Comparative Study of Rhodium and Iridium Porphyrin Diaminocarbene and N-Heterocyclic Carbene Complexes

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Abstract
Iridium meso-tetratolylporphyrinato (TTP) mono- and bis-diaminocarbene complexes, [Ir(TTP)[═C(NHBn)(NHR)]2-x(C≡NBn)x]BF4, where R = Bn, n-Bu and x = 1, 0, were synthesized by nucleophilic addition of amines to the bis-isocyanide complex [Ir(TTP)(C≡NBn)2]BF4. Rhodium and iridium porphyrinato N-heterocyclic carbene (NHC) complexes M(TTP)CH3(NHC), where NHC = 1,3-diethylimidazolylidene (deim) or 1-(n-butyl)-3-methylimidazolylidene (bmim), were prepared by the addition of the free NHC to M(TTP)CH3. The NHC complexes displayed two dynamic processes by variable-temperature NMR: meso-aryl–porphyrin C–C bond rotation and NHC exchange. meso-Aryl–porphyrin C–C bond rotation was exhibited by both rhodium and iridium complexes at temperatures ranging between 239 and 325 K. Coalescence data for four different complexes revealed ΔG ≠ ROT values of 59 ± 2 to 63 ± 1 kJ·mol–1. These relatively low rotation barriers may result from ruffling distortions in the porphyrin core, which were observed in the molecular structures of the rhodium and iridium bmim complexes. Examination of NHC exchange with rhodium complexes by NMR line-shape analyses revealed rate constants of 3.72 ± 0.04 to 32 ± 6 s–1 for deim displacement by bmim (forward reaction) and 2.7 ± 0.4 to 18 ± 2 s–1 for bmim displacement by deim (reverse reaction) at temperatures between 282 and 295 K, corresponding to ΔGf ≠ of 65.2 ± 0.6 kJ·mol–1 and ΔGr ≠ of 66.2 ± 0.5 kJ·mol–1, respectively. Rates of NHC exchange with iridium were far slower, with first-order dissociation rate constants of (1.75 ± 0.04) × 10–4 s–1 for the forward reaction and (1.2 ± 0.1) × 10–4 s–1 for the reverse reaction at 297.1 K. These rate constants correspond to ΔG ≠ values of 94.2 ± 0.6 and 95.2 ± 0.2 kJ·mol–1 for the forward and reverse reactions, respectively. Equilibrium constants for the exchange reactions were 1.6 ± 0.2 with rhodium and 1.56 ± 0.04 with iridium, favoring the bmim complex in both cases, and the log(K) values for NHC binding to M(TTP)CH3 were 4.5 ± 0.3 (M = Rh) and 5.4 ± 0.5 (M = Ir), as determined by spectrophotometric titrations at 23 °C. The molecular structures also featured unusually long metal–C carbene bonds for the bmim complexes (Rh–CNHC: 2.255(3) Å and Ir–CNHC: 2.194(4) Å).

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Comparative Study of Rhodium and Iridium Porphyrin Diaminocarbene and N-Heterocyclic Carbene Complexes

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Supporting Information

ABSTRACT: Iridium meso-tetratolylporphyrinato (TTP) mono- and bis-diaminocarbene complexes, [Ir(TTP)[═C(NHBn)(NHR)]_2]BF_4, where R = Bn, n-Bu and x = 1, 0, were synthesized by nucleophilic addition of amines to the bis-isocyancide complex [Ir(TTP)- (C═NBN)]=BF_4. Rhodium and iridium porphyrinato N-heterocyclic carbene (NHC) complexes M(TTP)CH₃(NHC), where NHC = 1,3-diethylimidazolyldiene (deim) or 1-(n-butyl)-3-methylimidazolyldiene (bimim), were prepared by the addition of the free NHC to M(TTP)CH₃. The NHC complexes displayed two dynamic processes by variable-temperature NMR line-shape analyses revealed rate constants of 3.72 ± 0.04 to 32 ± 6 s⁻¹ for deim displacement by bimim (forward reaction) and 2.7 ± 0.4 to 18 ± 2 s⁻¹ for bimim displacement by deim (reverse reaction) at temperatures between 282 and 295 K, corresponding to ΔGᵣₒₜ values of 65.2 ± 0.6 kJ·mol⁻¹ and ΔGᵣₒₜ of 66.2 ± 0.5 kJ·mol⁻¹, respectively. Rates of NHC exchange with iridium were far slower, with first-order dissociation rate constants of (1.75 ± 0.04) × 10⁻⁴ s⁻¹ for the forward reaction and (1.2 ± 0.1) × 10⁻⁴ s⁻¹ for the reverse reaction at 297.1 K. These rate constants correspond to ΔGᵣₒₜ values of 94.2 ± 0.6 and 95.2 ± 0.2 kJ·mol⁻¹ for the forward and reverse reactions, respectively. Equilibrium constants for the exchange reactions were 1.6 ± 0.2 with rhodium and 1.56 ± 0.04 with iridium, favoring the bimim complex in both cases, and the log(𝐾) values for NHC binding to M(TTP)CH₃ were 4.5 ± 0.3 (M = Rh) and 5.4 ± 0.5 (M = Ir), as determined by spectrophotometric titrations at 23 °C. The molecular structures also featured unusually long metal−C(carbene) bonds for the bimim complexes (Rh−C_NHC: 2.255(3) Å and Ir−C_NBn: 2.194(4) Å).

INTRODUCTION

Metalloporphyrin complexes containing Fe, Ru, Os, Co, Rh, and Ir are useful catalysts for carbon insertion including cyclopropanation, X−H insertion (X = C, N, O, and S), and ylide-forming reactions. Particularly noteworthy are the dramatic reactivity differences displayed among the group 9 metalloporphyrin catalysts. For example, cyclopropanation of electron-deficient olefins is achieved with remarkable efficiency using cobalt(II) porphyrin catalysts, whereas yields with the other group 9 metalloporphyrin catalysts are modest. This reactivity trend can be explained by examining the intermediate species. While cobalt(II) catalysts appear to form relatively nucleophilic radical carbene complexes, rhodium and iridium porphyrin catalysts are believed to form traditional electrophilic Fischer-type carbene complexes. Despite this similarity, however, rhodium and iridium catalysts also display notably divergent reactivity patterns. Rhodium porphyrins catalyze cyclopropanation and C−H insertion reactions with rare selectivity for cis cyclopropanes and primary insertion products, respectively. In addition, rhodium-catalyzed cyclo-

propanations are tolerant to sterically hindered di- and trisubstituted olefins, but reactions with rhodium catalysts often require higher reaction temperatures to achieve practical rates. Although iridium complexes do not induce remarkable diastere- or regioselectivity, they are extremely reactive and robust, generating cyclopropanation products rapidly at −78 °C with turnover numbers on the order of 10⁶. This dissimilarity in reactivity is particularly evident in N−H insertion reactions, where tetratolylporphyrinato methyliridium, Ir(TTP)CH₃, rapidly catalyzed product formation under mild conditions and methylrhodium tetratolylporphyrinato, Rh(TTP)CH₃, failed to generate products at refluxing temperatures. Additional insight into these reactivity differences may be achieved by further examination of rhodium and iridium porphyrin carbene complexes.

Rhodium and iridium porphyrin carbene complexes derived from alkyl diazoacetate compounds were observed spectro-
complex 1 appear limited, this study demonstrated that diaminocarbene and the related N-heterocyclic carbene (NHC) complexes are relatively robust, making them useful models for metalloporphyrin-carbene studies. Accordingly, the work herein describes the synthesis, characterization, and structural comparison of new rhodium and iridium porphyrin diaminocarbene and NHC complexes.

**RESULTS**

**Synthesis and Characterization of Diaminocarbene Complexes.** An iridium diaminocarbene complex was synthesized using a synthetic route similar to that described previously for Rh complex 1 (Scheme 2). Treating Ir(TTP)(CO) with silver tetrafluoroborate followed by excess benzylisocyanide led to the formation of the bis(isocyanide) iridium complex [Ir(TTP)(C(NHBn))2]BF4 (2), which was isolated in 61% yield after recrystallization. Complex 2 was characterized by 1H NMR, 13C NMR, and IR spectroscopy. New 1H NMR signals observed at 6.98 (t, 2H, CH2), 4.80 (d, 4H, o-H), and 2.65 (s, 4H, CH2) ppm were assigned to the isocyanide ligands. Significant upfield shifts, especially for the ortho and meta protons, were due to the porphyrin ring current effect. Coordination to iridium also caused a shift in the C=N bond stretching mode from 2151 cm−1 for the free isocyanide to 2228 cm−1, indicating that the bound isocyanide is susceptible to nucleophilic attack. This stretching frequency is similar to that of Rh(TTP)(C≡CNBn)2(PF6) found at 2248 cm−1. Single-crystal X-ray diffraction revealed that complex 2 crystallized in the C2/c space group with half of the molecule in the asymmetric unit (Figure 1). Iridium was coordinated in a nearly ideal octahedral environment (Table S4; Supporting Information), and the porphyrin ring displayed very little distortion from planarity (vide infra). However, complex 2 displayed axial ligand disorder through a mirror plane, which required the atomic positions for the axial ligands to be approximated.

Nucleophilic addition to one of the coordinated isocyanide carbon atoms with benzylamine afforded the target diamino-carbene complex [Ir(TTP)(C≡C(NHBn))2]BF4 (3). Signals corresponding to the diaminocarbene ligand were observed by 1H NMR spectroscopy at 7.17 (t, 2H, p-H), 7.02 (t, 4H, m-H), 6.79 (t, 4H, o-H), 5.31 (d, 4H, o-H), and 4.80 (d, 4H, o-H), and 4.80 (d, 4H, o-H), and 2.65 (s, 4H, CH2) ppm were assigned to the isocyanide ligands. Significant upfield shifts, especially for the ortho and meta protons, were due to the porphyrin ring current effect. Coordination to iridium also caused a shift in the C=N bond stretching mode from 2151 cm−1 for the free isocyanide to 2228 cm−1, indicating that the bound isocyanide is susceptible to nucleophilic attack. This stretching frequency is similar to that of Rh(TTP)(C≡CNBn)2(PF6) found at 2248 cm−1. Single-crystal X-ray diffraction revealed that complex 2 crystallized in the C2/c space group with half of the molecule in the asymmetric unit (Figure 1). Iridium was coordinated in a nearly ideal octahedral environment (Table S4; Supporting Information), and the porphyrin ring displayed very little distortion from planarity (vide infra). However, complex 2 displayed axial ligand disorder through a mirror plane, which required the atomic positions for the axial ligands to be approximated.

Nucleophilic addition to one of the coordinated isocyanide carbon atoms with benzylamine afforded the target diamino-carbene complex [Ir(TTP)(C≡C(NHBn))2]BF4 (3). Signals corresponding to the diaminocarbene ligand were observed by 1H NMR spectroscopy at 7.17 (t, 2H, p-H), 7.02 (t, 4H, m-H), 6.79 (t, 4H, o-H), 5.31 (d, 4H, o-H), and 4.80 (d, 4H, o-H), and 4.80 (d, 4H, o-H), and 2.65 (s, 4H, CH2) ppm were assigned to the isocyanide ligands. Significant upfield shifts, especially for the ortho and meta protons, were due to the porphyrin ring current effect. Coordination to iridium also caused a shift in the C=N bond stretching mode from 2151 cm−1 for the free isocyanide to 2228 cm−1, indicating that the bound isocyanide is susceptible to nucleophilic attack. This stretching frequency is similar to that of Rh(TTP)(C≡CNBn)2(PF6) found at 2248 cm−1. Single-crystal X-ray diffraction revealed that complex 2 crystallized in the C2/c space group with half of the molecule in the asymmetric unit (Figure 1). Iridium was coordinated in a nearly ideal octahedral environment (Table S4; Supporting Information), and the porphyrin ring displayed very little distortion from planarity (vide infra). However, complex 2 displayed axial ligand disorder through a mirror plane, which required the atomic positions for the axial ligands to be approximated.

**Scheme 1. Nucleophilic Attack on a Bis(isocyanide) Complex to Generate Complex 1**

**Scheme 2. Synthesis of Diaminocarbene (Tetra-p-tolylporphyrinato)iridium Complexes**

**Figure 1. ORTEP20 of [Ir(TTP)(C≡CNBn)2]BF4 (2) with 30% probability thermal ellipsoids. Selected bond distances (Å): Ir−N(1) = 2.045(4), Ir−N(2) = 2.045(4). Selected bond angles (deg): N(1)−Ir−N(2) = 90.02(14), N(1)−Ir−N(2) = 89.98(14). Atoms with index i are related to the basic atom with transformation 1/2 − x, 1/2 + y, 1 + z.**

**dx.doi.org/10.1021/om500081w | Organometallics 2014, 33, 2219−2229**
The 2218 cm\(^{-1}\) C≡N stretching band for complex 3 suggested that the remaining coordinated isocyanide is also susceptible to nucleophilic attack. Indeed, addition of benzylamine to complex 2 or 3 produced bis(diaminocarbene) complex \([\text{Ir}(\text{TTP})\{\text{C(NHBn)\_2}\}]\)\(_2\text{BF}_4\) (4a). Excess amine (~10 equiv) was required for the reaction to proceed at a practical rate; attempts with less than 5 equiv of benzylamine gave trace product formation in 24 h. The formation of complex 4a was established on the basis of its \(^1\text{H NMR}\) spectrum. Integrations of the diaminocarbene signals at 7.17 (t, 8H, CH\(_2\)) and 7.02 (t, 8H, CH\(_2\)) ppm were consistent with two equivalent axial ligands. Loss of the coordinated isocyanide was indicated by the disappearance of diagnostic signals at 4.85 ppm (d, CH\(_2\)). However, it was difficult to fully characterize complex 4a by \(^1\text{H NMR}\) because other metalloporphyrin impurities were present in substantial amounts, and attempts to purify complex 4a or obtain single crystals suitable for X-ray diffraction were unsuccessful. In lieu of definitive structural evidence for 4a, a similar bis(diaminocarbene) complex, \([\text{Ir}(\text{TTP})\{\text{C(NHBn)}\text{Bu}\_2\}]\)\(_2\text{BF}_4\) (4b), derived from the addition of excess \(n\)-butylamine to the bis(isocyanide) complex 2 was isolated and examined by X-ray diffraction (Supporting Information). This structure confirmed the formation of bis(diaminocarbene) complex 4b, but the axial ligands were disordered through symmetry, prohibiting a thorough metrical analysis of the axial atomic positions. Nevertheless, the structure of the porphyrin core was well-defined and exhibited significant ruffling and saddling deformations (vide infra).

### Synthesis and Characterization of NHC Complexes

Extensive comparisons of rhodium and iridium porphyrin diaminocarbene complexes are limited by the disorder in the iridium molecular structures. To find a more suitable basis for comparison, focus was shifted to complexes bearing NHC ligands 1,3-diethylimidazolylidene (deim) and 1-(n-buty1)-3-methylimidazolylidene (bmim). The free NHC ligands were synthesized by deprotonation of the corresponding imidazolium salt as reported by Arduengo et al.\(^{21}\) NHC complexes (NHC)\(_2\text{M(TTP)CH}_3\) (5a, M = Rh, NHC = deim; 5b, M = Rh, NHC = bmim; 6a, M = Ir, NHC = deim; 6b, M = Ir, NHC = bmim) were synthesized by treating the respective metalloporphyrins with a slight excess of the free NHC (Scheme 3).

In all cases, conversion of the metalloporphyrin was nearly quantitative, as indicated by the formation of one major \(\beta\)-pyrrole porphyrin signal in the \(^1\text{H NMR}\) spectrum of the reaction mixture. Pure samples were isolated by recrystallization from THF/hexanes and characterized by absorption spectroscopy, \(^{13}\text{C NMR}\) spectroscopy, and X-ray diffraction studies. Compounds 5a,b and 6a,b were moisture sensitive, especially in solution, generating M(\text{TTP})\text{CH}_3 (M = Rh, Ir) along with an imidazolium salt upon exposure to water. Although cobalt(III) porphyrin NHC complexes were isolated previously,\(^{22}\) complexes 5a,b and 6a,b serve as the first reported rhodium or iridium porphyrin NHC complexes.

Spectroscopic changes accompanied the coordination of the free NHC to \(\text{M(TTP)CH}_3\), producing an immediate color change from orange-red to a dark greenish-brown. The resulting absorption spectra displayed “split Soret” bands characteristic of hyperporphyrins at 374 and 444 nm for the rhodium NHC complexes and at 370 and 438 nm for the iridium NHC complexes (Figure 3).\(^{23}\) Similar hyper spectra were observed previously with the diazoacetate chemistry of iridium porphyrin complexes, including the metal–carbene and metal–ylide intermediates detected in \(\text{Ir(TTP)CH}_3\)-catalyzed C–H insertion and N–H insertion reactions, respectively.\(^{14,15,24}\) In contrast, the diaminocarbene complexes of rhodium (1) and iridium (3 and 4) did not display hyper spectra, suggesting that NHC complexes 5 and 6 provide a better model for the electronic structure of metal–carbene intermediates involved in catalysis than do the diaminocarbene complexes.

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**Scheme 3. Synthesis of (Tetra-p-tolylporphyrinato)rhodium and -iridium NHC Complexes**

![Scheme 3](image-url)
Transition metal hyperporphyrin complexes are typically classified as d-type metalloporphyrins, where the hyper character is the result of ligand-to-metal charge transfer (LMCT) from porphyrin \( \alpha(x) \), \( \alpha(y) \) orbitals to metal \( e_g(d_{ez}) \) orbitals.\textsuperscript{23,25} Metalloporphyrins with d\textsuperscript{6} electron configurations are an unusual case because the metal \( e_g(d_{ez}) \) orbitals \( (d_{ez} \text{ and } d_{yz}) \) with the z-axis perpendicular to the porphyrin plane are filled in the ground state. Iterative extended Hückel calculations on similar d\textsuperscript{6} hyperporphyrins, (OEP)Ru(py)\textsubscript{2} and (OEP)Os(py)\textsubscript{2}, suggested that orbital mixing with relatively low energy doubly excited states, \( [e_g(d_{ez})]_2 \lbrack \alpha(x), \alpha(y) \rbrack [e_u(x*)]_2 \), may be responsible for the hyper-type absorption bands.\textsuperscript{26} A similar phenomenon may be responsible for the hyper spectra displayed here.

The \(^1\)H NMR spectra of \( 5a, b \) and \( 6a, b \) displayed signals corresponding to the coordinated NHCS in the region of 5.3–5.1 ppm for the vinylic protons and 0.5 to –0.6 ppm for the aliphatic protons. These signals were upfield shifted 1–5 ppm relative to those of the free NHC. Coordination of the NHC also caused a significant upfield shift in the \( \alpha \) protons. The \( \alpha \)-methyl resonances. The \( \alpha \)-methyl shifted from –6.56 ppm to –7.44 and –7.38 ppm for rhodium NHC complexes \( (5a \text{ and } 5b, \text{ respectively}) \) and from –7.01 ppm to –8.03 and –7.94 ppm for the iridium NHC complexes \( (6a \text{ and } 6b, \text{ respectively}) \). In contrast, the \( \alpha \)-methyl signal of Ir(TTP)CH\textsubscript{3}(＝C\{Ph\}-CO\textsubscript{2}Me) shifted downfield to –4.8 ppm.\textsuperscript{15} The \(^{13}\)C NMR spectra for complexes \( 5a, 5b, 6a, \text{ and } 6b \) exhibited carbene \( \alpha \)-carbon signals at 179.98, 181.84, 164.33, and 164.86 ppm, respectively. These values are reasonable based on previously reported rhodium and iridium NHC complexes; carbene \( \alpha \)-carbon signals for RhCl(\( \eta^2\)-O\textsubscript{2})(IPr)\textsubscript{2} and IrCl(\( \eta^2\)-O\textsubscript{2})(IPr)\textsubscript{2} (IPr = N,N-diisopropyl imidazolylidene) were observed at 180.8 and 167.4 ppm, respectively.\textsuperscript{27–29} The carbene \( \alpha \)-carbon \(^{13}\)C NMR signals did not seem to be affected substantially by the porphyrin ring current effect.

**Variable-Temperature NMR Analysis.** At ambient temperature, complexes \( 5a, b \) and \( 6a, b \) displayed several broad NMR resonances. Further examination by variable-temperature NMR revealed multiple dynamic processes. At 302.6 K, signals corresponding to the ortho and meta protons on the meso-tolyl substituents appeared as two doublets at ca. 7.9 and 7.5 ppm, respectively. Decreasing the temperature split each of these signals in a range that was most evident for the ortho protons (Figure 4). Of the dynamic processes that have been identified for porphyrin complexes including N–H tautomerism, macrocyclic inversion, and substituent–porphyrin rotation,\textsuperscript{30} the behavior exhibited here is most consistent with meso-aryl rotation. Activation energies for meso-aryl rotation \( (\Delta G^+_{\text{ROT}}) \) were determined to be 59 ± 2 to 63 ± 1 kJ·mol\textsuperscript{-1} by NMR coalescence data (Table 1), which are within the previously established range of 40–78 kJ·mol\textsuperscript{-1} for metalloporphyrins.\textsuperscript{31–33}

Dynamic meso-aryl–porphyrin C–C bond rotation was observed previously in several metalloporphyrin complexes, including those with Ti, Ru, Ni, Zn, In, and Bi.\textsuperscript{31–33} Although aryl–porphyrin rotation has not been reported in rhodium or iridium porphyrins complexes, a study with ruthenium porphyrins measured relatively high barriers for meso-aryl rotation at 72–78 kJ·mol\textsuperscript{-1}.\textsuperscript{33} High rotation barriers are expected with relatively planar metalloporphyrins, which is usually the case with platinum group metals. Indeed, most axially asymmetric rhodium and iridium complexes typically display sharp inequivalent ortho proton signals at ambient temperature, implying that the activation energies for rotation are greater than 70 kJ·mol\textsuperscript{-1}. Thus, it is remarkable that NHC coordination lowers the barrier for aryl rotation to 59–63 kJ·mol\textsuperscript{-1}, especially considering that the nature of the axial ligand is not believed to have a significant impact on meso-aryl–porphyrin C–C bond rotation.\textsuperscript{35} More intriguing is that coordination with acyclic diaminocarbenes as in complexes 3 and 4 does not appear to lower the rotation barrier below 70 kJ·mol\textsuperscript{-1}. A reasonable explanation is that the low rotation barriers for complexes \( 5a, b \) and \( 6a, b \) result from deformations in the

![Figure 4](https://example.com/figure4.png)

**Figure 4.** Variable-temperature \(^1\)H NMR spectra of the ortho protons on the meso-tolyl substituents of \( (\text{NHC})M(\text{TTP})\text{CH}_3 \) (\( 5a, M = \text{Rh}, \text{NHC = deim}; 5b, M = \text{Rh}, \text{NHC = bmim}; 6a, M = \text{Ir}, \text{NHC = deim}; 6b, M = \text{Ir}, \text{NHC = bmim}) \). This dynamic behavior is consistent with meso-aryl–porphyrin C–C bond rotation.

**Table 1.** Kinetic Data for the Aryl–Porphyrin Rotation Shown by Complexes (NHC)M(\( \text{TTP})\text{CH}_3 \) (\( 5a, M = \text{Rh}, \text{NHC = deim}; 5b, M = \text{Rh}, \text{NHC = bmim}; 6a, M = \text{Ir}, \text{NHC = deim}; 6b, M = \text{Ir}, \text{NHC = bmim})

<table>
<thead>
<tr>
<th>complex</th>
<th>( \Delta G^+_{\text{ROT}} ) (kJ·mol\textsuperscript{-1})</th>
<th>coalescence T (K)</th>
</tr>
</thead>
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<tr>
<td>Rh(( \text{TTP})\text{CH}_3(\text{deim}) ) (5a)</td>
<td>61 ± 1</td>
<td>292</td>
</tr>
<tr>
<td>Rh(( \text{TTP})\text{CH}_3(\text{bmim}) ) (5b)</td>
<td>59 ± 2</td>
<td>270</td>
</tr>
<tr>
<td>Ir(( \text{TTP})\text{CH}_3(\text{deim}) ) (6a)</td>
<td>63 ± 1</td>
<td>303</td>
</tr>
<tr>
<td>Ir(( \text{TTP})\text{CH}_3(\text{bmim}) ) (6b)</td>
<td>62 ± 2</td>
<td>287</td>
</tr>
</tbody>
</table>
A second dynamic process was observed for rhodium complexes 5a and 5b. At 302.6 K, spectra of these complexes featured broad resonances for the NHC and the trans methyl protons. As the temperature was decreased to 239.0 K, these signals sharpened considerably (Figure S5), suggesting that NHC binding was fluxional with rhodium than with iridium.

**Kinetic Analysis of NHC Exchange.** Fluxional NHC binding was further established by examining NHC exchange reactions. In the initial studies, deim complexes 5a and 6a were treated with bmim, and NHC exchange (eq 1) was monitored by $^1$H NMR. The ratio of M(TTP)CH$_3$(deim) to M(TTP)-CH$_3$(deim), 6a, compared to Ir(TTP)-CH$_3$(deim), 6a. NHC exchange was more fluxional with rhodium than with iridium.

$$k_1 \approx k_2 \gg k_{-1}$$

where $k_1$ is the rate constant for NHC exchange, $k_2$ is the rate constant for ligand dissociation, and $k_{-1}$ is the rate constant for NHC dissociation. The ratio of $k_2$ to $k_{-1}$ is a measure of the rate of NHC exchange relative to the rate of ligand dissociation. The $k$ values were determined using pseudo-first-order kinetics, and the rate of NHC exchange was found to be independent of the concentration of the starting iridium complexes.

**Scheme 4. Pseudoirreversible NHC Exchange with Ir(TTP)CH$_3$**

The first series of kinetics reactions examined the exchange of deim in complex 6a with bmim as NHC, at 297.1 K. Reactions with varying concentrations of bmim (0.0227–0.0629 M, 8.3–21.6 equiv relative to the metalloporphyrin) showed little change with respect to reaction rate (Figure S34), as expected for rate-limiting ligand dissociation. In a second series of reactions, the concentration of Ir(TTP)CH$_3$(deim) was varied. Plotting the initial rate of these reactions versus [Ir(TTP)CH$_3$(deim)] gave a line with a slope of $(1.75 \pm 0.04) \times 10^{-4}$ s$^{-1}$, representing the rate constant for dissociation of the forward reaction ($k_{-1}$). The same treatment for the reverse reaction starting with Ir(TTP)-CH$_3$(bmim) gave a dissociation rate constant for the reverse reaction of $k_{-2}$.

**Figure 5.** Variable-temperature $^1$H NMR spectra of the coordinated NHC protons of Rh(TTP)CH$_3$(deim), 5a, compared to Ir(TTP)-CH$_3$(deim), 6a. NHC exchange was rapid on the NMR time scale. Iridium complexes 6a and 6b did not display rapid NHC fluxional behavior at temperatures ranging from 239.0 to 324.9 K, and decomposition became significant at temperatures above 325 K, prohibiting high-temperature studies.
reaction \( (k_f) \) equal to \((1.2 \pm 0.1) \times 10^{-4} \) s\(^{-1}\). Rate constants \( k_f \) and \( k_i \) at 297.1 K correspond to \( \Delta G^\ddagger \) values of 94.2 \pm 0.6 and 95.2 \pm 0.2 kJ\,mol\(^{-1}\), respectively, which are much higher than the \( \Delta G^\ddagger \) values observed for NHC exchange with rhodium (65.1 and 66.1 kJ\,mol\(^{-1}\)). Overall, the rate of NHC exchange is much slower for iridium than for rhodium, consistent with previously reported solvent exchange reactions using water, acetonitrile, and dimethyl sulfoxide.\(^{26-38}\)

**Determination of Equilibrium Binding Constants.** Equilibrium binding constants for NHC coordination to \( \text{M(TTP)CH}_3 \) were determined using a UV/vis titration method similar to that reported previously (Table 2).\(^{14,24}\)

**Table 2. Equilibrium Binding Constants for the Coordination of NHC to \( \text{M(TTP)CH}_3 \) at 296 K**

<table>
<thead>
<tr>
<th>metalloporphyrin</th>
<th>L</th>
<th>log(K)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Rh(TTP)CH}_3 )</td>
<td>deim</td>
<td>4.6 ± 0.2</td>
<td>this work</td>
</tr>
<tr>
<td>( \text{Rh(TTP)CH}_3 )</td>
<td>bmim</td>
<td>4.4 ± 0.3</td>
<td>this work</td>
</tr>
<tr>
<td>( \text{Ir(TTP)CH}_3 )</td>
<td>deim</td>
<td>5.5 ± 0.2</td>
<td>this work</td>
</tr>
<tr>
<td>( \text{Ir(TTP)CH}_3 )</td>
<td>bmim</td>
<td>5.3 ± 0.5</td>
<td>this work</td>
</tr>
<tr>
<td>( \text{Ir(OEP)(C}_3\text{H}_7 )</td>
<td>PPh(_3)</td>
<td>6.1 ± 0.4</td>
<td>ref 22</td>
</tr>
<tr>
<td>( \text{Ir(OEP)(C}_3\text{H}_7 )</td>
<td>N-Melm</td>
<td>5.6 ± 0.4</td>
<td>ref 22</td>
</tr>
<tr>
<td>( \text{Ir(OEP)(C}_3\text{H}_7 )</td>
<td>CO</td>
<td>5.0 ± 0.4</td>
<td>ref 22</td>
</tr>
<tr>
<td>( \text{Rh(OEP)CH}_3 )</td>
<td>PPh(_3)</td>
<td>3.3(^{a})</td>
<td>ref 37</td>
</tr>
</tbody>
</table>

\(^{a}\)Error was not reported.

Binding constants were nearly an order of magnitude smaller with \( \text{Rh(TTP)CH}_3 \) compared to \( \text{Ir(TTP)CH}_3 \) and, in both cases, were the same for deim and bmim within error. However, considering the relative equilibrium constants determined during kinetics studies (vide supra), the binding constant with bmim is expected to be slightly larger than that with deim. These equilibrium binding constants are reasonable compared to previous binding studies with rhodium and iridium complexes.\(^{3,39,40}\) Values for log(K) ranged between 1.6 and 8.2 for various L-type ligands. In particular, binding constants found for the coordination of PPh\(_3\), N-methylimidazole (N-Melm), and CO with \( \text{Ir(OEP)(C}_3\text{H}_7 \) were within an order of magnitude to the values observed for NHC ligands. In contrast, the binding constant previously reported for \( \text{Rh(OEP)CH}_3 \) and PPh\(_3\) was an order of magnitude lower than those with \( \text{Rh(TTP)CH}_3 \) and NHC ligands.

**Structural Analysis.** Structures of (bmim)\( \text{M(TTP)CH}_3 \) complexes \( 5b \) and \( 6b \) were determined unambiguously by single-crystal X-ray diffraction (Figures 6 and 7). Both complexes crystallized in the \( \text{P}1 \) space group, a triclinic unit cell, and displayed distorted octahedral geometry about the metal center. Selected bond distances and angles are listed in Table 3. Complexes \( 5b \) and \( 6b \) featured very long metal–C\(_\text{NHC}\) bonds at 2.255(3) and 2.194(4) Å, respectively, representative of nearly pure \( \sigma \)-bonding character.\(^{41-43}\) These M–C\(_\text{NHC}\) bonds are longer than any of those previously reported for rhodium or iridium NHC complexes, where the M–C\(_\text{NHC}\) bond length ranges from 1.919 to 2.122 Å.\(^{33-47}\) Moreover, the (TTP)\( \text{Rh–C}_\text{NHC} \) bond in \( 5b \) is notably longer than that for the iridium analogue, \( 6b \), which in conjunction with equilibrium binding constants and the kinetics of NHC exchange, suggests that the rhodium NHC complex \( 5b \) is at a higher relative potential energy than the iridium NHC complex \( 6b \).\(^{13,48}\)

Figure 7. ORTEP of complex \( 6b \) with 30% probability thermal ellipsoids.
Out-of-Plane Displacements (Å)

<table>
<thead>
<tr>
<th>complex</th>
<th>$D_{\text{oop}}$</th>
<th>$\delta_{\text{oop}}$</th>
<th>$B_{2\text{u,sad}}$</th>
<th>$B_{2\text{u,ref}}$</th>
<th>$A_{2\text{u,dom}}$</th>
<th>$E_I(x)$, $\text{wav}(x)$</th>
<th>$E_I(y)$, $\text{wav}(y)$</th>
<th>$A_{1\text{u,prop}}$</th>
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<td>-0.0004</td>
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</tr>
<tr>
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<td>0.0222</td>
<td>0.1425</td>
<td>-0.0602</td>
<td>-0.0445</td>
<td>-0.0242</td>
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<td>0.0074</td>
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<td>-0.9857</td>
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<td>0.0005</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0005</td>
</tr>
<tr>
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<td>1.1705</td>
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<td>0.0094</td>
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<td>Rh(TPP)CH$_3$N$_3$</td>
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<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>Ir(TTP)CH$_3$H$<em>2$O$</em>{30}$</td>
<td>0.1124</td>
<td>0.0053</td>
<td>0.0681</td>
<td>-0.0115</td>
<td>0.0754</td>
<td>-0.0234</td>
<td>0.0355</td>
<td>0.0192</td>
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In-Plane Displacements (Å)

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<th>$\delta_y$</th>
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<th>$B_{1\text{g,n-str}}$</th>
<th>$A_{2\text{g,rot}}$</th>
<th>$E_I(x)$, $\text{trn}(x)$</th>
<th>$E_I(y)$, $\text{trn}(y)$</th>
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<td>0.0001</td>
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<tr>
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<tr>
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<tr>
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<td>0.0163</td>
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</tr>
<tr>
<td>Rh(TPP)CH$_3$N$_3$</td>
<td>0.1154</td>
<td>0.0090</td>
<td>0.0000</td>
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<td>0.0000</td>
<td>0.0003</td>
<td>0.1154</td>
<td>0.0036</td>
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<tr>
<td>Ir(TTP)CH$_3$H$<em>2$O$</em>{30}$</td>
<td>0.0922</td>
<td>0.0158</td>
<td>0.0044</td>
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<td>0.0018</td>
<td>0.0097</td>
<td>0.0910</td>
<td>-0.0005</td>
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</table>

"Structures for referenced complexes were resolved previously. Displacements were calculated from the minimum basis set of core atoms in the porphyrin ring. Mean deviations."
rhodium analogue of complex 3, Rh(TPP)(=C(NHBn)₂)·(C≡NBn)(PF₆). Although these complexes show large in-plane displacements relative to 4b, 5b, and 6b, their Dₚ values are still small relative to other metalloporphyrin complexes.⁶⁵

Porphyrin deformations are ubiquitous in natural and synthetic systems,⁶⁶ and systematic analysis of heme complexes demonstrated that coordination with π-accepting ligands especially increases deformation in the ruffling mode.⁵⁷ Multiple studies have examined the importance of ring distortion on enzyme catalysis.⁵⁸—⁶⁰ A recent study examined the effect of ruffling and doming deformations on the N₄ cavity of the porphyrin.⁶¹ While doming expands the cavity, ruffling contracts it, resulting in up to a 24 nm red shift in the Soret band of the porphyrin. Such a shifting is consistent with the 443 and 438 nm Soret bands for complexes 5b and 6b, respectively (vide supra). Furthermore, the N₄ cavity contraction was suggested to increase the electron cloud density of a complexed metal ion, which was suggested to drive the formation of higher valent iron species.⁶² While it is unclear how these factors influence catalysis, the present and previous studies indicate that significant deformations are present during carbene transfer. For example, DFT optimization of a species that is active for carbene transfer, Ir(TTP)CH₃(=C(Ph)CO(CH₃)₂), revealed notable porphyrin distortion in the ruffling (−0.4513) and doming (−0.2309) modes, with an overall Dₚ of 0.5154.¹⁵ Medforth et al. previously proposed a deformability model, which suggests that the barrier for meso-aryl–porphyrin C–C bond rotation lowers upon increased ruffling of the metalloporphyrin. Rotation barriers and NMR data for NHC complexes 5b and 6b are consistent with this model. However, given the similar displacements in the B₁u ruffling mode, it is surprising that bis-diaminocarbene complex 4b does not show dynamic meso-aryl–porphyrin C–C bond rotation in the temperature range between 243 and 323 K. Complex 4b displays slightly more saddling, but previous studies suggest that increasing deformations in the B₂u saddling mode does not have a large impact on the meso group rotation barrier.³¹ Perhaps added steric bulk from the bis-diaminocarbene ligands relative to the NHCs raises the rotation barrier. The relationship between meso group rotation barriers and aryl–porphyrin C–C bond distances were also considered. Aryl–porphyrin C–C bond lengths for complexes 5b and 6b ranged from 1.491(5) to 1.506(7) Å. These bond distances are experimentally identical to those in other metalloporphyrin complexes, including 2 and 4b (1.487(6)–1.501(7) Å), which did exhibit dynamic aryl–porphyrin C–C bond rotation (ΔGᵣₒᵗ > 70 kJ·mol⁻¹). Thus, the low ΔGᵣₒᵗ values displayed by complex 5 and 6 cannot be explained by aryl–porphyrin C–C bond lengths.

### Experimental Section

**General Considerations.** Literature procedures were used to synthesize 1,3-diethylimidazolylidenediene and 1-(n-butyl)-3-methylimidazolylidene.²¹ Attempts to purify deim and bmim by distillation dissolved the free NHC. Crude samples of deim and bmim were dissolved in a known volume of THF and stored in the freezer. Stock-solution concentrations were in the range 0.10 to 0.50 M. Ir(TTP)Cl(CO) was generated by a known procedure for metalation of H₂TTP.⁶³ Rh(TTP)CH₃ and Ir(TTP)CH₃ were synthesized similarly using previously described methods for reductive alkylation of the corresponding metal halogeno porphyrin complexes.¹⁴ Methylenecarbamide and tetrahydrofuran were deoxygenated and dried by passage through columns of reduced copper and alumina. Hexanes and benzene-d₆ were dried over sieves, deoxygenated by successive freeze–pump–thaw cycles, and passed through a plug of activated alumina in the glovebox. All other chemicals were purchased as reagent grade and used without further purification. General NMR spectra were collected using Bruker DRX 400 MHz and AVIII 600 MHz spectrometers. Carbene ¹³C signals for the NHC complexes were verified with a 700 MHz instrument equipped with a cryoprobe. Variable-temperature and kinetics studies were done using the Bruker DRX 400 MHz spectrometer; the temperature gauge was calibrated by chemical shift analysis of methane and ethylene glycol. H and ¹³C NMR peak positions were referenced against residual proton resonances of deuterated solvents (δ ppm: CDCl₃, 7.26 and 77.16; THF, 3.58 and 67.57; CD₃D₄, 7.16). Absorption spectra were collected using a Hewlett-Packard/Agilent Technologies 8453 UV–vis spectrophotometer. Elemental analyses were performed by Iowa State University Instrument Services. Although hotter, longer combustion conditions were used, carbon analyses were often low. For metalloporphyrin complexes, this is likely due to the formation of metal carbides during combustion.⁶⁵

**X-ray Single-Crystal Structure Determination.** The crystal evaluation and data collection were performed at 173 K on a Bruker APEX II CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å). Full-sphere data with 0.3° frame width were collected until a resolution of 0.74 Å. The absorption correction was based on a fit of a spherical harmonic function to the empirical transmission surface as sampled by multiple equivalent measurements.⁶⁶ Structures were solved using direct methods and were refined using a full-matrix anisotropic approximation for all non-hydrogen atoms. All hydrogen atoms were placed in the structure factor calculation at idealized positions and refined using a “riding model”. The Uₘᵢₙ(H) values were set at 1.5 times the Uₑₐ value of the carrier atom. All calculations were performed using the APEX II software package.⁶⁷,⁶⁸ CCDC 943042–943046 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request cif.

**NHC Exchange with Rh(TTP)CH₃.** Stock solutions of bmim (6.0 mL from a 0.027 THF stock solution, 0.16 mmol) and deim (1.0 mL from a 0.18 M THF stock solution, 0.18 mmol) were collected in a vial, and THF was removed quickly in vacuo. Immediately after THF
removal, the residue was treated with a THF-d8 solution of Rh(TTP)CH3(deim) (32 mg, 0.0351 mmol). This solution was transferred to an NMR tube fitted with a Teflon stopcock, charged with mesitylene as an internal standard (2.0 μL, 0.01437 mmol), diluted to a final volume of 750 μL, and analyzed by 1H NMR. As verification, similar results were obtained when Rh(TTP)CH3(bimim) (18 mg, 0.0580 mmol) was treated with varied amounts of bimim (0.039 to 0.26 mmol) and deim (0.032 to 0.58 mmol).

Reversible NHC Exchange with Iridium Porphyrins. An NMR tube fitted with a Teflon stopcock was charged with 450 μL of a stock solution of Ir(TTP)CH3 (3.14 × 10−3 M, 1.41 μL). The solution was taken to dryness, and the NMR tube was brought into a glovebox. The NMR tube was charged with mesitylene standard (20 μL from a 5.16 × 10−3 M CdCl3 solution, 1.03 μmol), deim (108 μL from a 0.144 M CdCl3 stock solution, 15.5 μmol), and enough CdCl3 to attain a final solution volume of 420 μL. After mixing for 5–10 min, the solution was treated with varying amounts of bim (140–292 μL from a 0.0798 M CdCl3 solution, 11.2–23.3 μmol). The tube was sealed and transferred to an NMR instrument, where the temperature was raised to 308.1 K and reaction progress was monitored at 40–120 s intervals. This procedure was used for additional experiments where [bimim] was varied in order to determine k. The same procedure, except switching the order of NHC additions and varying only [deim], was extended to a second set of experiments to determine k. One of these sets was discards as a statistical outlier.

Pseudoirreversible NHC Exchange with Iridium Porphyrins. A medium-walled NMR tube was charged with Ir(TTP)CH3 (300 to 600 μL from a 3.60 × 10−3 M CH3Cl solution, 1.08 to 2.16 μmol). The tube was taken into a glovebox and loaded with NHCl3 (deim: 16 to 23 μL from a 0.141 M CdCl3 stock solution, 2.3 to 3.2 μmol; bim: 20 to 34 μL from a 0.0764 M CdCl3 stock solution, 1.5 to 2.6 μmol), mesitylene (20 μL from a 5.16 × 10−3 M CdCl3 stock solution, 1.0 μmol), and enough CdCl3 to reach a final volume of 420 μL. The tube was sealed with a septum and taken to the NMR spectrometer. Spectrometer settings were prepared and the temperature was equilibrated to 297.1 K. Finally, the solution was treated with NHCl3 (deim: 110 μL from a 0.141 M CdCl3 stock solution, 15.1 μmol; bim: 200 μL from a 0.0764 M CdCl3 stock solution, 15.3 μmol), and data collection began ca. 2 min after addition.

1H NMR Chemical Shifts. All chemical shifts were referenced to residual proton signals of 2.50 ppm (d, 2H) for CDCl3 and 1.28 ppm (s, 3H) for CD3OD. The chemical shifts are presented in ppm and are referenced to the signals of the solvent. Spectra were recorded at 250.1 MHz for 1H NMR.

19F NMR Chemical Shifts. All chemical shifts were referenced to residual fluorine signals of 0 ppm. The chemical shifts are presented in ppm and are referenced to the signals of the solvent. Spectra were recorded at 250.1 MHz for 19F NMR.

IR Spectra. IR spectra were recorded on a PerkinElmer Spectrum 100 spectrometer, using the KBr method. Spectra were recorded in the range of 4000–400 cm−1.

UV-Vis Spectra. UV-Vis spectra were recorded using a JASCO V-570 spectrophotometer. All spectra were recorded in CH3Cl.

Organometallics: Pseudoirreversible NHC Exchange with Iridium Porphyrins. A medium-walled NMR tube was charged with Ir(TTP)CH3 (300 to 600 μL from a 3.60 × 10−3 M CH3Cl solution, 1.08 to 2.16 μmol). The tube was taken into a glovebox and loaded with NHCl3 (deim: 16 to 23 μL from a 0.141 M CdCl3 stock solution, 2.3 to 3.2 μmol; bim: 20 to 34 μL from a 0.0764 M CdCl3 stock solution, 1.5 to 2.6 μmol), mesitylene (20 μL from a 5.16 × 10−3 M CdCl3 stock solution, 1.0 μmol), and enough CdCl3 to reach a final volume of 420 μL. The tube was sealed with a septum and taken to the NMR spectrometer. Spectrometer settings were prepared and the temperature was equilibrated to 297.1 K. Finally, the solution was treated with NHCl3 (deim: 110 μL from a 0.141 M CdCl3 stock solution, 15.1 μmol; bim: 200 μL from a 0.0764 M CdCl3 stock solution, 15.3 μmol), and data collection began ca. 2 min after addition.

1H NMR Chemical Shifts. All chemical shifts were referenced to residual proton signals of 2.50 ppm (d, 2H) for CDCl3 and 1.28 ppm (s, 3H) for CD3OD. The chemical shifts are presented in ppm and are referenced to the signals of the solvent. Spectra were recorded at 250.1 MHz for 1H NMR.

19F NMR Chemical Shifts. All chemical shifts were referenced to residual fluorine signals of 0 ppm. The chemical shifts are presented in ppm and are referenced to the signals of the solvent. Spectra were recorded at 250.1 MHz for 19F NMR.

IR Spectra. IR spectra were recorded on a PerkinElmer Spectrum 100 spectrometer, using the KBr method. Spectra were recorded in the range of 4000–400 cm−1.

UV-Vis Spectra. UV-Vis spectra were recorded using a JASCO V-570 spectrophotometer. All spectra were recorded in CH3Cl.
meso-m-tolyl), 7.50 (d, $^{3}J(\text{HH}) = 7.2$ Hz, 4H, meso-m-tolyl), 5.32 (s, 2H, vinyl–CH), 2.63 (s, 12H, tolyl–CH$_3$), $-0.02$ (q, $^{3}J(\text{HH}) = 6.8$ Hz, 4H, ethyl–CH$_2$–), $-0.42$ (t, $^{3}J(\text{HH}) = 6.8$ Hz, 6H, ethyl–CH$_2$–), $-8.03$ (s, 3H, Ir–CH$_3$), $131.1$ (s, $^{13}C$ (THF–d$_4$)), 143.43, 139.92, 137.31, 134.44, 131.51, 127.99, 127.60, 133.71, 118.03, 40.16 (ethyl–CH$_2$–), 21.30 (toyl–CH$_3$), 15.12 (ethyl–CH$_2$–), $-21.97$ (Ir–CH$_3$); $^{13}$C signals, especially those for the coordinated NHC and axial methyl carbons, were verified by HMOC experiments. UV–vis (THF): nm (log $e$) 370 (4.54), 438 (4.94).

$\text{Ir(TTP)(bmim)}$ CH$_3$, 6b. $\text{Ir(TTP)}$ CH$_3$ (27.9 mg, 31.8 $\mu$mol) was treated with bnmim (0.10 mL from a 0.40 M stock solution, 40 $\mu$mol). Dark brown crystals (10.1 mg, 100 $\mu$mol, 31% yield) were collected after drying in vacuo. $^{1}H$ NMR (THF–d$_4$, 400 MHz, 239.0 K): $\delta$ 8.80 (s, 8H, $\beta$-pyrrole), 7.91 (dd, $^{3}J(\text{HH}) = 7.8$, 1.6 Hz, 4H, meso-o-tolyl), 7.85 (dd, $^{3}J(\text{HH}) = 7.8$, 1.6 Hz, 4H, meso-o-tolyl), 7.50 (d, $^{3}J(\text{HH}) = 7.8$ Hz, 8H, meso-o-tolyl), 5.22 (d, $^{3}J(\text{HH}) = 12$ Hz, 1H, vinyl–CH), 5.15 (d, $^{3}J(\text{HH}) = 1.2$ Hz, 1H, vinyl–CH), 2.63 (s, 12H, tolyl–CH), 0.52 (t, $^{3}J(\text{HH}) = 7.2$ Hz, 2H, butyl–CH$_2$–), 0.54 (m, 2H, butyl–CH)$_2$–), 0.05 (s, 3H, methyl–CH$_3$–), $-0.03$ (t, $^{3}J(\text{HH}) = 7.2$ Hz, 2H, butyl–CH$_2$–), $-0.32$ (m, 2H, butyl–CH$_2$–), $-7.94$ (s, 3H, Ir–CH$_3$), $131.1$ (s, $^{13}C$ (THF–d$_4$)), 143.40, 139.91, 137.31, 134.66, 134.34, 131.47, 127.96, 127.58, 123.74, 120.61, 117.23, 45.15 (butyl–CH$_2$–), 32.70 (butyl–CH$_2$–), 32.68 (NCH$_3$), 21.30 (tolyl–CH$_3$); 19.61 (butyl–CH$_2$–), 13.67 (butyl–CH$_3$); $-21.92$ (Ir–CH$_3$); $^{13}$C signals, especially those for the coordinated NHC and axial methyl carbons, were verified by HMOC experiments. UV–vis (THF): nm (log $e$) 370 (4.49), 438 (4.89).
(42) McGuinness, D. S.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Organometallics* 1999, 18, 2211.
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