ORGANOMETALLICS

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

Bernie J. Anding, Arkady Ellern, and L. Keith Woo*

Department of Chemistry, Iowa State University, Ames, Iowa 50011-3111, United States

Supporting Information

ABSTRACT: Iridium *meso*-tetratolylporphyrinato (TTP) mono- and bisdiaminocarbene complexes, $[Ir(TTP)]=C(NHBn)(NHR)]_{2-x}(C \equiv NBn)_x]BF_4$, where R = Bn, *n*-Bu and x = 1, 0, were synthesized by nucleophilic addition of amines to the bis-isocyanide complex $[Ir(TTP)-(C \equiv NBn)_2]BF_4$. Rhodium and iridium porphyrinato N-heterocyclic carbene (NHC) complexes M(TTP)CH₃(NHC), where NHC = 1,3diethylimidazolylidene (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 variabletemperature 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 ΔG_f^{\pm} of 65.2 ± 0.6 kJ·mol⁻¹ and ΔG_r^{\pm} 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 $(1.75 \pm 0.04) \times 10^{-4}$ s⁻¹ for the forward reaction and $(1.2 \pm 0.1) \times 10^{-4}$ s⁻¹ for the reverse reaction at 297.1 K. These rate constants correspond to ΔG^{\ddagger} values of 94.2 \pm 0.6 and 95.2 \pm 0.2 kJ·mol⁻¹ for the forward and reverse reactions, respectively. Equilibrium constants for the exchange reactions were 1.6 \pm 0.2 with rhodium and 1.56 \pm 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 \pm 0.3 (M = Rh) and 5.4 \pm 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–C_{NHC}: 2.255(3) Å and Ir–C_{NHC}: 2.194(4) Å).

INTRODUCTION

Metalloporphyrin complexes containing Fe, Ru, Os, Co, Rh, and Ir are useful catalysts for carbene transfer reactions including cyclopropanation, X-H insertion (X = C, N, O, and S), and ylide-forming reactions.¹ 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.^{2,3} This reactivity trend can be explained by examining the intermediate species. While cobalt(II) catalysts appear to form relatively nucleophilic radical carbene complexes,⁴⁻⁶ d⁶ 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 cyclopropanations are tolerant to sterically hindered di- and trisubstituted olefins, but reactions with rhodium catalysts often require higher reaction temperatures to achieve practical rates.^{7–12} Although iridium complexes do not induce remarkable diastereo- or regioselectivity, they are extremely reactive and robust, generating cyclopropanation products rapidly at -78 °C with turnover numbers on the order of $10^{5,13}$ 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.¹⁴ 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-

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scopically,^{15,16} but have not been successfully isolated in pure form. The only group 9 metalloporphyrin carbene complex that has been isolated and structurally characterized by single-crystal X-ray analysis is a rhodium diaminocarbene complex, [Rh-(TTP)[$=C(NHBn)_2$]($C\equiv NBn$)]PF₆, (1), which was synthesized via nucleophilic addition of benzylamine to bis-(benzylisocyanide)(tetraphenylporphyrinato)rhodium(III) hexafluorophosphate (Scheme 1).¹⁷ Although applications of

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



^{*a*}meso-Phenyl groups are omitted for clarity.

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).^{17,18} Treating Ir(TTP)Cl(CO) with silver tetrafluoroborate followed by excess benzylisocyanide led to the formation of the bis-(isocyanide) iridium complex $[Ir(TTP)(C \equiv NBn)_2]BF_4$ (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, p-H), 6.79 (t, 4H, m-H), 4.80 (d, 4H, o-H), and 2.65 (s, 4H, (CH_2) 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 IR stretching mode from 2151 cm⁻¹ for the free isocyanide to 2228 cm⁻¹ indicating that the bound isocyanide is susceptible to nucleophilic attack.¹⁹ This stretching frequency is similar to that of $Rh(TTP)(C \equiv NBn)_2(PF_6)$ found at 2248 cm^{-1.17} 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-





^ameso-p-Tolyl groups are omitted for clarity.



Figure 1. ORTEP²⁰ of $[Ir(TTP)(C \equiv NBn)_2]BF_4$ (2) with 30% probability thermal ellipsoids. Selected bond distances (Å): Ir-N(1) = 2.045(4), Ir-N(2) = 2.044(4). Selected bond angles (deg): N(1)-Ir-N(2) = 90.02(14), N(1)-Ir-N(2i) = 89.98(14). Atoms with index *i* are related to the basic atom with transformation 1/2 - x, 1/2 + y, 1 + z.

carbene complex $[Ir(TTP)[=C(NHBn)_2](C\equivNBn)]BF_4$ (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), 5.31 (d, 4H, *o*-H), 2.07 (d, 4H, CH₂), and -1.89 (br, 2H, NH). Signals corresponding to one remaining bound isocyanide ligand were observed with shifts similar to those observed in complex 2. The presence of a bound isocyanide ligand was confirmed further by IR with a C=N stretching band at 2218 cm⁻¹. Complex 3 crystallized in a C-centered monoclinic unit cell in the C2/*c* space group with a half of the molecule in the asymmetric unit (Figure 2). Similar to complex 2, the axial ligands were disordered through symmetry, and the interatomic distances in those groups were constrained. Iridium inhabited a nearly ideal octahedral environment, and the porphyrin core was planar with very little distortion (*vide infra*).



Figure 2. ORTEP of $[Ir(TTP)[=C(NHBn)_2](C=NBn)]BF_4$ (3) with 30% probability thermal ellipsoids. Selected bond distances (Å): Ir-N(1) = 2.044(4), Ir-N(2) = 2.042(4). Selected bond angles (deg): N(1)-Ir-N(2) = 90.03(13), N(2)-Ir-N(1) = 89.97(13). Atoms with index *i* are related to the basic atom with transformation 1/2 - x, 1/2 - y, 2 - z.

The 2218 cm⁻¹ C \equiv 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 $[Ir(TTP){=C(NHBn)_2}_2]_2BF_4$, 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 ¹H NMR spectrum. Integrations of the diaminocarbene signals at 7.17 (t, 4H, p-H), 7.02 (t, 8H, m-H), 5.31 (d, 8H, o-H), 2.07 (d, 8H, CH_2), and -1.72 (br, 4H, NH) ppm were consistent with two equivalent axial ligands. Loss of the coordinated isocyanide was indicated by the disappearance of diagnostic signals at 4.85-4.80 ppm (d, o-H) and 2.65-2.63 ppm (s, CH₂). However, it was difficult to fully characterize complex 4a by ¹H 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, [Ir(TTP)]=C(NHBn)- $(NHBu)_{2}]BF_{4}$ (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-diethylimidazolylidiene (deim) and 1-(*n*-butyl)-3-methylimidazolylidene (bmim). The free NHC ligands were synthesized by deprotonation of the corresponding imidazo-lium salt as reported by Arduengo et al.²¹ NHC complexes (NHC)M(TTP)CH₃ (**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 metal-loporphyrins with a slight excess of the free NHC (Scheme 3).

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



^ameso-p-Tolyl groups are omitted for clarity.

In all cases, conversion of the metalloporphyrin was nearly quantitative, as indicated by the formation of one major β -pyrrole porphyrin signal in the ¹H NMR spectrum of the reaction mixture. Pure samples were isolated by recrystallization from THF/hexanes and characterized by absorption spectroscopy, NMR spectroscopy, and X-ray diffraction studies. Compounds **5a,b** and **6a,b** were moisture sensitive, especially in solution, generating M(TTP)CH₃ (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 $M(TTP)CH_3$, 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



Figure 3. Absorption spectra for Rh(TTP)CH₃ (4.41 × 10⁻⁵ M, right axis) and complex **5b** (1.11 × 10⁻⁴ M, left axis) in THF. Absorption axes were scaled to demonstrate the actual relative band intensities. Complexes **5a**, **6a**, and **6b** all exhibit similar absorption spectra.

were observed previously with the diazoacetate chemistry of iridium porphyrin complexes, including the metal–carbene and metal–ylide intermediates detected in $Ir(TTP)CH_3$ -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.

Transition metal hyperporphyrin complexes are typically classified as d-type metalloporphryins, where the hyper character is the result of ligand-to-metal charge transfer (LMCT) from porphyrin $a_{1u}(\pi)$, $a_{2u}(\pi)$ orbitals to metal $e_g(d_{\pi})$ orbitals.^{23,25} Metalloporphyrins with d⁶ electron configurations are an unusual case because the metal $e_g(d_{\pi})$ orbitals (d_{xz} and d_{yz} , with the z-axis perpendicular to the porphyrin plane) are filled in the ground state. Iterative extended Hückel calculations on similar d⁶ hyperporphyrins, (OEP)Ru(py)₂ and (OEP)Os(py)₂, suggested that orbital mixing with relatively low energy doubly excited states, $[e_g(d_{\pi})]^3[a_{1u}(\pi), a_{2u}(\pi)]^3[e_g(\pi^*)]^2$, may be responsible for the hyper-type absorption bands.²⁶ A similar phenomenon may be responsible for the hyper spectra displayed here.

The ¹H 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 trans-methyl resonances. The trans-methyl shifted from -6.56 ppm to -7.44and -7.38 ppm for rhodium NHC complexes (5a and 5b, respectively) and from -7.01 ppm to -8.03 and -7.94 ppm for the iridium NHC complexes (6a and 6b, respectively). In contrast, the *trans*-methyl signal of $Ir(TTP)CH_3(=C(Ph))$ - CO_2Me) shifted downfield to -4.8 ppm.¹⁵ The ³¹³C NMR spectra for complexes 5a, 5b, 6a, and $\overline{6b}$ exhibited carbene α 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 α carbon signals for RhCl(η^2 -O₂)(IPr)₂ and IrCl(η^2 -O₂)(IPr)₂ $(IPr = N_i N$ -diisopropyl imidazolylidene) were observed at 180.8 and 167.4 ppm, respectively.^{27–29} The carbon α -carbon ¹³C 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,³⁰ the behavior exhibited here is most consistent with meso-aryl rotation. Activation energies for *meso*-aryl rotation (ΔG^{\dagger}_{ROT}) were determined to be 59 \pm 2 to 63 \pm 1 kJ·mol⁻¹ by NMR coalescence data (Table 1), which are within the previously established range of 40-78 kJ·mol⁻¹ for metalloporphyrins.^{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.^{31–33} Although aryl–porphyrin rotation has not been reported in rhodium or iridium porphyrin complexes, a study with ruthenium porphyrins measured relatively high barriers for *meso*-aryl rotation at 72–78 kJ·mol⁻¹.³³ 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



Figure 4. Variable-temperature ¹H NMR spectra of the *ortho* protons on the *meso*-tolyl substituents of $(NHC)M(TTP)CH_3$ (**5a**, M = Rh, NHC = deim; **5b**, M = Rh, NHC = bmim; **6a**, M = Ir, NHC = deim; **6b**, M = Ir, 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 $(NHC)M(TTP)CH_3$ (5a, M = Rh, NHC = deim; 5b, M = Rh, NHC = bmim; 6a, M = Ir, NHC = deim; 6b, M = Ir, NHC = bmim)

complex	$\Delta G^{\ddagger}_{ROT} \ (kJ \cdot mol^{-1})$	coalescence T (K)
Rh(TTP)CH ₃ (deim) (5a)	61 ± 1	292
$Rh(TTP)CH_3(bmim)$ (5b)	59 ± 2	270
Ir(TTP)CH ₃ (deim) (6a)	63 ± 1	303
Ir(TTP)CH ₃ (bmim) (6b)	62 ± 2	287

temperature, implying that the activation energies for rotation are greater than 70 kJ·mol⁻¹. Thus, it is remarkable that NHC coordination lowers the barrier for aryl rotation to 59–63 kJ·mol⁻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.³³ 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⁻¹. A reasonable explanation is that the low rotation barriers for complexes **5a**,**b** and **6a**,**b** result from deformations in the porphyrin ring, which are caused by coordination with bulky NHC ligands (*vide infra*).^{34,35}

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 5), suggesting that



Figure 5. Variable-temperature ¹H NMR spectra of the coordinated NHC protons of $Rh(TTP)CH_3(deim)$, 5a, compared to $Ir(TTP)-CH_3(deim)$, 6a. NHC binding is more fluxional with rhodium than with iridium.

NHC binding was fluxional and 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.

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 ¹H NMR. The ratio of M(TTP)CH₃(deim) to M(TTP)-CH₃(bmim) was determined by proton integration of the cleanly separated *trans* methyl proton signals. At 260 K, signals for the rhodium complexes resonated at -7.43 ppm (**5a**) and -7.36 ppm (**5b**), and those for the iridium complexes appeared at -8.00 ppm (**6a**) and -7.92 ppm (**6b**). NHC exchange was observed for all complexes, but the rates of exchange were dramatically different for Rh versus Ir. For a mixture of **5a** and **5b** produced by combining Rh(TTP)CH₃ (18 μ mol), deim (32 μ mol), and bmim (39 μ mol), the coordinated NHC signals were broad and unresolved at 303 K. Cooling the sample to 249 K produced sharp Rh-CH₃ signals, with integrations that indicated the sample contained a mixture of **5a** and **5b** in a ratio of 1:1.7. This ratio did not change after repeated cycles of

heating and cooling, demonstrating that the sample had reached equilibrium before the initial cooling that took place within 5 min of mixing. Rate constants for NHC exchange, under conditions with a ca. 10-fold excess of both bmim and deim, were calculated by line shape analysis using the slow exchange approximation at temperatures between 282 and 295 K (Figure S29; Supporting Information). Using the reaction direction defined in eq 1, rate constants for the forward reaction ranged between $3.72 \pm 0.04 \text{ s}^{-1}$ (282 K) and 31 ± 6 s⁻¹ (295 K), corresponding to a $\Delta G_{\rm f}^{\ddagger}$ of 65.2 \pm 0.6 kJ·mol⁻¹. Rate constants for the reverse reaction were $2.7 \pm 0.4 \text{ s}^{-1}$ (282) K) to $18 + 2 \text{ s}^{-1}$ (295 K), and ΔG_{*}^{\pm} was $66.2 + 0.5 \text{ kI} \cdot \text{mol}^{-1}$. Although these activation barriers are unresolved within the error limits, the equilibrium constant at these temperatures was 1.6 \pm 0.2, verifying that $k_{\rm f}$ is indeed greater than $k_{\rm r}$. Rate constants were similar under a variety of different NHC concentrations, indicating that these first-order rate constants are representative of rate-limiting ligand dissociation. As expected for this rate-limiting step, the pentacoordinate intermediate Rh(TTP)CH₃ was not observed under these conditions.

NHC exchange with $Ir(TTP)CH_3$ was much slower. Preliminary kinetics experiments under saturated, reversible conditions demonstrated that the system was well behaved (Supporting Information). First-order rate constants for NHC exchange were determined by initial rate kinetics under pseudoirreversible conditions, which were created with ca. 1 equiv of the dissociating NHC (NHC_d) and a large excess of the incoming NHC (NHC_i) (Scheme 4). A steady-state

Scheme 4. Pseudoirreversible NHC Exchange with $Ir(TTP)CH_3$



approximation was applicable since the pentacoordinate intermediate was not present in observable amounts. Under these pseudoirreversible conditions, the steady-state approximation follows the limiting case where $k_2 \gg k_{-1}$. Thus, the reaction rate depended only on the rate constant for NHC dissociation (k_1) and the concentration of the starting iridium NHC complex (eqs S5 and S6, Supporting Information).

The first series of kinetics reactions examined the exchange of deim in complex **6a** with bmim as NHC_i 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, Supporting Information), as expected for rate-limiting ligand dissociation. In a second series of reactions, the concentration of Ir(TTP)CH₃(deim) was varied. Plotting the initial rate of these reactions versus [Ir(TTP)CH₃(deim)] gave a line with a slope of (1.75 ± 0.04) × 10⁻⁴ s⁻¹, representing the rate constant of dissociation for the forward reaction (k_{1f}). The same treatment for the reverse reaction starting with Ir(TTP)-CH₃(bmim) gave a dissociation rate constant for the reverse reaction (k_{1r}) equal to $(1.2 \pm 0.1) \times 10^{-4} \text{ s}^{-1}$. Rate constants k_{1f} and k_{1r} at 297.1 K correspond to ΔG^{\ddagger} values of 94.2 \pm 0.6 and 95.2 \pm 0.2 kJ·mol⁻¹, respectively, which are much higher than the ΔG^{\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.^{36–38}

Determination of Equilibrium Binding Constants. Equilibrium binding constants for NHC coordination to $M(TTP)CH_3$ 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 M(TTP)CH₃ at 296 K

metalloporphyrin	L	$\log(K)$	ref
Rh(TTP)CH ₃	deim	4.6 ± 0.2	this work
Rh(TTP)CH ₃	bmim	4.4 ± 0.3	this work
Ir(TTP)CH ₃	deim	5.5 ± 0.2	this work
$Ir(TTP)CH_3$	bmim	5.3 ± 0.5	this work
$Ir(OEP)(C_3H_7)$	PPh ₃	6.1 ± 0.4	ref 22
$Ir(OEP)(C_3H_7)$	N-MeIm	5.6 ± 0.4	ref 22
$Ir(OEP)(C_3H_7)$	CO	5.0 ± 0.4	ref 22
Rh(OEP)CH ₃	PPh ₃	3.3 ^{<i>a</i>}	ref 37
^a Error was not report	ed.		

Binding constants were nearly an order of magnitude smaller with Rh(TTP)CH₃ compared to $Ir(TTP)CH_3$ 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 porphyrin complexes.^{24,39,40} 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 PPh₃, *N*-methylimidazole (N-MeIm), and CO with Ir(OEP)C₃H₇ were within an order of magnitude to the values observed for NHC ligands. In contrast, the binding constant previously reported for Rh-(OEP)CH₃ and PPh₃ was an order of magnitude lower than those with Rh(TTP)CH₃ and NHC ligands.

Structural Analysis. Structures of $(bmim)M(TTP)CH_3$ complexes **5b** and **6b** were determined unambiguously by single-crystal X-ray diffraction (Figures 6 and 7). Both complexes crystallized in the $P\overline{1}$ space group, a triclinic unit



Figure 6. ORTEP of complex 5b with 30% probability thermal ellipsoids.



Figure 7. ORTEP of complex 6b with 30% probability thermal ellipsoids.

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– $C_{\alpha\text{-carbene}}$ bonds at 2.255(3) and 2.194(4) Å, respectively, representative of nearly pure σ -bonding character.^{41–43} These M– $C_{\alpha\text{-carbene}}$ bonds are longer than any of those previously reported for rhodium or iridium NHC complexes, where the M– $C_{\alpha\text{-carbene}}$ bond length ranges from 1.919 to 2.122 Å.^{43–47} Moreover, the (TTP)Rh– $C_{\alpha\text{-carbene}}$ 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}

The results reported here provide additional insight for trends observed in metalloporphyrin-catalyzed cyclopropanation reactions. Cyclopropanation is believed to proceed through metal carbene intermediates with the product-forming step being carbene transfer to an olefin substrate. Indirect analysis of the carbene transfer step using secondary kinetic isotope effects suggested that rhodium catalysts involved earlier transition states than those observed with iridium and iron analogues;⁴³ an inverse secondary isotope effect was observed for iridium but not for rhodium.^{13'} The longer $Rh-C_{\alpha-carbene}$ bond in NHC complex 5b and a higher potential energy of the rhodium carbene complex, relative to the iridium analogue 6b, are consistent with an earlier transition state model for Rh porphyrin catalysts and are in accord with the reactivity differences reported for Ir- and Rh-catalyzed cyclopropanation reactions.

M-C bond distances for the trans methyl ligands of 5b and 6b were 2.068(3) and 2.097(4) Å, respectively. These bonds were significantly longer than those of the pentacoordinate complexes Rh(TPP)CH₃ (1.968(12) Å) and Ir(TTP)CH₃. H_2O (2.059(11) Å), demonstrating the strong *trans* influence of the carbene ligand.^{49,50} In addition, multiple structural deformations were observed in complexes 5b and 6b. Distortion in the bonding angle of the NHC ligand is described by pitch (out-of-plane tilting, relative to the imidazolylidene plane) and yaw (in-plane tilting) angles (Figure 8).51 While both complexes display a trivial yaw angle $(<1^\circ)$, the pitch angle was 7.9° in **5b** and 6.4° in **6b**. This distortion may result from steric interactions with the porphyrin, as pitch angles up to 23° have been reported with other sterically hindered NHC complexes.^{52,53} Considerable distortion was also observed in the porphyrin ligand. Deformations of the porphyrin core are quantitatively described using the normal-coordinate structural

Rh(TTP)CH ₃ (bmin	m), 5b	Ir(TTP)CH ₃ (br	nim), 6b
$Rh-C(49)^a$	2.255(3) Å	$Ir-C(50)^a$	2.194(4) Å
$Rh-C(57)^b$	2.068(3) Å	$Ir - C(49)^{b}$	2.097(4) Å
Rh-N(1)	2.021(3) Å	Ir-N(1)	2.028(3) Å
Rh-N(2)	2.019(3) Å	Ir-N(2)	2.023(3) Å
Rh-N(3)	2.015(3) Å	Ir-N(3)	2.207(3) Å
Rh-N(4)	2.022(3) Å	Ir-N(7)	2.024(3) Å
C(49)-Rh-C(57)	$178.11(14)^{\circ}$	C(50)-Ir-C(49)	178.15(15)°
C(49)-Rh-N(1)	92.81(12)°	C(50)-Ir-N(1)	91.40(11)°
C(49) - Rh - N(2)	90.75(12)°	C(50)-Ir-N(2)	91.01(12)°
C(49) - Rh - N(3)	91.35(12)°	C(50)-Ir-N(3)	92.83(12)°
C(49) - Rh - N(4)	93.39(12)°	C(50)-Ir-N(7)	93.42(12)°
C(57)-Rh-N(1)	88.34(13)°	C(49)-Ir-N(1)	87.59(14)°
C(57)-Rh-N(2)	87.75(13)°	C(49)-Ir-N(2)	87.44(14)°
C(57)-Rh-N(3)	87.50(13)°	C(49)-Ir-N(3)	$88.18(14)^{\circ}$
C(57)-Rh-N(4)	88.12(13)°	C(49)-Ir-N(7)	88.13(14)°
$Rh-C(49)-N(5)^{c}$	128.0(3)°	$Ir-C(50)-N(5)^{c}$	128.2(3)°
$Rh-C(49)-N(6)^d$	128.9(3)°	$Ir-C(50)-N(4)^{d}$	129.1(3)°
N(5)-Rh-N(6)	102.7(3)°	N(5)-Ir- $N(4)$	102.5(3)°

^{*a*}Carbene carbon. ^{*b*}*trans* methyl carbon. ^{*c*}Imidazolylidene nitrogen bound to the methyl substituent. ^{*d*}Imidazolylidene nitrogren bound to the *n*-butyl substituent.



Figure 8. Graphical representations of pitch and yaw angles.

decomposition (NSD) analysis.^{54,55} This method describes the total out-of-plane (D_{oop}) and in-plane (D_{ip}) displacements as a

function of the 12 lowest frequency normal modes of the porphyrin core. Minimal basis calculations for complexes **5b** and **6b** are shown in Table 4. Analogous to previously reported cobalt porphyrin NHC complexes,²² **5b** and **6b** displayed substantial out-of-plane distortions primarily in the ruffling mode (B_{1u}). Similar deformations were observed with the bisdiaminocarbene complex **4b**, albeit with a larger displacement in the saddling mode (B_{2u}). The calculated D_{oop} values of 1.4937 (**4b**), 1.2165 (**5b**), and 1.2097 (**6b**) were moderate as compared to the values for other metalloporphyrin complexes, where highly distorted complexes have D_{oop} values greater than 3.⁵⁵ In comparison, small D_{oop} values were measured for Rh(TTP)CH₃, Ir(TTP)CH₃, complex **2**, complex **3**, and the

Table 4. NSD Analy	ysis of Selected	Rhodium and	Iridium	Metallopo	rphyrins ^a
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Out-of-Plane Displacements (Å)								
complex	D_{oop}	$\delta_{oop}^{\ \ b}$	B _{2w} sad	B _{1u,} ruf	A _{2w} dom	$E_g(x)$, $wav(x)$	$E_g(y)$, $wav(y)$	A _{1w} prop
2	0.0590	0.0214	-0.0001	-0.0003	0.0000	-0.0587	0.0056	-0.0003
3	0.0185	0.0180	0.0006	-0.0004	-0.0004	0.0171	0.0070	0.0002
$Rh(TPP)(=C(NHBn)_2)(C\equiv NBn)(PF_6)^{17}$	0.1803	0.0222	0.1425	-0.0602	-0.0445	-0.0242	-0.0773	0.0074
4b	1.4937	0.0182	-0.9857	1.1223	-0.0005	0.0000	0.0000	0.0005
5b	1.2165	0.0119	-0.2479	1.1705	-0.2108	-0.0057	0.0613	0.0088
6b	1.2097	0.0119	0.2521	1.1551	0.2493	-0.0046	-0.0568	0.0094
Rh(TPP)CH ₃ ⁴⁹	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
$Ir(TTP)CH_3 \cdot H_2O^{50}$	0.1124	0.0053	0.0681	-0.0115	0.0754	-0.0234	0.0355	0.0192
		In-Pla	ne Displaceme	nts (Å)				
complex	$D_{ m ip}$	$\delta_{\mathrm{ip}}{}^{b}$	B _{2g} , m-str	B _{1g} , n-str	A _{2g} , rot	$E_u(x)$, trn	$E_u(y)$, trn	A _{1g} , bre
2	0.1840	0.0110	-0.0080	0.0190	0.0002	0.0005	0.1826	-0.0084
3	0.1430	0.0151	-0.0034	-0.0064	0.0001	-0.0006	0.1428	0.0038
$Rh(TPP)(=C(NHBn)_2)(C\equiv NBn)(PF_6)^{17}$	0.1716	0.0215	-0.0017	0.0481	-0.0063	-0.0240	0.1626	-0.0102
4b	0.0361	0.0235	0.0000	0.0001	-0.0005	0.0003	0.0035	-0.0360
5b	0.0613	0.0199	0.0518	0.0211	0.0193	0.0010	-0.0034	-0.0157
6b	0.0665	0.0198	-0.0570	0.0195	-0.0144	0.0011	0.0163	0.0178
Rh(TPP)CH ₃ ⁴⁹	0.1154	0.0090	0.0000	0.0000	0.0000	0.0003	0.1154	0.0036
$Ir(TTP)CH_3 \cdot H_2O^{50}$	0.0922	0.0158	0.0044	-0.0105	0.0018	0.0097	0.0910	-0.0005

^aStructures for referenced complexes were resolved previously. Displacements were calculated from the minimum basis set of core atoms in the porphyrin ring. ^bMean deviations.

rhodium analogue of complex 3, Rh(TPP)(=C(NHBn)₂)-(C=NBn)(PF₆). Although these complexes show large inplane displacements relative to 4b, 5b, and 6b, their D_{ip} values are still small relative to other metalloporphyrin complexes.⁵⁵

Porphyrin deformations are ubiquitous in natural and synthetic systems,⁵⁶ 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 N_4 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 444 and 438 nm Soret bands for complexes 5b and 6b, respectively (vide supra). Furthermore, the N_4 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, $Ir(TTP)CH_3 = C(Ph)CO_2CH_3$, revealed notable porphyrin distortion in the ruffling (-0.4513)and doming (-0.2309) modes, with an overall D_{oop} of 0.5154.

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.³¹ Rotation barriers and NSD data for NHC complexes 5b and 6b are consistent with this model. However, given the similar displacements in the B_{1u} 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 B_{2u} 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 arylporphyrin C-C bond distances were also considered. Arylporphyrin 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 $(\Delta G^{\ddagger}_{ROT} > 70 \text{ kJ} \cdot \text{mol}^{-1})$. Thus, the low $\Delta G^{\ddagger}_{ROT}$ values displayed by complex 5 and 6 cannot be explained by arylporphyrin C-C bond lengths.

CONCLUSION

Several metalloporphyrin diaminocarbene and NHC complexes were prepared and characterized. Iridium diaminocarbene complexes 3 and 4 were synthesized by nucleophilic addition of an amine to the bis-isocyanide complex $[Ir(TTP)(C \equiv$ NBn)₂](BF₄). Characterization data for 3 are similar to thse for the previously reported rhodium diaminocarbene complexes, $[Rh(por)(=C(NHBn)_2)(C \equiv NBn)](PF_6)$. However, axial ligand disorder in the crystal structures of 3 and 4b prohibited a thorough metrical comparison. More direct comparisons were observed between rhodium and iridium NHC complexes. Equilibrium binding constants and ligand exchange rate constants demonstrated that NHCs were bound more strongly to iridium than rhodium. This was further established by examining metal– $C_{\alpha\text{-carbene}}$ bond lengths, which revealed that the rhodium– $C_{\alpha\text{-carbene}}$ bond was ca. 0.06 Å longer than the iridium– $C_{\alpha\text{-carbene}}$ bond. These data are consistent with the transition-state model proposed for rhodium porphyrincatalyzed cyclopropanation, where the selectivity of rhodium catalysts was proposed to arise from a relatively high energy rhodium–carbene complex, leading to an earlier transition state for carbene transfer. In addition, isolated NHC complexes exhibited significant porphyrin ring distortions. As has been shown repeatedly in biological systems, porphyrin distortion plays an important role in catalysis and should be considered for the continuing development of synthetic metalloporphyrin catalysts.

EXPERIMENTAL SECTION

General Considerations. Literature procedures were used to synthesize 1,3-diethylimidazolylidiene and 1-(n-butyl)-3-methylimidazolylidene.²¹ Attempts to purify deim and bmim by distillation decomposed the free NHC. Crude samples of deim and bmim were dissolved in a known volume of THF and stored in the freezer. Stocksolution 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 halogenato porphyrin complex.⁶⁴ Methylene chloride and tetrahydrofuran were deoxygenated and dried by passage through columns of reduced copper and alumina. Hexanes and benzene- d_6 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 methanol and ethylene glycol. ¹H 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; C₆D₆, 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 K α 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 $U_{iso}(H)$ values were set at 1.5 times the $U_{\rm eq}$ 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- d_8 solution of Rh(TTP)CH₃(deim) (32.0 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 μ L, 0.01437 mmol), diluted to a final volume of 750 μ L, and analyzed by ¹H NMR. As verification, similar results were obtained when Rh(TTP)CH₃(bmim) (16.7 mg, 0.0180 mmol) was treated with varying amounts of bmim (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 μ L of a stock solution of Ir(TTP)CH₃ (3.14×10^{-3} M, 1.41μ mol). The solution was taken to dryness, and the NMR tube was brought into a glovebox. The NMR tube was charged with mesitylene standard (20 μ L from a 5.16×10^{-2} M C₆D₆ stock solution, 1.03 μ mol), deim (108 μ L from a 0.144 M C₆D₆ stock solution, 15.5 μ mol), and enough C₆D₆ to attain a final solution volume of 420 μ L. After mixing for 5–10 min, the solution was treated with varying amounts of bmim (140-292 μ L from a 0.0798 M C₆D₆ stock solution, 11.2–23.3 μ mol). 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 [bmim] was varied in order to determine $k_{\rm f}$. 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 discarded as a statistical outlier.

Pseudoirreversible NHC Exchange with Iridium Porphyrins. A medium-walled NMR tube was charged with Ir(TTP)CH₃ (300 to 600 μ L from a 3.60 × 10⁻³ M CH₂Cl₂ stock solution, 1.08 to 2.16 μ mol). The tube was taken into a glovebox and loaded with NHC_d (deim: 16 to 23 μ L from a 0.141 M C₆D₆ stock solution, 2.3 to 3.2 μ mol; bmim: 20 to 34 μ L from a 0.0764 M C₆D₆ stock solution, 1.5 to 2.6 μ mol), mesitylene (20 μ L from a 5.16 × 10⁻² M C₆D₆ stock solution, 1.5 to 2.4 μ L. 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 NHC_i (deim: 110 μ L from a 0.141 M C₆D₆ stock solution, 15.1 μ mol; bmim: 200 μ L from a 0.0764 M C₆D₆ stock solution, 3.1 μ mol; bmim: 200 μ L from a 0.141 M C₆D₆ stock solution, 3.1 μ mol; bmim: 200 μ L from a 0.141 M C₆D₆ stock solution, 3.1 μ mol; bmim: 200 μ L from a 0.141 M C₆D₆ stock solution, 3.1 μ mol; bmim: 200 μ L from a 0.0764 M C₆D₆ stock solution, 3.1 μ mol; bmim: 200 μ L from a 0.0764 M C₆D₆ stock solution, 3.1 μ mol; bmim: 200 μ L from a 0.0764 M C₆D₆ stock solution, 3.1 μ mol; bmim: 200 μ L from a 0.0764 M C₆D₆ stock solution, 3.1 μ mol; bmim: 200 μ L from a 0.0764 M C₆D₆ stock solution, 3.1 μ mol; bmim: 200 μ L from a 0.0764 M C₆D₆ stock solution, 3.1 μ mol; bmim: 200 μ L from a 0.0764 M C₆D₆ stock solution, 3.1 μ mol; bmim: 200 μ L from a 0.0764 M C₆D₆ stock solution, 3.1 μ mol; bmim: 200 μ L from a 0.0764 M C₆D₆ stock solution, 3.3 μ mol), and data collection began ca. 2 min after addition.

 $[Ir(TTP)(C \equiv NBn)_2](BF_4)$, 2. Following a procedure similar to that described previously for $[Rh(TPP)(C \equiv NtBu)](PF_6)^{18}$ and $[Ir-(TTP)(BF_4)/Ir(TTP)(CO)](BF_4)^{69}$ Ir(TTP)Cl(CO) (44.8 mg, 0.0485 mmol) and silver tetrafluoroborate (16.9 mg, 0.0868 mmol) were collected in a vial under a glovebox atmosphere, wrapped with aluminum foil, dissolved in CH2Cl2, and stirred at ambient temperature for 2 days. Solids were removed by filtration through a pad of Celite. The filtrate was treated with benzyl isocyanide (25.0 μ L, 0.205 mmol) and stirred at ambient temperature overnight. Volatiles were removed in vacuo, and the crude sample was evaluated by ¹H NMR. If conversion to complex 2 was incomplete, the residue was recollected in CH_2Cl_2 (5.0 mL) under air and treated with additional portions of benzyl isocyanide until ¹H NMR signals corresponding to $[Ir(TTP)/Ir(TTP)(CO)](BF_4)$ were completely consumed. Complex 2 was isolated by recrystallization from CH2Cl2/hexanes (33.3 mg, 0.0295 mmol, 61% yield), though benzene was also a suitable recrystallization solvent. ¹H NMR (CDCl₃, 300 MHz): δ 8.96 (s, 8H, β -pyrrole), 7.96 (d, ³J(HH) = 7.8 Hz, 8H, meso-o-tolyl), 7.56 (d, ³J(HH) = 7.8 Hz, 8H, meso-m-tolyl), 6.98 (t, ³J(HH) = 7.5 Hz, 2H, pphenyl), 6.79 (t, ${}^{3}J(HH) = 7.5$ Hz, 4H, *m*-phenyl), 4.80 (d, ${}^{3}J(HH) =$ 7.5 Hz, 4H, o-phenyl), 2.72 (s, 12H, tolyl -CH₃), 2.65 (s, 4H, $-CH_2-$). ¹³C{¹H} NMR (CDCl₃, 75 MHz): δ 183.07 (Ir $-C\equiv$ N), 141.72, 138.18, 137.77, 134.26, 132.43, 128.51, 128.02, 127.81, 124.16, 122.55, 45.16 (-CH₂-), 21.67 (tolyl -CH₃). UV-vis (CH₂Cl₂): nm $(\log_{\epsilon} \epsilon)$ 419 (5.44), 531 (4.36), 566 (3.86). IR (KBr): C=N 2228 cm⁻

[Ir(TTP)(=C(NHBn)₂)(C=NBn)](BF₄), 3. Complex 2 (26.1 mg, 0.0221 mmol) was collected in a 20 mL scintillation vial and dissolved in CH₂Cl₂ (3.5 mL) under air. The solution was treated with benzylamine ($5.40 \times 10^2 \,\mu$ L from a 0.0411 M CDCl₃ stock solution, 0.0222 mmol) and heated to 40 °C overnight in a tightly closed

container sealed with a poly-lined cap. Volatiles were removed in vacuo. Single crystals suitable for X-ray diffraction were obtained by slow evaporation from a CH₂Cl₂/hexanes solution (20.7 mg, 0.0161 mmol, 73% yield). ¹H NMR (CDCl₃, 400 MHz): δ 8.80 (s, 8H, β pyrrole), 7.91 (d, ${}^{3}J(HH) = 7.6$ Hz, 4H, meso-o-tolyl), 7.53 (m, 12H, meso-o-tolyl and meso-p-tolyl), 7.17 (t, ³J(HH) = 7.6 Hz, 2H, pphenyl(carbene)), 7.04–6.96 (m, 5H, p-phenyl(isocyanide) and m-phenyl(carbene)), 6.81 (t, ${}^{3}J(HH) = 7.6$ Hz, 2H, m-phenyl-(isocyanide)), 5.31 (d, ${}^{3}J(HH) = 7.6$ Hz, 4H, o-phenyl(carbene)), 4.85 (d, ³J(HH) = 7.6 Hz, 2H, o-phenyl(isocyanide)), 2.70 (s, 12H, tolyl – CH₃), 2.63 (s, 2H, isocyanide – CH₂–), 2.07 (d, J = 3.2 Hz, 4H, carbene – CH₂–), –1.98 (br, 2H, –NH). ¹³C{¹H} NMR (CDCl₃, 151 MHz): δ 162.92 (Ir-C(NHR)₂), 141.56, 138.20, 137.58, 134.43, 134.09, 134.05, 132.50, 129.47, 129.00, 128.48, 128.21, 127.89, 127.85, 127.73, 126.17, 124.18, 122.66, 48.12 (carbene -CH₂-), 44.85 (isocyanide $-CH_2$ -), 21.65 (tolyl $-CH_3$). A carbon signal corresponding to bound isocyanide was not observed. Anal. Calcd for C₇₁H₅₉BF₄IrN₇·H₂O: C, 65.23; H, 4.70; N, 7.50. Found: C, 65.01; H, 4.93; N, 7.26. UV-vis (CH₂Cl₂): nm (log ε) 419 (5.38), 530 (4.34), 564 (3.85). IR (KBr): C≡N 2218 cm⁻

General Procedure for Synthesis and Isolation of NHC Complexes. A 20 mL scintillation vial was charged with M(TTP)-CH₃ and transferred into the glovebox. The metalloporphyrin was dissolved in 1–3 mL of THF and treated with the NHC complex (ca. 1.5 equiv). The resulting solution was layered with hexanes (ca. 3× greater volume than THF) and stored in the freezer overnight. Dark crystals were collected by filtration and physical separation.

Rh(TTP)(deim)(CH₃), 5a. Rh(TTP)CH₃ (58.0 mg, 73.7 µmol) was treated with bmim (0.30 mL from a 0.40 M stock solution, 120 μ mol). Dark green crystals (16.7 mg, 18.0 µmol, 24% yield) were collected after drying in vacuo. ¹H NMR (THF- d_8 , 400 MHz, 239.0 K): δ 8.53 (s, 8H, β -pyrrole), 7.97 (dd, ³J(HH) = 7.6, 2.4 Hz, 4H, meso-o-tolyl), 7.89 (dd, ${}^{3}J(HH) = 7.6$, 2.4 Hz, 4H, meso-o-tolyl), 7.52 (d, ${}^{3}J(HH) =$ 7.6 Hz, 8H, meso-m-tolyl), 5.27 (s, 2H, vinyl-CH), 2.65 (s, 12H, tolyl- CH_3), -0.31 (q, ³J(HH) = 7.0 Hz, 4H, ethyl- CH_2 -), -0.56 (t, ${}^{3}J(HH) = 7.0$ Hz, 6H, ethyl-CH₃), -7.44 (d, ${}^{3}J(RhH) = 2.0$ Hz, 3H, Rh–CH₃). ¹³C{¹H} NMR (THF- d_{8} , 151 MHz, 260 K): δ 179.98 (d, $^{1}J(RhC) = 88.2$ Hz, Rh $-C_{NHC}$), 143.07, 140.45, 137.35, 134.69, 134.57, 131.79, 127.96, 127.59, 121.44, 117.89, 40.19 (ethyl-CH₂-), 21.38 (tolyl-CH₃), 15.32 (ethyl-CH₃), -4.55 (br, Rh-CH₃). ¹³C signals, especially those for the coordinated NHC and axial methyl carbons, were verified by HMQC experiments and in a separate acquisition with a 700 MHz instrument using Cr(acac)₃. UV-vis (THF): nm (log ε) 374 (4.80), 444 (4.94).

Rh(TTP)(bmim)(CH₃), 5b. Rh(TTP)CH₃ (40.0 mg, 50.8 μ mol) was treated with bmim (0.350 mL from a 0.18 M stock solution, 65 $\mu mol).$ Dark green crystals (32.0 mg, 35.1 $\mu mol,$ 69% yield) were collected after drying in vacuo. ¹H NMR (THF-d₈, 400 MHz, 239.0 K): δ 8.53 (s, 8H, β -pyrrole), 7.93 (d, ³J(HH) = 7.6 Hz, 4H, meso-otolyl), 7.91 (d, ${}^{3}J(HH) = 7.6$ Hz, 4H, meso-o-tolyl), 7.52 (d, ${}^{3}J(HH) =$ 7.6 Hz, 8H, meso-m-tolyl), 5.20 (d, ${}^{3}J(HH) = 1.2$ Hz, 1H, vinyl –*CH*), 5.13 (d, ${}^{3}J(HH) = 1.2$ Hz, 1H, vinyl –CH), 2.65 (s, 12H, tolyl–CH₃), 0.44 (t, ${}^{3}J(HH) = 7.4$ Hz, 3H, butyl $-CH_{3}$), 0.20 (m, 2H, butyl- $C\gamma H_2$ -), -0.20 (s, 3H, methyl- CH_3), -0.31 (m, 2H, butyl- C_aH_2 -), -0.42 (m, 2H, butyl $-C_{\beta}H_2-$), -7.38 (d, ¹J(RhH) = 1.6 Hz, 3H, Rh-CH₃). ¹³C{¹H} NMR (THF-*d*₈, 151 MHz, 260 K): δ 181.84 (br, Rh-С_{NHC}), 143.00, 140.41, 137.35, 134.61, 134.46, 131.74, 127.97, 127.57, 121.41, 120.31, 117.16, 45.12 (butyl– $C_{\alpha}H_2$ –), 32.88 (butyl– $C_{\beta}H_2$ –), 32.47 (NCH₃), 21.39 (tolyl-CH₃), 19.57 (butyl-C_rH₂-), 13.79 (butyl-CH₃), and -5.01 (Rh-CH₃). The axial methyl carbon at -5.01 ppm was observed only by HMQC. The carbene signal at 181.84 ppm (br) was observed only in a separate acquisition using Cr(acac)₃ and a 700 MHz NMR instrument. UV-vis (THF): nm (log ϵ) 374 (4.80), 444 (4.94).

Ir(TTP)(deim)(CH₃), 6a. Ir(TTP)CH₃ (17.7 mg, 20.2 μmol) was treated with bmim (0.15 mL from a 0.18 M stock solution, 27 μmol). Dark brown crystals (11.0 mg, 11.0 μmol, 55% yield) were collected after drying *in vacuo*. ¹H NMR (THF- d_8 , 400 MHz, 239.0 K): δ 8.30 (s, 8H, β-pyrrole), 7.95 (d, ³J(HH) = 7.2 Hz, 4H, *meso-o*-tolyl), 7.84 (d, ³J(HH) = 7.2 Hz, 4H, *meso-o*-tolyl), 7.52 (d, ³J(HH) = 7.2 Hz, 4H,

meso-m-tolyl), 7.50 (d, ${}^{3}J(HH) = 7.2$ Hz, 4H, meso-m-tolyl), 5.32 (s, 2H, vinyl-CH), 2.63 (s, 12H, tolyl-CH₃), -0.02 (q, ${}^{3}J$ (HH) = 6.8 Hz, 4H, ethyl– CH_2 –), –0.42 (t, ³J(HH) = 6.8 Hz, 6H, ethyl– CH_3), –8.03 (s, 3H, Ir– CH_3). ¹³C{¹H} NMR (THF- d_8 , 151 MHz, 298 K): δ 164.33 (Ir-C_{NHC}), 143.43, 139.92, 137.31, 134.64, 134.44, 131.51, 127.99, 127.60, 123.71, 118.03, 40.16 (ethyl-CH2-), 21.30 (tolyl-CH₃), 15.12 (ethyl-CH₃), -21.97 (Ir-CH₃). ¹³C signals, especially those for the coordinated NHC and axial methyl carbons, were verified by HMQC experiments. UV-vis (THF): nm (log ε) 370 (4.54), 438 (4.94).

Ir(TTP)(bmim)(CH₃), 6b. Ir(TTP)CH₃ (27.9 mg, 31.8 µmol) was treated with bmim (0.10 mL from a 0.40 M stock solution, 40 μ mol). Dark brown crystals (10.1 mg, 10.0 μ mol, 31% yield) were collected after drying in vacuo. ¹Η NMR (THF-d₈, 400 MHz, 239.0 K): δ 8.30 (s, 8H, β -pyrrole), 7.91 (dd, ${}^{3}J(HH) = 7.8$, 1.6 Hz, 4H, meso-o-tolyl), 7.85 (dd, ${}^{3}J(HH) = 7.8$, 1.6 Hz, 4H, meso-o-tolyl), 7.50 (d, ${}^{3}J(HH) =$ 7.8 Hz, 8H, meso-m-tolyl), 5.22 (d, ${}^{3}J(HH) = 1.2$ Hz, 1H, vinyl-CH), 5.15 (d, ${}^{3}J(HH) = 1.2$ Hz, 1H, vinyl-CH), 2.63 (s, 12H, tolyl-CH₃), 0.52 (t, ${}^{3}J(HH) = 7.2$ Hz, 3H, butyl-CH₃), 0.40 (m, 2H, butyl $-C_{y}H_{2}$ -), 0.05 (s, 3H, methyl $-CH_{3}$), -0.03 (t, ${}^{3}J(HH) = 7.2$ Hz, 2H, butyl- $C_{a}H_{2}$ -), -0.32 (m, 2H, butyl- $C_{b}H_{2}$ -), -7.94 (s, 3H, Ir-CH₃). ${}^{13}C{\tilde{1}H}$ NMR (THF- d_{8} , 151 MHz, 298 K): δ 164.86 (Ir– С_{NHC}), 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- $C_{\alpha}H_2$ -), 32.70 (butyl- $C_{\beta}H_2$ -), 32.68 (NCH₃), 21.30 (tolyl- CH_3), 19.61 (butyl- C_yH_2 -), 13.67 (butyl-CH₃), -21.92 (Ir-CH₃). ¹³C signals, especially those for the coordinated NHC and axial methyl carbons, were verified by HMQC experiments. UV-vis (THF): nm (log ɛ) 370 (4.49), 438 (4.89).

ASSOCIATED CONTENT

Supporting Information

Absorption and NMR spectra of complexes 2, 3, 5, and 6, variable-temperature NMR spectra, spectra for NHC exchange with $Rh(TTP)CH_3$, kinetics data, structure refinement data, and crystal data. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: kwoo@iastate.edu.

Author Contributions

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Notes

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ABBREVIATIONS

NHC, N-heterocyclic carbene; deim, 1,3-diethylimidazolylidene; bmim, 1-(n-butyl)-3-methylimidazolylidene; TTP, tetratolylporphyrinato dianion; OEP, octaethylporphyrinato dianion; NSD, normal-coordinate structural decomposition analysis; D_{oop} , out-of-plane distortion; D_{ip} , in-plane distortion; THF, tetrahydrofuran

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