remaining in the Ir−methylene positions, it is deduced that there is no substantial kinetic isotope effect associated with the final hydrogen transfer to the pyridyl nitrogen. Note also that the NH hydrogen of

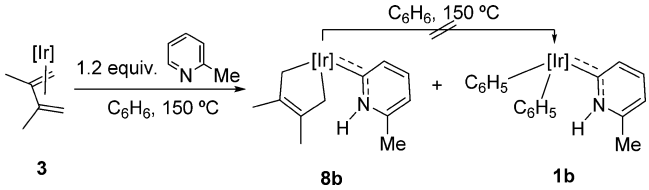
**Scheme 9. Reaction of Complex 3-$d_4$ with 2.2 equiv of 2-Picoline in $C_6D_{12}$ at 120 °C**




complex **8b** in this scheme is the result, at least partially, of a very easy ND → NH exchange with adventitious water.

When the reaction of 3 with 2-picoline was carried out in $C_6H_6$ at 150 °C (1.2 equiv; i.e. a ratio much lower than that required for pseudo-first-order conditions), a mixture of **8b** and the diphenyl species **1b** was obtained in a ca. 1.5:1 ratio (Scheme 10). A control experiment revealed that complex **8b**

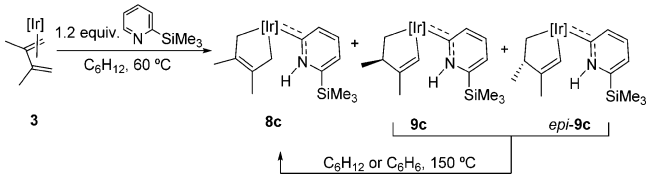
**Scheme 10. Reaction of Complex 3 with a Small Excess of 2-Picoline in $C_6H_6$ at 150 °C**




did not react with benzene at this temperature and, if the concentration of 2-picoline was increased by an order of magnitude, no **1b** was formed. It is concluded therefore that the ratio of these pyridylidenes reflects the kinetic ability of 2-picoline and benzene to enter the reactivity shown in Schemes 8 and 5, respectively.

**Reaction of Complex 3 with 2-Trimethylsilylpyridine.** Heating complex **3** with 1.2 equiv of 2-trimethylsilylpyridine in $C_6H_{12}$ at 60 °C (Scheme 11) gave the pyridylidene **8c**, but it

**Scheme 11. Reaction of Complex 3 with 2-Trimethylsilylpyridine, Under Kinetic and Thermodynamic Conditions ($C_6H_{12}$, 60 and 150 °C, Respectively)**




was accompanied by two related compounds **9c** and its epimer *epi*-**9c** in a ratio **8c**:(**9c**+*epi*-**9c**) of ca. 1:0.7 with **9c** predominating (**9c**:*epi*-**9c** ca. 2:1), and these ratios were independent of 2-trimethylsilylpyridine concentration (1.2−15 equiv). The structure of complex **8c** was confirmed by X-ray diffraction (Figure 3). The complexes **9c** and *epi*-**9c** are vinyl isomers of **8c** which are derived from the latter by formal 1,3-H shifts from one of the $CH_2$ termini to the double bond. Complex **8c** is the thermodynamically more stable compound, as both **9c** and *epi*-**9c** completely transformed into the former, **9c** more slowly than *epi*-**9c**, when the above mixture was heated to 150 °C, in both $C_6H_{12}$ and $C_6H_6$. The fact that in the last solvent the diphenyl species **8a** was not observed is clearly in accord with these rearrangements being intramolecular.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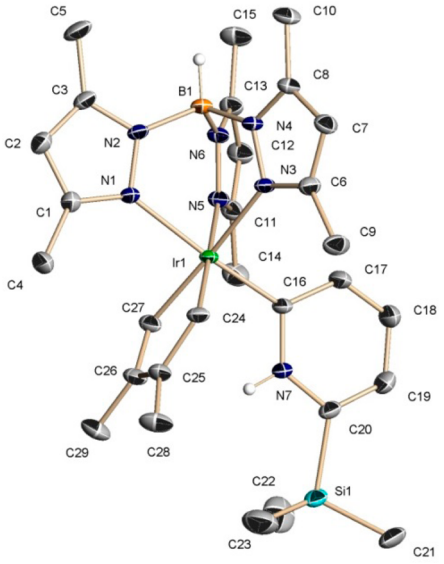
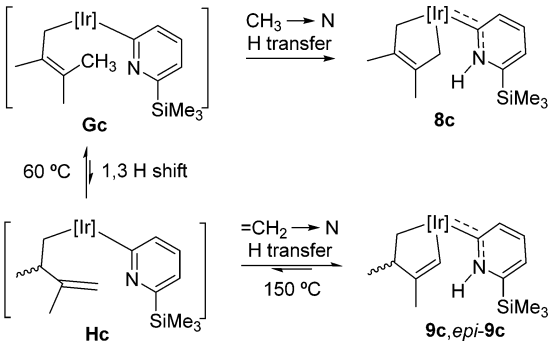



**Figure 3.** ORTEP drawing of complex **8c**. Thermal ellipsoids are set at 30% probability. Selected bond lengths (Å) and angles (deg): Ir1−C16 1.951(2), Ir1−C24 2.074(2), Ir1−C27 2.069(2), C25−C26 1.370(4); C16−Ir1−C24 88.95(9), C16−Ir1−C27 90.26(9), C24−Ir1−C27 81.53(10).

Only compound **8c** could be purified by column chromatography, as *epi*-**9c** did not appear in any fraction and the species **9c** was always obtained mixed with **8c** at the outlet of the column, but these more concentrated samples served for its complete NMR characterization. Thus, the Ir−CH═ functionality gives rise to $^{1}$H and $^{13}$C{$^{1}$H} NMR signals at 7.18 and 132.4 ppm, respectively, while the stereochemistry of the CHMe group is deduced from the NOESY spectrum. In turn, the vinyl species *epi*-**9c** was only partially characterized by spectroscopy using the whole mixture, while its stereochemistry was deduced according to an exclusion reasoning and by the structure of its hydrolysis product (see Scheme 13 below).

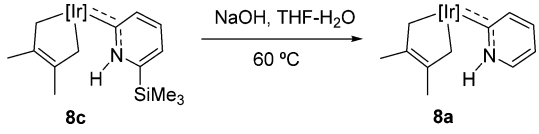
The formation of complexes **9c** and *epi*-**9c** is best explained by invoking the mechanism of Scheme 12. The unsaturated intermediate **Gc** that gives rise to the pyridylidene **8c** is in equilibrium with the less thermodynamically favored species **Hc**, with the vinyl $CH_2$ hydrogen transfer to the nitrogen pyridyl ligand being kinetically competitive with the corresponding H transfer from the methyl group of **Gc**. At 150 °C these transfers became reversible and the compounds **9c** and *epi*-**9c** revert to the thermodynamically more stable product **8c**.

**Scheme 12. Proposed Mechanism for the Formation of 8c, 9c, and *epi*-9c under Kinetic (60 °C) and Thermodynamic Control (150 °C)**




**System of Complex 3 with Pyridine.** The parent pyridylidene **8a** could be easily obtained by alkaline hydrolysis of the trimethylsilyl derivative **8c**: i.e., following the procedure used[1a] for the case of the related diphenyl compound (NaOH(aq), THF, 60 °C, 12 h; Scheme 13). Interestingly,

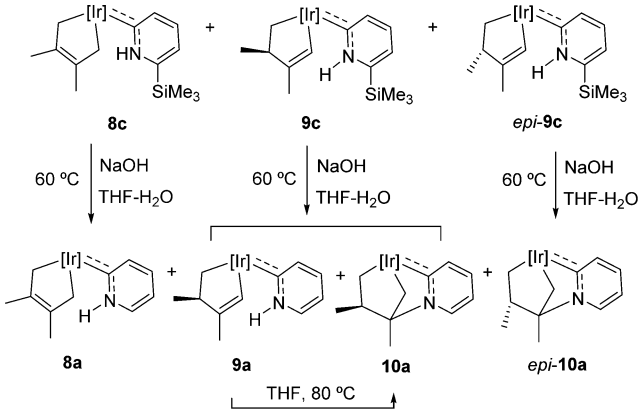
**Scheme 13. Formation of the Parent Pyridylidene 8a by Basic Hydrolysis of Pyridylidene 8c**




only the rotamer depicted in the scheme exists in $CDCl_3$ or $CD_2Cl_2$ solution, and this is in contrast with the diphenyl carbene, where the location of the NH group was not biased and equal amounts of the two possible rotamers were interchanging on the NMR time scale. This behavior may reflect the existence of a stabilizing, but weak, interaction between the N−H dipole and the C═C double bond.

When the mixture of the $SiMe_3$-containing pyridylidenes of Scheme 11 was subjected to the hydrolysis protocol, the three new species **9a**, **10a**, and *epi*-**10a** were formed in a ratio which reflected that of the starting species: i.e., **9a** and **10a** being derived from **9c** and *epi*-**10a** from *epi*-**9c** (Scheme 14). Further

**Scheme 14. Removal of the $SiMe_3$ Groups of Complexes 8c, 9c, and *epi*-9c by Basic Hydrolysis in THF−$H_2O$ Mixtures (60−80 °C)**




heating of the hydrolyzed mixture at 80 °C resulted only in the conversion of the remaining **9a** into **10a**. None of these species were obtained in a pure state even after careful chromatography from these reaction conditions. However, a ca. 2:1 mixture of **10a** and *epi*-**10a** could be separated by preparative thin-layer chromatography in *n*-hexane/$Et_2O$ (4/1) and this was used for the complete NMR characterization of both isomers. Thus, the carbon nuclei of the two Ir−$CH_2$ groups of **10a** resonate at 10.6 and −3.6 ppm while the quaternary carbon bound to the nitrogen appears at 88.5 ppm. Interestingly, the $^{1}$H NMR chemical shifts and $J_{HH}$ coupling constants of the Ir−$CH_2$CHMe− moiety follow consistent trends depending on the stereochemistry of the CHMe group, as deduced from a comparison of the corresponding values for **10a** and *epi*-**10a** with those obtained for the complex *epi*-**10e**, the only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stereoisomer derived from 2-methoxypyridine (see below) that has been completely characterized by X-ray studies and NOESY spectroscopy. *epi*-**10a** was also characterized by single-crystal X-ray diffraction (Figure 4). In turn, the vinyl species **9a** was only

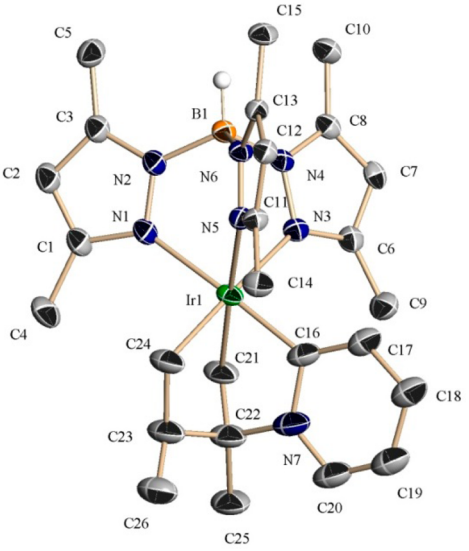
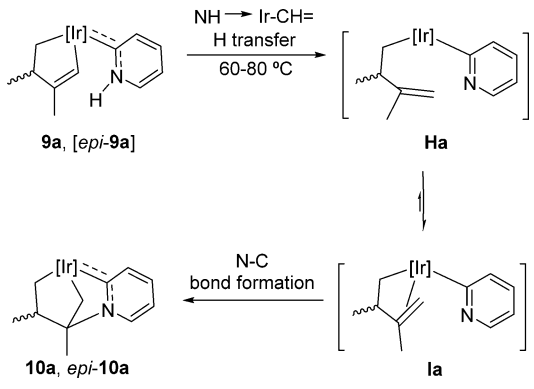



**Figure 4.** ORTEP drawing of complex *epi*-**10a**. Thermal ellipsoids are set at 30% probability. Selected bond lengths (Å) and angles (deg): Ir1−C16 1.930(10), Ir1−C21 2.067(9), Ir1−C24 2.076(10), C22−C23 1.566(18), N7−C22 1.520(18); C16−Ir1−C21 79.7(5), C16−Ir1−C24 84.9(5), C21−Ir1−C24 81.7(5), C21−C22−N7 104.9(10).

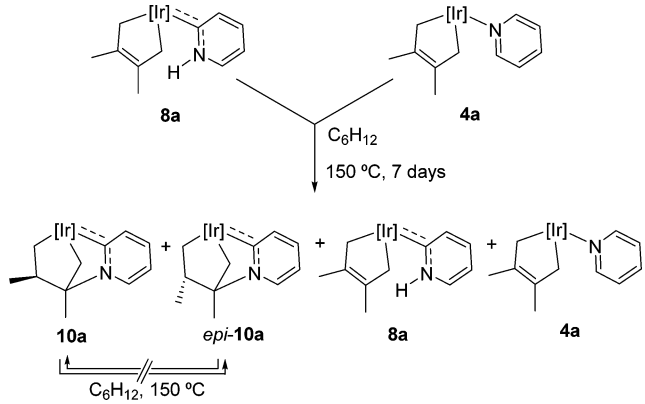
partially characterized by the $^{1}H$ and $^{13}C$ resonances of the Ir−CH═ moiety (7.21 and 133.7 ppm, respectively), while its stereochemistry was deduced by its conversion into **10a**. The species *epi*-**9a** was not observed, but it is proposed that once generated it transformed into *epi*-**10a** at ≤60 °C. Pyridylidenes **10a** and *epi*-**10a** are the formal result of the transfer of the N−H hydrogen of the corresponding species **9a** and [*epi*-**9a**] to the *α*-carbon of the vinyl chain coupled to a N−C bond formation process. It is proposed (Scheme 15) that the N−H hydrogen of the latter species is back-transferred to the Ir−CH═ carbon to give intermediate **Ia** (probably through **Ha**) followed by nucleophilic attack of pyridyl nitrogen at the coordinated olefin, a reactivity already observed in this kind of species.[1b]

**Scheme 15. Proposed Mechanism for the Thermal (60−80 °C) Conversion of Complexes 9a and [*epi*-9a] (the Latter Not Observed) Into the Corresponding 10a and *epi*-10a**




Pure pyridylidene **8a** and the known adduct **4a** very slowly partially transformed, in $C_6H_{12}$ at 150 °C, into each other with concomitant formation of **10a** and *epi*-**10a**, but in neither case was a thermodynamic equilibrium attained, even after 7 days at this temperature (Scheme 16). After this heating period the

**Scheme 16. Formation of Complexes 10a and *epi*-10a from the Thermal Activation of the N Adduct 4a and the Pyridylidene 8a ($C_6H_{12}$, 150 °C, 7 Days)**




species **10a** and *epi*-**10a** were strongly predominating, but quite different **10a**:*epi*-**10a** ratios were obtained (the **10a**:*epi*-**10a**:**8a**:**4a** ratios were 1:0.05:0.02:0.08 and 1:0.57:0.30:0.64 starting from **8a** and **4a**, respectively). This and the fact that the ca. 2:1 mixture of **10a** and *epi*-**10a** noted above did not change in any respect after heating for 1 week at 150 °C permit us to conclude that these compounds are the more stable species in this system, although we do not know which of the noninterchangeable epimers is thermodynamically preferred.

**Reaction of Complex 3 with 2-Fluoropyridine and 2-Methoxypyridine.** Upon the reaction of complex **3** with 1.2 equiv of 2-fluoropyridine, in $C_6H_{12}$ at 60 °C, the adduct **4d** was cleanly obtained. When the temperature was increased to 120 °C, the reaction afforded stereospecifically the bicyclic product *epi*-**10d** as the only product observed. For the case of 2-methoxypyridine, the adduct **4e** was again the kinetic product ($C_6H_{12}$, 60 °C), but increasing the reaction temperature gave mixtures of the carbene **8e** and the bicyclic product *epi*-**10e** in a ratio that depended on the reaction temperature (ca. 1:0.6 and 1:1 at 90 and 120 °C, respectively). These distributions are not under thermodynamic control, as once formed, they do not appreciably change upon further heating and furthermore complex **8e** does not transform into *epi*-**10e** under these conditions (Scheme 17). These complexes were easily separated by column chromatography. The X-ray structures of complexes **8e** and *epi*-**10e** are shown in Figures 5 and 6, respectively.

**Reactivity of Complex 3 with 2-Dimethylaminopyridine and 2-Acetylpyridine.** In contrast to the chemistry described so far, these last two pyridines behaved very simply in their reactions with complex **3**. Thus, the first reacted (60 °C, $C_6H_{12}$) with exclusive formation of carbene **8f** (Scheme 18), and the same was the case for 2-acetylpyridine. Pyridylidenes **8f,g** were both stable at 150 °C for at least 3 days. Complex **8f** was also characterized by single-crystal X-ray diffraction (Figure 7).

**Kinetic and Thermodynamic Considerations on the Reactivity of Complex 3 with Pyridines.** From the results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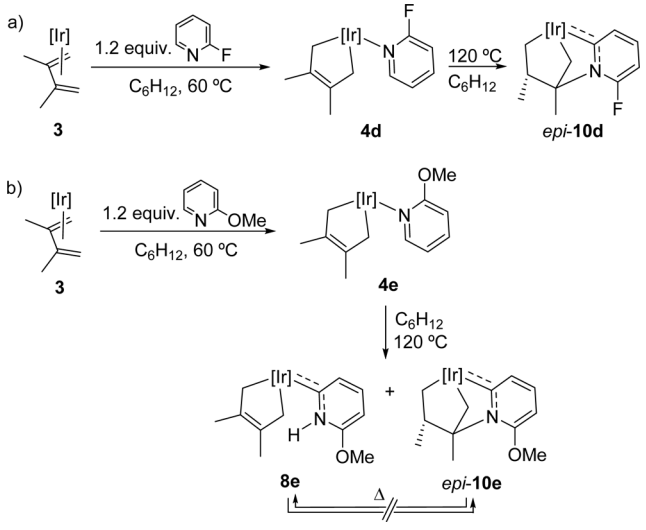
**Scheme 17. Temperature-Dependent Reactivity of Complex 3 with 2-Fluoropyridine (a) and 2-Methoxypyridine (b)**



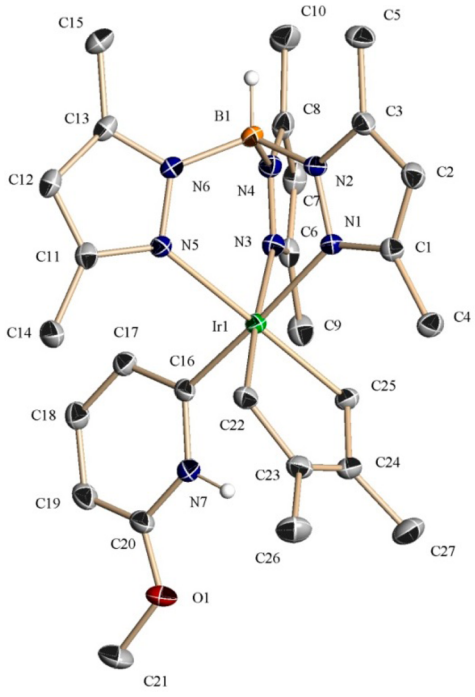




**Figure 5.** ORTEP drawing of complex **8e**. Thermal ellipsoids are set at 30% probability. Selected bond lengths (Å) and angles (deg): Ir1−C16 1.946(3), Ir1−C22 2.076(3), Ir1−C25 2.080(3), C23−C24 1.332(5); C16−Ir1−C22 89.87(11), C16−Ir1−C25 89.27(11), C22−Ir1−C25 82.15(11).

presented so far it can be concluded that, in the reaction of complex **3** with pyridine and its 2-substituted analogues, the nature of the 2-substituent strongly conditions the nature of the products obtained both under kinetic and thermodynamic (real or apparent) control, conditions which correspond roughly to 60 and 120−150 °C, respectively. When R = Me, the adduct **4b** is the kinetic product and the carbene **8b** *seems* to be the thermodynamic product (see below). For R = $SiMe_3$ carbene **8c** is accompanied by the vinylic species **9c** and *epi*-**9c**, resulting from C−H activation of the $=CH_2$ termini, as kinetic products but the carbene **8c** is the only species stable at 150 °C. If R = H,

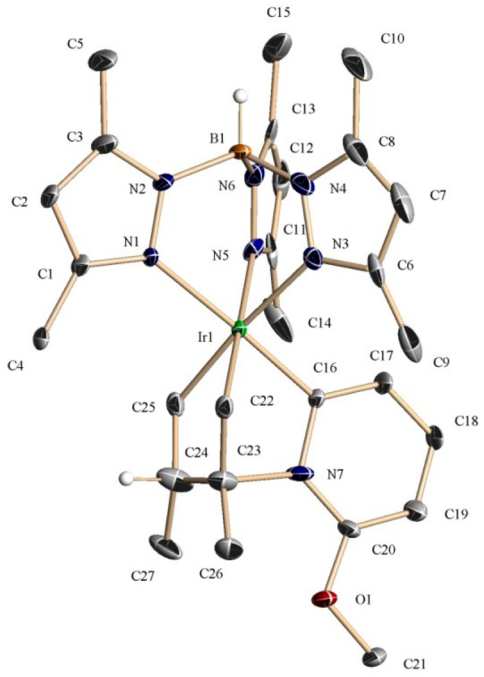
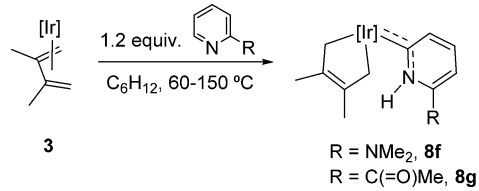



**Figure 6.** ORTEP drawing of complex *epi*-**10e**. Thermal ellipsoids are set at 30% probability. Selected bond lengths (Å) and angles (deg): Ir1−C16 1.933(8), Ir1−C22 2.059(8), Ir1−C25 2.061(9), C23−C24 1.341(17), N7−C23 1.729(15); C16−Ir1−C22 81.0(4), C16−Ir1−C25 80.5(4), C22−Ir1−C25 80.7(4), C23−C22−N7 113.4(9).

**Scheme 18. Temperature-Independent Reactivity of Complex 3 with 2-Dimethylaminopyridine and 2-Acetylpyridine**




the adduct **4a** is the kinetic product but, in contrast with the two already noted systems, the more stable species appear to be **10a** and e*pi*-**10a**: i.e., bicyclic carbenic structures resulting from a C−N bond forming process. For R = F, OMe the adducts **4d,e** are the kinetic products but the bicyclic compounds *epi*-**10d** and *epi*-**10e** are much more and almost equally favored, respectively, with respect to the corresponding N−H pyridylidene isomer, at 150 °C. Finally, when R = $NMe_2$, C(=O)Me the corresponding pyridylidenes **8f,g** are the only products observed under all the experimental conditions tested (60−150 °C).

With respect to adduct formation, i.e. the simplest reaction outcome of complex **3** with pyridines, it can be said that when it is observed, it is always under kinetic control. As was the case for the $[Tp^{Me2}Ir(C_6H_5)_2]$ system F strain prevents their formation with the bulky $SiMe_3$ and $NMe_2$ substituents but in the case of the 2-acetylpyridine its failure to act as a Lewis base is clearly due to the electron-withdrawing properties of the acetyl group.

For the formation of all other products observed in the system under consideration it is proposed that the 16e unsaturated pyridyl intermediates of structure **G** are the first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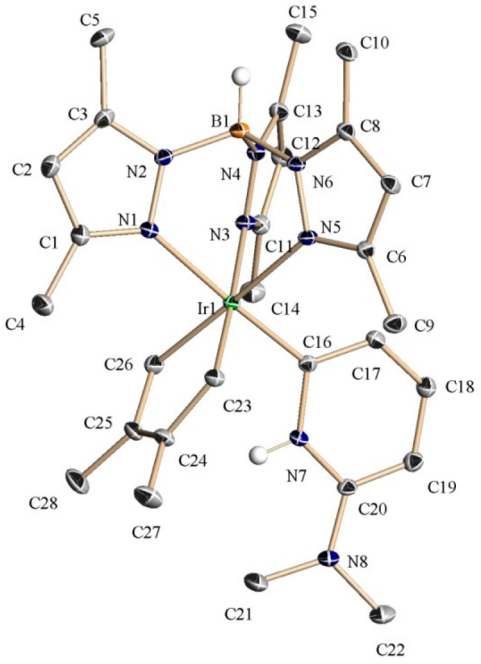
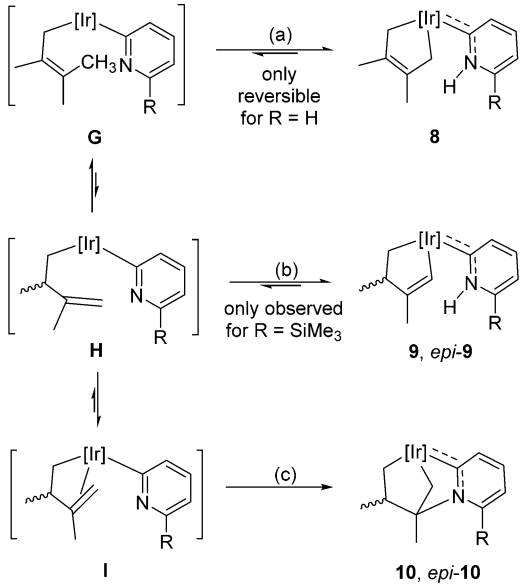



**Figure 7.** ORTEP of complex **8f**. Thermal ellipsoids are set at 30% probability. Selected bond lengths (Å) and angles (deg): Ir1−C16 1.951(2), Ir1−C23 2.0746(19), Ir1−C26 2.069(2), C24−C25 1.331(3); C16−Ir1−C26 90.18(8), C16−Ir1−C23 90.03(8), C23−Ir1−C26 82.23(8).

to form and that, depending on R, they evolve to give three different kind of carbenic species: i.e., but-1-enediyl and but-2-enediyl N−H pyridylidenes (**9** and **8**, respectively) and N−C-containing iridabicyclic structures (**10**). Starting from **3** and the corresponding pyridine, only the first type is observed, for unknown reasons, for R = $SiMe_3$ and its formation is under kinetic control. DFT calculations of the energetics of the three types of products suggest that with the exception of the 2-trimethylsilylpyridine, for obvious steric reasons, the more stable structures are the bicyclic pyridylidenes (for example, *epi*-**10e** and **10e** are ca. 6.1 and 3.3 kcal·mol$^{-1}$ more stable than **8e**, respectively). The N−H pyridylidenes are, even after prolonged heating at 150 °C, unable to afford the thermodynamic products. The only exception to this behavior is when R = H with the parent pyridylidene **8a** transferring, although very slowly at 150 °C, its N−H hydrogen to give **10a** and *epi*-**10a**.

Therefore, to account for the product distribution observed under prolonged heating at 150 °C a kinetic reasoning is necessary, i.e. to reveal the factors that are at work with the different pyridines, assuming that intermediates **G** and **I** are in equilibrium (Scheme 19). We expect that decreasing the electron density in the pyridyl nitrogen of intermediate **I** (route (c)) will disfavor the N−C bonding process but this is also the case with respect to hydrogen transfer from the methyl group of intermediate **G** (route (a)). Clearly, subtle factors should determine the disparate reaction products formed depending on R, and only broad trends can be considered herein. First, the strong EWG C(=O)Me clearly favors pathway (a), and the same is true for the weak EDG Me substituent. Second, fluorine, somewhat ambiguous electronically as an aromatic substituent[13] (it is considered in a separate group by Ingold in their well-known studies on aromatic activation), gives rise to only the bicyclic pyridylidene (route (c)). Third, strong EDG substituents such as OMe and $NMe_2$ seem to increasingly favor

**Scheme 19. The Three Possible Outcomes of Intermediates G and Their Corresponding Mechanistic Pathways ((a)−(c))**




N−H pyridylidene formation (route (a)) as the electron-donating properties are increased (**8f** is the only observed product when R = $NMe_2$ but the formation of **8e** and *epi*-**10e** have almost the same kinetic barrier in the case of R = OMe). Clearly, DFT theoretical studies are needed to explain all the experimental findings and the mechanistic proposals made in this paper.

## CONCLUSION

The reactions of the Ir$^{I}$ diene complex $Tp^{Me2}Ir(\eta^4\text{-}CH_2{=}C(Me)C(Me){=}CH_2)$ (**3**) with pyridine and 2-substituted pyridines are strongly dependent on the reaction conditions and the nature of the substituent. Four kinds of complexes have been observed in this system: N adducts, but-1-enediyl, but-2-enediyl N−H pyridylidenes, and N−C bond containing bicyclic carbenes. In addition, the temperature-dependent reactivity of complex **3** in $C_6H_6$ has been studied and particularly the interesting deuteration of its $=CH_2$ termini by $C_6D_6$ at 60 °C.

## EXPERIMENTAL SECTION

**General Considerations.** Microanalyses were performed by the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla, Spain). The mass spectra were obtained at the Mass Spectroscopy Service of the University of Sevilla. The NMR instruments were Bruker DRX-500 and DRX-400 spectrometers. Spectra were referenced to external $SiMe_4$ (0 ppm) using the residual protio solvent peaks of the deuterated solvents as internal standards ($^1$H NMR experiments) or the characteristic resonances of the solvent nuclei ($^{13}$C NMR experiments). Spectral assignments were made by routine one- and two-dimensional NMR experiments where appropriate. All the $^3J_{H-H}$ aromatic coupling constants are ca. 7.5 Hz with the exception of that exhibited by the C−H proton next to heterocyclic nitrogen (ca. 5.5 Hz). Almost all manipulations were performed under a dry, oxygen-free dinitrogen atmosphere, following conventional Schlenk techniques. The complex $Tp^{Me2}Ir(\eta^4\text{-}CH_2{=}C(Me)C(Me){=}CH_2)$ (**3**) was synthesized according to the published procedure.[6]

**X-ray Structure Analysis for 8c, *epi*-10a, 8e, *epi*-10e, and 8f.** A summary of crystallographic data and structure refinement details of these new crystalline compounds is given at the end of the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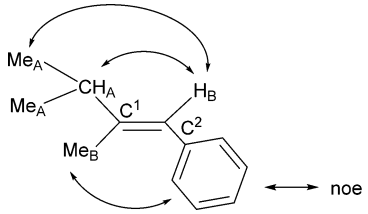
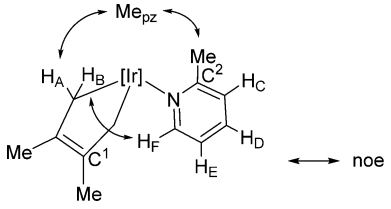
experimental and spectroscopic data for each compound. Crystals of suitable size for X-ray diffraction analysis were coated with dry perfluoropolyether (Fomblin Y H-VAC 140/13) and mounted on glass fibers and fixed in a cold nitrogen stream ($T$ = 100 K) to the goniometer head. Data collections were performed on a Bruker-Nonius X8Apex-II CCD diffractometer, using monochromatic radiation $\lambda$(Mo K$\alpha$) = 0.71073 Å, by means of $\omega$ and $\varphi$ scans with a width of 0.50°. The data were reduced (SAINT)[14] and corrected for absorption effects by the multiscan method (SADABS).[15] The structures were solved by direct methods (SIR-2002)[16] and refined against all $F^2$ data by full-matrix least-squares techniques (SHELXTL-6.12)[17] minimizing $w[F_o^2 - F_c^2]^2$. All of the non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms (except the N−H of pyridylidenes) were included in calculated positions and allowed to ride on the attached atoms with the isotropic temperature factors ($U_{iso}$ values) fixed at 1.2 times (1.5 times for methyl groups) those $U_{eq}$ values of the corresponding attached atoms. The N−H of pyridylidene (**8c,e,f**) was localized by difference Fourier maps and its distance restrained to 0.88 Å (DFIX command) and refined isotropically.

**Synthesis and Characterization of Compound *E*-7.**



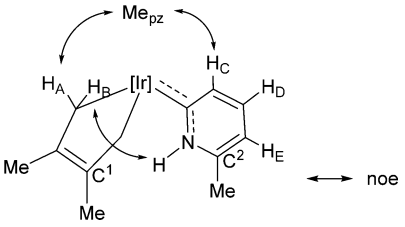

A solution of complex **3** (100 mg, 0.17 mmol) in 5 mL of benzene was heated to 120 °C for 12 h. The solvent was removed under reduced pressure and the residue subjected to column chromatography on silica gel (*n*-hexane) to give **7**, a colorless liquid (65% yield), as a mixture of the two stereoisomers *E* and *Z* in the ratio 1:0.3. The following NMR data correspond to the major isomer. $^1$H NMR ($CDCl_3$, 500 MHz, 25 °C): $\delta$ 7.31−7.16 (m, 5 H, Ph), 6.28 (br s, 1 H, $H_B$), 2.41 (sept, 1 H, $H_A$), 1.81 (d, 3 H, $^4J_{HH}$ = 1.2 Hz, $Me_B$), 1.10 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, 2 $Me_A$). $^{13}$C{$^1$H} NMR ($CDCl_3$, 125 MHz, 25 °C): $\delta$ 144.8 ($C^1$), 138.9 ($C^2$), 129.0, 128.0, 125.8 (2:2:1, $CH_{Ph}$), 122.7 ($CH_B$), 37.7 ($CH_A$), 21.5 (2 $Me_A$), 15.1 ($Me_B$). HRMS (FAB): $m/z$ calcd for $C_{12}H_{16}$ 160.1252, found 160.1288.

**Synthesis and Characterization of Complex 4b.**



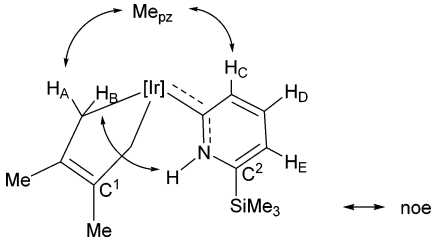

A suspension of complex **3** (200 mg, 0.35 mmol) in 5 mL of cyclohexane was heated to 60 °C for 12 h with 1.2 equiv of 2-picoline (42 $\mu$L, 0.42 mmol). The solvent was removed under reduced pressure and the solid residue subjected to column chromatography on silica gel (*n*-hexane/$Et_2O$, 100/1) to give compound **4b**, as a yellow solid, in 60% yield. $^1$H NMR ($CDCl_3$, 400 MHz, 25 °C): $\delta$ 8.50 (d, 1 H, $H_F$), 7.38 (t, 1 H, $H_D$), 6.87 (t, 1 H, $H_E$), 6.73 (d, 1 H, $H_C$), 5.67, 5.59 (s, 2:1, 3 $CH_{pz}$), 3.24, 2.55 (d, 2 H each, $^2J_{AB}$ = 14.0 Hz, 2 $H_A$, 2 $H_B$), 2.41, 2.32, 2.01, 1.59 (s, 2:1:1:2, 6 $Me_{pz}$), 1.77 (s, 6 H, 2 $C^1$ Me), 1.08 (s, 3 H, $C^2$ Me). $^{13}$C{$^1$H} NMR ($CDCl_3$, 100 MHz, 25 °C): $\delta$ = 164.7 ($C^2$), 157.1 ($CH_F$), 151.5, 150.2, 142.9, 142.6 (1:2:1:2, $C_{qpz}$), 140.3 (2 $C^1$), 133.4 ($CH_D$), 125.1 ($CH_C$), 123.0 ($CH_E$), 108.5, 106.3 (1:2, $CH_{pz}$), 21.6 ($C^2$*Me*), 18.6 (2 $C^1$*Me*), 13.4, 13.0, 12.5, 12.4 (1:2:1:2, $Me_{pz}$), 13.2 ppm (2 $IrCH_2$, $^1J_{CH}$ = 121 Hz). HRMS (FAB): $m/z$ calcd for $C_{27}H_{39}BIrN_7$ ($M - H^+$) 664.2911, found 664.2936. Anal. Calcd for $C_{27}H_{39}BIrN_7$: C 48.7; H, 5.9; N, 14.7. Found: C, 48.3; H, 6.1; N, 14.2.

**Synthesis and Characterization of Complex 8b.**




A suspension of complex **3** (100 mg, 0.17 mmol) in 4 mL of cyclohexane was heated to 150 °C for 12 h with 1.2 equiv of 2-picoline (21 $\mu$L, 0.21 mmol). The solvent was removed under reduced pressure, and the solid residue was subjected to column chromatography on silica gel (*n*-hexane/$Et_2O$, 100/1) to give compound **8b**, as a pale yellow solid, in 75% yield. $^1$H NMR ($CDCl_3$, 500 MHz, 25 °C): $\delta$ 11.10 (br s, 1 H, NH), 6.87 (d, 1 H, $H_C$), 6.74 (t, 1 H, $H_D$), 6.38 (d, 1 H, $H_E$), 5.71, 5.67 (s, 1:2, 3 $CH_{pz}$), 3.12 (d, 2 H, $^2J_{AB}$ = 14.3 Hz, 2 $H_A$), 2.40, 2.38 (s, 2:1, 3 $Me_{pz}$), 2.29 (s, 3 H, $C^2$ Me), 2.26 (d, 2 H, 2 $H_B$), 2.06 (s, 3 H, $Me_{pz}$), 1.83 (s, 6 H, 2 $C^1$ Me), 1.60 (s, 6 H, 2 $Me_{pz}$). $^{13}$C{$^1$H} NMR ($CDCl_3$, 125 MHz, 25 °C): $\delta$ 184.5 (Ir=C), 150.8, 149.2 (1:2, $C_{qpz}$), 147.0 ($C^2$), 143.1, 142.1 (1:2, $C_{qpz}$), 142.4 (2 $C^1$), 139.0 ($CH_C$), 131.1 ($CH_D$), 111.9 ($CH_E$), 107.5, 106.3 (1:2, $CH_{pz}$), 19.7 (2 $C^1$*Me*), 19.3 ($C^2$*Me*), 14.0, 13.1, 12.8, 11.3 (2:1:2:1, $Me_{pz}$), 11.6 ppm (2 $IrCH_2$). HRMS (FAB): $m/z$ calcd for $C_{27}H_{39}BIrN_7$ ($M - H^+$) 664.2911, found 664.2904. Anal. Calcd for $C_{27}H_{39}BIrN_7$: C, 48.7; H, 5.9; N, 14.7. Found: C, 48.6; H, 5.7; N, 15.1.

**Synthesis and Characterization of Complex 8c.**




A suspension of complex **3** (100 mg, 0.17 mmol) in 3 mL of cyclohexane was heated to 150 °C for 24 h with 1.2 equiv of 2-trimethylsilylpyridine (34.9 $\mu$L, 0.21 mmol). The solvent was removed under reduced pressure, and the solid residue was washed with *n*-pentane at −20 °C to give compound **8c** as a yellow solid in 85% yield. Single crystals suitable for X-ray diffraction were obtained by the slow evaporation of the solvent from a saturated solution in *n*-hexane/$Et_2O$ (1/1) at room temperature. $^1$H NMR ($CDCl_3$, 500 MHz, 25 °C): $\delta$ 11.07 (br s, 1 H, NH), 6.92 (d, 1 H, $H_C$), 6.68 (m, 2 H, $H_D$, $H_E$), 5.67, 5.64 (s, 1:2, 3 $CH_{pz}$), 3.03 (d, 2 H, $^2J_{AB}$ = 14.0 Hz, 2 $H_A$), 2.37, 2.35 (s, 2:1, 3 $Me_{pz}$), 2.28 (d, 2 H, 2 $H_B$), 2.00 (s, 3 H, $Me_{pz}$), 1.79 (s, 6 H, 2 $C^1$ Me), 1.54 (s, 6 H, 2 $Me_{pz}$), 0.31 (s, 9 H, $SiMe_3$). $^{13}$C{$^1$H} NMR ($CDCl_3$, 125 MHz, 25 °C): $\delta$ 185.1 (Ir=C), 154.3 ($C^2$), 150.8, 149.2 (1:2, $C_{qpz}$), 144.1 ($CH_C$), 143.0, 142.0 (1:2, $C_{qpz}$), 142.3 (2 $C^1$), 128.7 ($CH_D$), 119.2 ($CH_E$), 107.5, 106.3 (1:2, $CH_{pz}$), 19.6 (2 $C^1$*Me*), 13.7, 13.1, 12.8, 11.1 (2:1:2:1, $Me_{pz}$), 11.7 (2 $IrCH_2$, $^1J_{CH}$ = 122 Hz), −2.5 ppm ($SiMe_3$). Anal. Calcd for $C_{29}H_{45}BIrN_7Si$: C, 48.1; H, 6.2; N, 13.5. Found: C, 48.0; H, 6.4; N, 13.3. Crystal data for **8c**: $C_{29}H_{45}BIrN_7Si$, $M_r$ = 722.82, monoclinic, $a$ = 10.5281(5) Å, $b$ = 16.3714(9) Å, $c$ = 18.5506(10) Å, $\alpha$ = 90.00°, $\beta$ = 94.1900(10)°, $\gamma$ = 90.00°, $V$ = 3188.8(3) Å$^3$, $T$ = 173(2) K, space group $P2_1/c$, $Z$ = 4, $\mu$ = 4.254 mm$^{-1}$, 168408 reflections measured, 9753 independent reflections ($R_{int}$ = 0.0479). The final R1 value was 0.0241 ($I > 2\sigma(I)$). The final wR2($F^2$) value was 0.0602 ($I > 2\sigma(I)$). The final R1 value was 0.0300 (all data). The final wR2($F^2$) value was 0.0631 (all data). The goodness of fit on $F^2$ was 1.033. CCDC-943065 (**8c**).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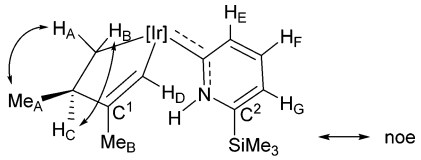
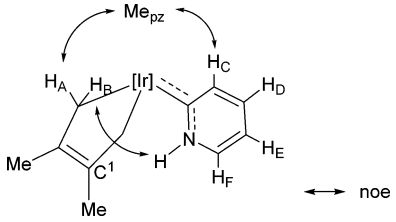
**Synthesis and Characterization of Complex 9c.**



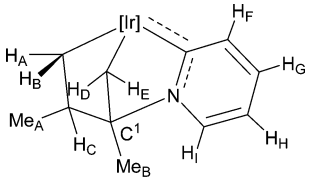

Following the procedure used in the synthesis of complex **8c**, but with heating at 60 °C, a mixture of complexes **8c**, **9c**, and *epi*-**9c** was obtained in a ca. 1:0.5:0.2 ratio. Column chromatography on silica gel (*n*-hexane/$Et_2O$, 100/0.1) allowed complex **9c** to be isolated but always in admixture with considerable amounts of the carbene **8c**. $^1$H NMR ($CDCl_3$, 400 MHz, 25 °C): $\delta$ 12.7 (br s, 1 H, NH), 7.18 (s, 1 H, $H_D$), 6.90 (m, 1 H, $H_E$), 6.68 (m, 2 H, $H_F$, $H_G$), 5.70, 5.63, 5.60 (s, 1 H each, 3 $CH_{pz}$), 3.02 (from cosy, 1 H, $H_B$), 2.62 (m, 1 H, $H_C$), 2.38, 2.34, 2.31, 2.29 (s, 3 H each, 4 $Me_{pz}$), 2.08 (dd, 1 H, $^2J_{HH}$ = 12.2, $^3J_{HH}$ = 3.9 Hz, $H_A$), 1.94 (s, 3 H, $Me_B$), 1.84, 1.36 (s, 3 H each, 2 $Me_{pz}$), 1.25 (d, 3 H, $^3J_{HH}$ = 7.0 Hz, $Me_A$), 0.36 (s, 9 H, $SiMe_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): $\delta$ 180.2 (Ir=C), 152.3, 152.2 ($C^2$, $C^1$), 150.0, 149.6, 149.0, 142.9, 142.4, 141.9 ($C_{qpz}$), 142.5 ($CH_E$), 132.4 ($CH_D$), 129.7, 120.5 ($CH_F$, $CH_G$), 107.5, 106.4, 106.0 ($CH_{pz}$), 46.8 ($CH_C$), 23.8 ($Me_A$), 21.9 ($Me_B$), 14.4, 14.0, 13.0, 12.5, 12.2, 12.1 ($Me_{pz}$), 3.1 ($IrCH_2$), −1.8 ppm ($SiMe_3$).

**Synthesis and Characterization of Complex 8a.**



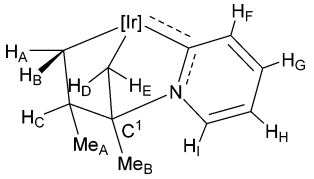

Complex **8c** (300 mg, 0.415 mmol) was dissolved in 20 mL of THF, an excess of NaOH in water was added (4 mL, 1.5 M), and the resulting solution was heated for 24 h at 60 °C. The solvent was evaporated under vacuum, and after addition of water, the yellow product was extracted with $CH_2Cl_2$ (3 × 20 mL). The organic phase was dried with $MgSO_4$ and evaporated to give complex **8a** in 85% yield. Crystallization could be achieved by the slow solvent evaporation of its solutions in $CH_2Cl_2$/MeOH mixtures (1/1) at room temperature. $^1$H NMR ($CDCl_3$, 400 MHz, 25 °C): $\delta$ 11.1 (br s, 1 H, NH), 7.65 (d, 1 H, $H_F$), 7.02 (d, 1 H, $H_C$), 6.79 (t, 1 H, $H_D$), 6.58 (t, 1 H, $H_E$), 5.67, 5.64 (s, 1:2, 3 $CH_{pz}$), 3.05 (d, 2 H, $^2J_{AB}$ = 14.5 Hz, 2 $H_A$), 2.37, 2.34 (s, 2:1, 3 $Me_{pz}$), 2.26 (d, 2 H, 2 $H_B$), 2.00 (s, 3 H, 1 $Me_{pz}$), 1.78 (s, 6 H, 2 $C^1$ Me), 1.56 (s, 6 H, 2 $Me_{pz}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): $\delta$ 184.9 (Ir=C), 150.7, 149.0 (1:2, $C_{qpz}$), 143.4 ($CH_C$), 142.9 ($C_{qpz}$), 142.0 (2 $C^1$, 2 $C_{qpz}$), 137.3 ($CH_F$), 130.2 ($CH_D$), 112.3 ($CH_E$), 107.4, 106.2 (1:2, $CH_{pz}$), 19.4 (2 $C^1Me$), 13.7, 12.9, 12.6, 11.0 (2:1:2:1, $Me_{pz}$), 11.4 ppm (2 $IrCH_2$, $^1J_{CH}$ = 122 Hz). HRMS (FAB): *m*/*z* calcd for $C_{26}H_{37}BIrN_7$ ($M - H^+$) 650.2755, found 650.2771. Anal. Calcd for $C_{26}H_{37}BIrN_7$: C, 48.0; H, 5.7; N, 15.0. Found: C, 48.3; H, 6.0; N, 14.6.

**Synthesis and Characterization of Complex 10a.**



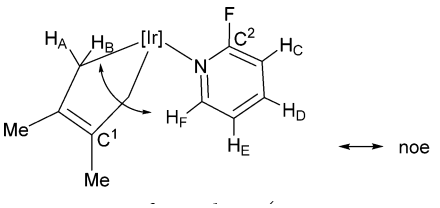

A suspension of complex **8a** (40 mg, 0.0.06 mmol) in 4 mL of cyclohexane was heated to 150 °C for 7 days and the solvent removed to dryness to give a yellow solid that was shown by $^1$H NMR spectroscopy to be almost pure **10a**. $^1$H NMR ($C_6D_6$, 400 MHz, 25 °C): $\delta$ 7.40 (d, 1 H, $H_I$), 7.34 (d, 1 H, $H_F$), 6.34 (t, 1 H, $H_G$), 6.12 (t, 1 H, $H_H$), 5.72, 5.63, 5.58 (s, 1 H each, 3 $CH_{pz}$), 3.34 (d, 1 H, $^2J_{HH}$ = 10.4 Hz, $H_D$), 2.85 (s, 3 H, $Me_{pz}$), 2.75 (dd, 1 H, $^2J_{HH}$ = 11.4, $^3J_{HH}$ = 9.3 Hz, $H_B$), 2.61 (dd, 1 H, $^2J_{HH}$ = 11.4, $^3J_{HH}$ = 5.3 Hz, $H_A$), 2.31, 2.28, 2.25, 2.00, 1.59 (s, 3 H each, 5 $Me_{pz}$), 2.33 (d, 1 H, $H_E$), 1.47 (m, 1 H, $H_C$), 1.45 (d, 3 H, $^3J_{HH}$ = 7.0 Hz, $Me_A$), 1.44 (s, 3 H, $Me_B$). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 100 MHz, 25 °C): $\delta$ 198.1 (Ir=C), 151.6, 149.4, 149.2, 142.8, 142.1, 142.0 ($C_{qpz}$), 140.3 ($CH_I$), 134.8 ($CH_F$), 129.4 ($CH_H$), 113.7 ($CH_G$), 108.3, 107.1, 107.0 ($CH_{pz}$), 88.5 ($C^1$), 44.9 ($CH_C$), 21.7 ($Me_A$), 25.0 ($Me_B$), 15.6, 14.9, 14.0, 13.2, 12.9 (1:2:1:1:1, $Me_{pz}$), 10.6 ($IrCH_{2\ (D/E)}$, $^1J_{CH}$ = 126 Hz), −3.6 ppm ($IrCH_{2\ (A/B)}$, $^1J_{CH}$ = 126 Hz). HRMS (FAB): *m*/*z* calcd for $C_{26}H_{37}BIrN_7$ 651.2833, found 651.2858.

**Synthesis and Characterization of Complex *epi*-10a.**




Following the procedure used in the synthesis of complex **8a**, but beginning from a mixture of complexes **8c**, **9c**, and *epi*-**9c** and heating to 80 °C, a mixture of complexes **8a**, **10a**, and *epi*-**10a** was obtained in a ca. 1:0.5:0.2 ratio. Separation by preparative thin-layer chromatography (*n*-hexane/$Et_2O$, 4/1) gave a ca. 2/1 mixture of **10a** and *epi*-**10a**. $^1$H NMR ($C_6D_6$, 500 MHz, 25 °C): $\delta$ 7.50 (d, 1 H, $H_F$), 7.31 (d, 1 H, $H_I$), 6.40 (t, 1 H, $H_G$), 6.09 (t, 1 H, $H_H$), 5.69, 5.68, 5.60 (s, 1 H each, 3 $CH_{pz}$), 3.15, 2.45 (d, 1 H each, $^2J_{HH}$ = 10.1 Hz, $H_D$, $H_E$), 2.98 (dd, 1 H, $^2J_{HH}$ = 11.8, $^3J_{HH}$ = 9.8, $H_B$), 2.76, 2.29, 2.27, 2.25, 2.08, 1.58 (s, 3 H each, 6 $Me_{pz}$), 2.20 (m, 1 H, $H_C$), 1.78 (m, 1 H, $H_A$), 1.43 (s, 3 H, $Me_B$), 0.89 (d, 3 H, $^3J_{HH}$ = 7.0 Hz, $Me_A$); $^{13}C\{^1H\}$ NMR ($C_6D_6$, 125 MHz, 25 °C) selected data: $\delta$ 191.1 (Ir=C), 42.4 ($CH_C$), 17.6 ($Me_A$), 15.0 ($IrCH_{2\ (D/E)}$), −2.94 ppm ($IrCH_{2\ (A/B)}$). Crystal data for ***epi*-10a**: $C_{26}H_{37}BIrN_7$, *Mr* = 650.64, orthorhombic, *a* = 10.4723(6) Å, *b* = 14.5591(7) Å, *c* = 17.0061(9) Å, $\alpha$ = 90.00°, $\beta$ = 90.00°, $\gamma$ = 90.00°, *V* = 2592.9(2) Å$^3$, *T* = 173(2) K, space group $P2_12_12_1$, *Z* = 4, $\mu$ = 5.178 mm$^{-1}$, 58266 reflections measured, 7921 independent reflections ($R_{int}$ = 0.0737). The final R1 value was 0.0549 ($I > 2\sigma(I)$). The final wR2($F^2$) value was 0.1122 ($I > 2\sigma(I)$). The final R1 value was 0.0913 (all data). The final wR2($F^2$) value was 0.1267 (all data). The goodness of fit on $F^2$ was 1.107. CCDC-943067 (*epi*-**10a**).

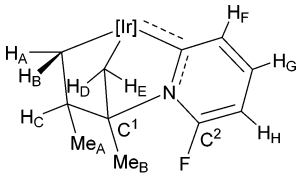
**Synthesis and Characterization of Complex 4d.**




A suspension of complex **3** (100 mg, 0.17 mmol) in 6 mL of cyclohexane was heated to 60 °C for 24 h with 1.2 equiv of 2-fluoropyridine (18 $\mu$L, 0.21 mmol). The solvent was removed under reduced pressure, and the solid residue was subjected to column chromatography on silica gel (*n*-hexane/$Et_2O$, 20/1) to obtain compound **4d** as a yellow-green solid (60% yield). $^1$H NMR ($CDCl_3$, 400 MHz, 25 °C): $\delta$ 8.28 (m, 1 H, $H_F$), 7.63 (q, 1 H, $^4J_{FH}$ = 7.4 Hz, $H_D$), 7.0 (t, 1 H, $H_E$), 6.46 (dd, 1 H, $^3J_{FH}$ = 3.2 Hz, $H_C$), 5.65, 5.60 (s, 2:1, 3 $CH_{pz}$), 3.24 (d, 2 H, $^2J_{HH}$ = 14.3 Hz, 2 $H_A$), 2.45 (d, 2 H, 2 $H_B$), 2.39, 2.33, 1.99, 1.56 (s, 2:1:1:2, 6 $Me_{pz}$), 1.75 (s, 6 H, 2 $C^1$ Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): $\delta$ 168.4 (d, $^1J_{CF}$ = 260 Hz, $C^2$), 155.2 ($CH_F$), 151.5, 149.0, 143.1, 142.7 (1:2:1:2, $C_{qpz}$), 140.2 (2 $C^1$), 138.0 (d, $^3J_{CF}$ = 9 Hz, $CH_D$), 122.6 (d, $^4J_{CF}$ = 4 Hz, $CH_E$), 108.8 (d, $^2J_{CF}$ = 30 Hz, $CH_C$), 108.4, 105.9 (1:2, $CH_{pz}$), 18.6 (2 $C^1Me$), 13.4, 13.0, 12.4, 12.0 (1:2:2:1, $Me_{pz}$), 12.0 ppm (2 $IrCH_2$). HRMS (FAB): *m*/*z* calcd for $C_{26}H_{36}BFIrN_7$ 669.2739, found: 669.2744. Anal. Calcd for $C_{26}H_{36}BFIrN_7$: C, 46.7; H, 5.4; N, 14.6. Found: C, 46.5; H, 5.9; N, 13.9.

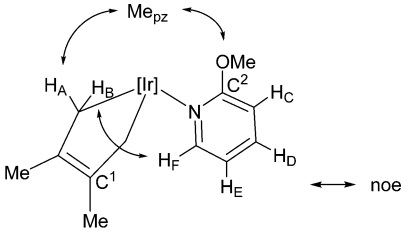

dx.doi.org/10.1021/om400968s | *Organometallics* 2014, 33, 498−510

### Synthesis and Characterization of Complex *epi*-10d.



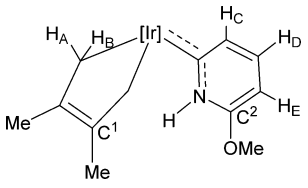

A suspension of complex **3** (100 mg, 0.17 mmol) in 4 mL of cyclohexane was heated to 150 °C for 24 h with 1.2 equiv of 2-fluoropyridine (18 μL, 0.21 mmol). The solvent was removed under reduced pressure and the solid residue subjected to column chromatography on silica gel (*n*-hexane/$Et_2O$, 60/1) to give *epi*-**10d**, as a pale yellow solid, in 40% yield. $^1$H NMR ($CDCl_3$, 500 MHz, 25 °C): $\delta$ 7.28 (d, 1 H, $H_F$), 7.01 (q, 1 H, $^4J_{HF}$ = 7.5 Hz, $H_G$), 6.27 (t, 1 H, $^3J_{HF}$ = 7.5 Hz, $H_H$), 5.77, 5.65, 5.61 (s, 1 H each, 3 $CH_{pz}$), 2.77 (d, 1 H, $^2J_{HH}$ = 10.3 Hz, $H_D$), 2.57 (s, 3 H, $Me_{pz}$), 2.45 (dd, 1 H, $^2J_{HH}$ = 12.1, $^3J_{HH}$ = 10.2 Hz, $H_B$), 2.35, 2.34, 2.33 (s, 3 H each, 3 $Me_{pz}$), 2.28 (d, 1 H, $H_E$), 2.0 (m, 1 H, $H_C$), 1.84 (s, 6 H, $Me_{pz}$, $Me_B$), 1.59 (s, 3 H, $Me_{pz}$), 1.43 (dd, 1 H, $^2J_{HH}$ = 12.1, $^3J_{HH}$ = 7.8 Hz, $H_A$), 0.93 (d, 3 H, $^3J_{HH}$ = 6.6 Hz, $Me_A$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, 25 °C): $\delta$ 193.0 (d, $^3J_{CF}$ = 9 Hz, Ir=C), 159.1 (d, $^1J_{CF}$ = 270 Hz, $C^2$), 151.2, 149.3, 143.1, 142.3, 142.1 (1:2:1:1:1, $C_{qpz}$), 136.2 (d, $^4J_{CF}$ = 3 Hz, $CH_F$), 132.8 (d, $^3J_{CF}$ = 9 Hz, $CH_G$), 107.6, 106.6, 106.5 ($CH_{pz}$), 96.9 (d, $^2J_{CF}$ = 24 Hz, $CH_H$), 93.8 ($C^1$), 42.5 ($CH_C$), 26.0 (d, $^4J_{CF}$ = 17 Hz, $Me_B$), 17.8 ($Me_A$), 17.7 ($IrCH_{2\ (D/E)}$, $^1J_{CH}$ = 127 Hz), 14.4, 14.3, 14.0, 12.9, 12.8, 12.7 ($Me_{pz}$), −2.9 ppm ($IrCH_{2\ (A/B)}$, $^1J_{CH}$ = 126 Hz). HRMS (FAB): *m*/*z* calcd for $C_{26}H_{36}BFIrN_7$ 669.2739, found 669.2731.

### Synthesis and Characterization of Complex 4e.



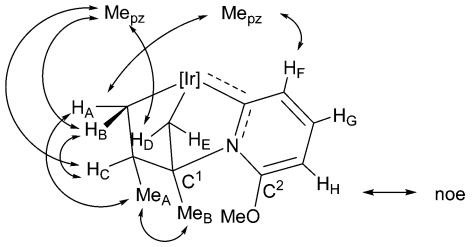

Complex **3** (200 mg, 0.35 mmol) was dissolved in benzene (4 mL), 2-methoxypyridine was added (44 μL, 0.42 mmol), and the mixture was heated with stirring for 3 h at 60 °C. The solvent was removed under reduced pressure and the solid residue washed with *n*-pentane to give **4e** as a yellow solid in 90% yield. $^1$H NMR ($C_6D_6$, 400 MHz, 25 °C): $\delta$ 8.56 (d, 1 H, $H_F$), 6.79 (t, 1 H, $H_D$), 6.27 (t, 1 H, $H_E$), 5.55, 5.53 (s, 2:1, 3 $CH_{pz}$), 5.44 (d, 1 H, $H_C$), 3.90 (d, 2 H, $^2J_{AB}$ = 13.6 Hz, 2 $H_A$), 2.99 (d, 2 H, 2 $H_B$), 2.42 (s, 3 H, OMe), 2.35, 2.34, 2.20, 1.68 (s, 1:2:1:2, 6 $Me_{pz}$), 2.18 (s, 6 H, 2 $C^1$ Me); $^{13}C\{^1H\}$ NMR ($C_6D_6$, 100 MHz, 25 °C): $\delta$ 169.2 ($C^2$), 156.1 ($CH_F$), 151.1, 149.1, 143.1, 141.0 (1:2:1:2, $C_{qpz}$), 141.4 (2 $C^1$), 136.8 ($CH_D$), 119.0 ($CH_E$), 108.8, 106.0 (1:2, $CH_{pz}$), 103.5 ($CH_C$), 55.3 (OMe), 19.6 (2 $C^1Me$), 13.7, 13.6, 12.8, 12.7 (1:2:1:2, $Me_{pz}$), 13.2 ppm (2 $IrCH_2$, $^1J_{CH}$ = 120 Hz). HRMS (FAB): *m*/*z* calcd for $C_{27}H_{39}BIrN_7O$ 681.2938, found 681.2917. Anal. Calcd for $C_{27}H_{39}BIrN_7O$: C, 47.6; H, 5.7; N, 14.4. Found: C, 47.2; H, 5.9; N, 14.4.

### Synthesis and Characterization of Complex 8e.



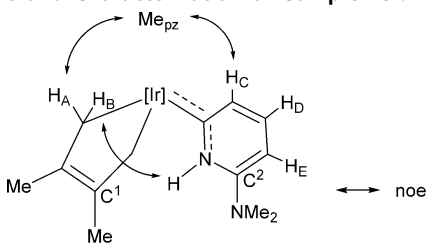

Complex **3** (100 mg, 0.17 mmol) was suspended in $C_6H_{12}$ (3 mL), 2-methoxypyridine was added (22 μL, 0.21 mmol), and the mixture was heated with stirring for 15 h at 90 °C. The solvent was removed under reduced pressure, and the $^1$H NMR spectrum of the residue confirmed the presence of compounds **8e** and *epi*-**10e** in a ca. 1:0.6 ratio. Column chromatography on silica gel (*n*-hexane/$Et_2O$, 100/1) allowed separation of the two species with **8e** isolated, in the first fraction, as an orange solid in 20% yield. $^1$H NMR ($C_6D_6$, 500 MHz, 25 °C): $\delta$ 11.28 (br s, 1 H, NH), 6.85 (d, 1 H, $H_C$), 6.27 (t, 1 H, $H_D$), 5.70, 5.66 (s, 1:2, 3 $CH_{pz}$), 5.12 (d, 1 H, $H_E$), 3.68 (d, 2 H, $^2J_{AB}$ = 14.4 Hz, 2 $H_A$), 2.78 (d + s, 5 H, 2 $H_B$ and OMe), 2.36, 2.30, 2.26, 2.15, (s, 1:2:1:2, 6 $Me_{pz}$), 1.87 (s, 6 H, 2 $C^1$ Me). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 125 MHz, 25 °C): $\delta$ 185.6 (Ir=C), 159.5 ($C^2$), 150.6, 149.2 (1:2, $C_{qpz}$), 142.7 (2 $C^1$), 142.5, 141.8 (1:2, $C_{qpz}$), 135.4 ($CH_C$), 132.7 ($CH_D$), 107.6, 106.5 (1:2, $CH_{pz}$), 90.6 ($CH_E$), 54.2 (OMe), 19.7 (2 $C^1Me$), 14.1, 12.7, 12.5, 11.4 (2:1:2:1, $Me_{pz}$), 12.0 ppm (2 $IrCH_2$). Crystal data for **8e**: $C_{27}H_{39}BIrN_7O{\cdot}C_6H_6$, $M_r$ = 758.77, triclinic, *a* = 9.8842(4) Å, *b* = 10.3715(4) Å, *c* = 17.4179(7) Å, $\alpha$ = 81.9220(10)°, $\beta$ = 76.8800(10)°, $\gamma$ = 72.2920(10)°, *V* = 1651.65(11) Å$^3$, *T* = 173(2) K, space group $P\bar{1}$, *Z* = 2, $\mu$ = 4.079 mm$^{-1}$, 57121 reflections measured, 9872 independent reflections ($R_{int}$ = 0.0481). The final R1 value was 0.0278 ($I > 2\sigma(I)$). The final wR2($F^2$) value was 0.0597 ($I > 2\sigma(I)$). The final R1 value was 0.0366 (all data). The final wR2($F^2$) value was 0.0632 (all data). The goodness of fit on $F^2$ was 1.032. CCDC-943066 (**8e**).

### Synthesis and Characterization of Complex *epi*-10e.




Complex *epi*-**10e** was obtained in the second fraction of the chromatography noted above, as a brown solid in 35% yield. $^1$H NMR ($C_6D_6$, 400 MHz, 25 °C): $\delta$ 7.34 (d, 1 H, $H_F$), 6.56 (t, 1 H, $H_G$), 5.78, 5.72 (s, 2:1, 3 $CH_{pz}$), 5.41 (d, 1 H, $H_H$), 3.26 (d, 1 H, $^2J_{HH}$ = 10.3 Hz, $H_D$), 3.10 (dd, 1 H, $^2J_{HH}$ = 11.5, $^3J_{HH}$ = 10.1 Hz, $H_B$), 2.93 (s, 3 H, OMe), 2.85 (s, 3 H, $Me_{pz}$), 2.82 (d, 1 H, $H_E$), 2.33 (m, 1 H, $H_C$), 2.31, 2.30, 2.28, 2.13 (s, 3 H each, 4 $Me_{pz}$), 2.08 (s, 3 H, $C^1$ $Me_B$), 1.98 (dd, 1 H, $^2J_{HH}$ = 11.5, $^3J_{HH}$ = 7.8 Hz, $H_A$), 1.88 (s, 3 H, $Me_{pz}$), 1.28 (d, 3 H, $^3J_{HH}$ = 6.5 Hz, $Me_A$). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 100 MHz, 25 °C): $\delta$ 194.4 (Ir=C), 161.3 ($C^2$), 151.2, 149.6, 149.5, 142.7, 142.2, 142.0 ($C_{qpz}$), 133.3 ($CH_F$), 132.1 ($CH_G$), 107.8, 107.1 (1:2, $CH_{pz}$), 93.8 ($CH_H$), 92.8 ($C^1$), 54.8 (OMe), 43.9 ($CH_C$), 28.4 ($Me_B$), 19.7 ($IrCH_{2(D/E)}$, $^1J_{CH}$ = 124 Hz), 19.1 ($Me_A$), 15.0, 14.7, 14.6, 13.0 (1:1:1:3, $Me_{pz}$), −1.5 ppm ($IrCH_{2(A/B)}$, $^1J_{CH}$ = 124 Hz). HRMS (FAB): *m*/*z* calcd for $C_{27}H_{39}BIrN_7O$ 681.2938, found 681.2961. Anal. Calcd for $C_{27}H_{39}BIrN_7O$: C, 47.6; H, 5.7; N, 14.4. Found: C, 47.4; H, 5.3; N, 14.3. Crystal data for ***epi*-10e**: $C_{27}H_{39}BIrN_7O{\cdot}C_6H_6$, $M_r$ = 758.77, triclinic, *a* = 10.327(3) Å, *b* = 11.229(3) Å, *c* = 16.031(3) Å, $\alpha$ = 83.361(6)°, $\beta$ = 76.900(6)°, $\gamma$ = 64.141(4)°, *V* = 1628.9(7) Å$^3$, *T* = 173(2) K, space group $P\bar{1}$, *Z* = 2, $\mu$ = 4.136 mm$^{-1}$, 18827 reflections measured, 6529 independent reflections ($R_{int}$ = 0.0793). The final R1 value was 0.0540 ($I > 2\sigma(I)$). The final wR2($F^2$) value was 0.1145 ($I > 2\sigma(I)$). The final R1 value was 0.0881 (all data). The final wR2($F^2$) value was 0.1267 (all data). The goodness of fit on $F^2$ was 1.029. CCDC-943068 (*epi*-**10e**).

### Synthesis and Characterization of Complex 8f.




A suspension of complex **3** (100 mg, 0.17 mmol) in 4 mL of cyclohexane was heated to 90 °C for 15 h with 1.2 equiv of 2-dimethylaminopyridine (25.5 μL, 0.21 mmol). The solvent was removed under reduced pressure, and the solid residue was subjected to column chromatography on silica gel (*n*-hexane/$Et_2O$, 20/1) to give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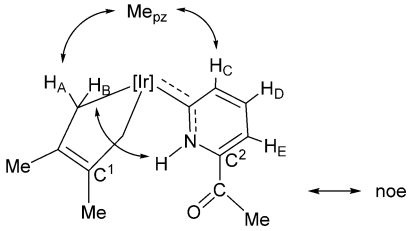
compound **8f**, as a yellow solid, in 70% yield. $^1$H NMR ($C_6D_6$, 400 MHz, 25 °C): $\delta$ 10.72 (br s, 1 H, NH), 6.60 (d, 1 H, $H_C$), 6.35 (t, 1 H, $H_D$), 5.71, 5.70 (s, 2:1, 3 $CH_{pz}$), 5.19 (d, 1 H, $H_E$), 3.59 (d, 2 H, $^2J_{AB}$ = 14.4 Hz, 2 $H_A$), 2.81 (d, 2 H, 2 $H_B$), 2.36, 2.31, 2.28, 1.94, (s, 1:2:1:2, 6 $Me_{pz}$), 2.18 (s, 6 H, $NMe_2$), 2.00 (s, 6 H, 2 $C^1$ Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): $\delta$ 197.6 (Ir=C), 152.3 ($C^2$), 150.5, 149.2 (1:2, $C_{qpz}$), 142.7, 141.7 (3:2, 2 $C^1$, $C_{qpz}$), 133.1 ($CH_D$), 129.0 ($CH_C$), 107.3, 106.1 (1:2, $CH_{pz}$), 93.8 ($CH_E$), 38.1 ($NMe_2$), 19.3 (2 $C^1$*Me*), 14.0, 12.9, 12.7, 11.0 (2:1:2:1, $Me_{pz}$), 10.6 ppm (2 $IrCH_2$, $^1J_{CH}$ = 121 Hz). IR (KBr): $\nu$ 2521.5 (B−H), 3218 (N−H) cm$^{-1}$. Anal. Calcd for $C_{28}H_{42}BIrN_8$: C, 48.4; H, 6.1; N, 16.1. Found: C, 48.3; H, 6.1; N, 15.8. Crystal data for **8f**: $C_{28}H_{42}BIrN_8$, $M_r$ = 693.71, triclinic, $a$ = 10.0039(4) Å, $b$ = 10.3168(5) Å, $c$ = 14.6755(6) Å, $\alpha$ = 82.575(2)°, $\beta$ = 81.865(2)°, $\gamma$ = 81.578(2)°, $V$ = 1474.09(11) Å$^3$, $T$ = 173(2) K, space group $P\bar{1}$, $Z$ = 2, $\mu$ = 4.560 mm$^{-1}$, 38288 reflections measured, 9068 independent reflections ($R_{int}$ = 0.0336). The final R1 value was 0.0199 ($I > 2\sigma(I)$). The final wR2($F^2$) value was 0.0457 ($I > 2\sigma(I)$). The final R1 value was 0.0247 (all data). The final wR2($F^2$) value was 0.0469 (all data). The goodness of fit on $F^2$ was 1.026. CCDC-945612 (**8f**).

**Synthesis and Characterization of Complex 8g.**




A suspension of complex **3** (100 mg, 0.17 mmol) in 4 mL of cyclohexane was heated to 90 °C for 15 h with 1.2 equiv of 2-acetylpyridine (23 $\mu$L, 0.21 mmol). The solvent was removed under reduced pressure, and the solid residue was subjected to column chomatography on silica gel (*n*-hexane/$Et_2O$, 10/1) to give compound **8g**, as a brown solid, in 75% yield. $^1$H NMR ($CDCl_3$, 500 MHz, 25 °C): $\delta$ 11.91 (br s, 1 H, NH), 7.15 (d, 1 H, $H_C$), 7.11 (d, 1 H, $H_E$), 6.87 (t, 1 H, $H_D$), 5.69, 5.64 (s, 1:2, 3 $CH_{pz}$), 3.17 (d, 2 H, $^2J_{AB}$ = 14.4 Hz, 2 $H_A$), 2.49 (s, 3 H, COMe), 2.25 (d, 2 H, 2 $H_B$), 2.37, 2.35, 2.07, 1.56, (s, 2:1:1:2, 6 $Me_{pz}$), 1.84 (s, 6 H, 2 $C^1$ Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, 25 °C): $\delta$ 191.0 (COMe), 188.4 (Ir=C), 151.3, 149.2 (1:2, $C_{qpz}$), 148.6 ($CH_C$), 143.2 ($C^2$), 143.0, 142.3 (1:2, $C_{qpz}$), 141.9 (2 $C^1$), 128.3 ($CH_D$), 115.6 ($CH_E$), 107.6, 106.4 (1:2, $CH_{pz}$), 24.7 (CO*Me*), 19.5 (2 $C^1$*Me*), 13.9, 13.1, 12.8, 11.3 (2:1:2:1, $Me_{pz}$), 12.6 ppm (2 $IrCH_2$, $^1J_{CH}$ = 120 Hz). Anal. Calcd for $C_{28}H_{39}BIrN_7O$: C, 48.0; H, 5.6; N, 14.1. Found: C, 48.1; H, 5.7; N, 13.2.

## ■ ASSOCIATED CONTENT

### Supporting Information

Figures giving NMR spectra of compounds **7**, **10a**, *epi*-**10d**, and **8e** as proof of purity, CIF files giving crystallographic data for the crystal structure determinations, and a table containing the corresponding crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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