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Addition of Amines to a Carbonyl Ligand: Syntheses, Characterization, and Reactivities of Iridium(III) Porphyrin Carbamoyl Complexes

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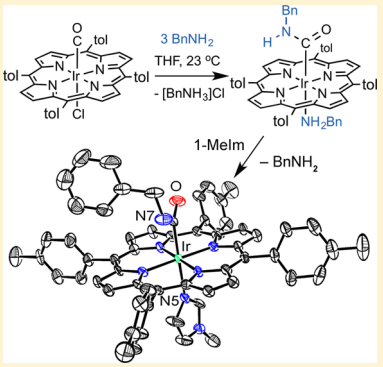
Supporting Information

ABSTRACT: Treatment of (carbonyl)chloro(*meso*-tetra-*p*-tolylporphyrinato)iridium-(III), (TTP)Ir(CO)Cl (**1**), with excess primary amines at 23 °C in the presence of Na_2CO_3 produces the *trans*-amine-coordinated iridium carbamoyl complexes (TTP)Ir-(NH_2R)[C(O)NHR] (R = Bn (**2a**), *n*-Bu (**2b**), *i*-Pr (**2c**), *t*-Bu (**2d**)) with isolated yields up to 94%. The *trans*-amine ligand is labile and can be replaced with quinuclidine (1-azabicyclo[2.2.2]octane, ABCO), 1-methylimidazole (1-MeIm), triethyl phosphite ($P(OEt)_3$), and dimethylphenylphosphine (PMe_2Ph) at 23 °C to afford the hexacoordinated carbamoyl complexes (TTP)Ir(L)[C(O)NHR] (for R = Bn: L = ABCO (**3a**), 1-MeIm (**4a**), $P(OEt)_3$ (**5a**), PMe_2Ph (**6a**)). On the basis of ligand displacement reactions and equilibrium studies, ligand binding strengths to the iridium metal center were found to decrease in the order PMe_2Ph > $P(OEt)_3$ > 1-MeIm > ABCO > $BnNH_2$ ≫ Et_3N, PCy_3. The carbamoyl complexes (TTP)Ir(L)[C(O)NHR] (L = RNH_2 (**2a,b**), 1-MeIm (**4a**)) undergo protonolysis with HBF_4 to give the cationic carbonyl complexes [(TTP)Ir(NH_2R)(CO)]BF_4 (**7a,b**) and [(TTP)Ir(1-MeIm)(CO)]BF_4 (**8**), respectively. In contrast, the carbamoyl complexes (TTP)Ir(L)[C(O)NHR] (L = $P(OEt)_3$ (**5a**), PMe_2Ph (**6a,c**)) reacted with HBF_4 to afford the complexes [(TTP)Ir(PMe_2Ph)]BF_4 (**9**) and [(TTP)Ir$P(OEt)_3$]BF_4 (**10**), respectively. The carbamoyl complexes (TTP)Ir(L)[C(O)NHR] (L = RNH_2 (**2a−d**), 1-MeIm (**4a**), $P(OEt)_3$ (**5b**), PMe_2Ph (**6c**)) reacted with methyl iodide to give the iodo complexes (TTP)Ir(L)I (L = RNH_2 (**11a−d**), 1-MeIm (**12**), $P(OEt)_3$ (**13**), PMe_2Ph (**14**)). Reactions of the complexes [(TTP)Ir(PMe_2Ph)]BF_4 (**9**) and [(TTP)Ir$P(OEt)_3$]BF_4 (**10**) with $[Bu_4N]I$, benzylamine ($BnNH_2$), and PMe_2Ph afforded (TTP)Ir(PMe_2Ph)I (**14**), (TTP)Ir$[P(OEt)_3]$I (**13**), [(TTP)Ir$(PMe_2Ph)(NH_2Bn)$]BF_4 (**16**), and *trans*-[(TTP)Ir$(PMe_2Ph)_2$]-BF_4 (**17**), respectively. Metrical details for the molecular structures of **4a** and **17** are reported.



INTRODUCTION

Metal carbonyl complexes play a significant role in industrial and organometallic chemistry, serving as important starting materials and catalysts.[1] A key reaction for these complexes is the addition of nucleophiles to the carbonyl ligand. This reactivity provides access to useful organic molecules such as dimethylformamide, methanol, etc.[2] Furthermore, the nucleophilic addition of the hydroxide anion to the CO ligand in metal carbonyl complexes has been identified as a key step in the water-gas shift reaction.[3]

Addition of amines to a transition-metal-bound carbonyl ligand is a convenient route to the synthesis of metal carbamoyl (or carboxamido) complexes (eq 1).[4] In general, metal carbonyl

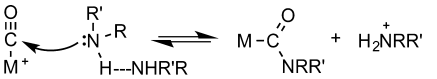
$$L_nM^{+}\text{–CO} + 2\,HNRR' \rightleftharpoons L_nM\text{–}C(=O)NRR' + H_2NRR'^{+} \quad (1)$$

R, R' = H or alkyl

complexes that are susceptible to nucleophilic amine addition to form metal carbamoyl complexes have υ(CO) above 2000 cm^{-1}, an indication of the electrophilicity of the CO ligand.[5,6] Some of the earliest reported examples of carbamoyl complexes prepared by this route include those of Mn, Ru, Pt, and Fe.[4] Kinetic studies involving the reaction of amines with *trans*-$[M(CO)_4L_2]PF_6$ (where M = Mn, Re and L = PPh_3, $PMePh_2$, PMe_2Ph), have revealed that the rate of formation of carbamoyl complexes has a second order dependence on the amine concentration. To rationalize this rate dependence, a mechanism involving amine assisted nucleophilic attack at the carbonyl carbon atom was proposed (Scheme 1).[7]

Subsequently, metal carbamoyl complexes were either observed or suggested to be involved in several catalytic and stoichiometric chemical transformations. For example, the catalytic oxidative carbonylation of *n*-butylamine to the 1,3-substituted urea, using $[(CO)_2W(NPh)I_2]_2$ as a catalyst, was

Scheme 1. Carbamoyl Complexes via Nucleophilic Attack of Amine on M−CO



Rate = k [M$^+$-CO][NHR'R]^2

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proposed to involve the tungsten carbamoyl complex (CO)-$W[C(O)NHBu](NH_2R)_2(NPh)I$ as an intermediate.[8] This was supported further by IR spectroscopic studies with stoichiometric reactions of excess secondary and primary amines with $[(CO)_2W(NPh)I_2]_2$, which produced formamides and 1,3-disubstituted ureas, respectively, in the presence of air as an oxidizing agent.[9] In addition, treatment of palladium carbamoyl complexes with halogens or other oxidizing agents produced isocyanates, in quantitative yields (eq 2).[10]

$$PdClL_2[C(O)NHR] + X_2 \xrightarrow[-HX]{} PdClXL_2 + RNCO \quad X = Cl,\ I \qquad (2)$$

Despite the diversity of metal carbamoyl complexes that exist,[11−17] reports on the synthesis and isolation of metalloporphyrin carbamoyl complexes are rare. One example involves the formation of the carbamoyl complex (TPP)Rh-$[C(O)NEt_2]$ from the reaction of (TPP)Rh(CO)Cl with $LiNEt_2$ in $HNEt_2$. Treatment of the Rh carbamoyl product with HCl re-formed the starting chlorocarbonyl complex.[18] In addition, octaethyl- and tetraphenylporphyrinato rhodium carbamoyl complexes, (OEP)Rh[C(O)NHR] and (TPP)Rh-[C(O)NHR], were observed as trace products in reactions of the bis(isocyanide) porphyrinato rhodium(III) complexes $[(OEP)Rh(CNR)_2]PF_6$ and $[(TPP)Rh(CNR)_2]PF_6$ with nucleophiles, such as methanol, to form the cationic rhodium diaminocarbene species $[(OEP)Rh\{=C(NHR)_2\}]PF_6$ and $[(TPP)Rh\{=C(NHR)_2\}]PF_6$.[19] Furthermore, Wayland and co-workers[20] isolated pentacoordinate carbamoyl complexes of rhodium octaethylporphyrin, (OEP)Rh[C(O)NHR], by treating $[(OEP)Rh]_2$ with CO and primary amines (eq 3). In this case, the reaction was proposed to proceed via a hydroxyaminocarbene complex, $[(OEP)Rh{=}C(OH)NHR]^+$.

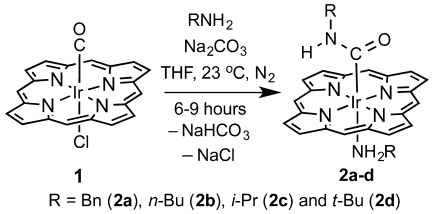
$$^1/_2[(OEP)Rh]_2 + CO + RNH_2 \xrightarrow[-^1/_2H_2]{} (OEP)RhC(O)NHR \qquad (3)$$

Although the isolation and characterization of the pentacoordinate octaethylporphyrinato rhodium carbamoyl complexes were described, the reactivities of these metalloporphyrin carbamoyl complexes were not explored. We report herein the syntheses, characterization, and reactivities of novel hexacoordinate porphyrinato iridium carbamoyl complexes.

RESULTS AND DISCUSSION

Reactions of (TTP)Ir(CO)Cl with Amines. Generally, carbonyl groups react with amines, to give carbamoyl ligands, when ν(CO) is greater than 2000 cm^{-1}.[5,6] The ν(CO) value of (TTP)Ir(CO)Cl (2056 cm^{-1})[21] suggested that the carbonyl ligand should be susceptible to nucleophilic attack. Thus, treatment of THF solutions of (TTP)Ir(CO)Cl (**1**) with primary amines, at 23 °C, immediately resulted in a color change from red to brown. ^{1}H NMR monitoring of the reactions revealed that product formation was complete within 3 min. Amine-coordinated iridium carbamoyl complexes, $(TTP)Ir(NH_2R)[C(O)NHR]$, were isolated from the reaction mixtures in 73−94% yields (Scheme 2). Use of 2 equiv of the amine resulted in quantitative reactions, as monitored by NMR. In order to facilitate product isolation, both excess amine (up to 67 equiv) and excess sodium carbonate were needed. Without

Scheme 2. Syntheses of Carbamoyl Complexes $(TTP)Ir(NH_2R)[C(O)NHR]$ (2a−d)[a]



1 **2a-d**

R = Bn (**2a**), *n*-Bu (**2b**), *i*-Pr (**2c**) and *t*-Bu (**2d**)

[a] *meso*-tolyl groups are omitted.

Na_2CO_3, workup resulted in some contamination with (TTP)Ir(CO)Cl, presumably due to reversion of the reaction. Similar observations were reported in the syntheses of the carbamoyl complexes *cis*-$Mn(CNR)[C(O)NHMe](CO)_2(bipy)$ from *fac*-$[Mn(CNR)(CO)_3(bipy)]^+$ and $MeNH_2$.[17]

Formation of the carbamoyl complexes was readily followed spectroscopically, as evidenced by the replacement of the ^{1}H NMR β-pyrrole signal of (TTP)Ir(CO)Cl (**1**) with the β-pyrrole signal of the corresponding carbamoyl products **2a−d**. The ^{1}H NMR spectra also showed upfield shifts for the carbamoyl and the *trans*-amine ligands, relative to the free amine chemical shifts. These upfield shifts of the axial ligand signals are attributed to the well-known ring current effect of the porphyrin macrocycle.[19,22] For example, the methylene protons of free benzylamine resonate at 3.55 ppm, in C_6D_6. In comparison, the methylene signal of the *N*-benzylcarbamoyl ligand in complex **2a** appeared as a two-proton doublet at 2.00 ppm, while the methylene protons of the *trans*-benzylamine in **2a** resonated at −1.78 ppm (2H, br), also in C_6D_6. Generally, the proton signals of the amine ligand are shifted more upfield than those of the carbamoyl fragment, due to the closer proximity of the amine to the porphyrin macrocycle. This is illustrated by $(TTP)Ir(NH_2{}^iPr)[C(O)NHPr^i]$ (**2c**), in which the isopropyl methyl signal of the amine ligand resonated at −2.31 ppm, in comparison to the isopropyl methyl signal of the carbamoyl ligand at −0.75 ppm.

At 26 °C, the amine proton signals in the carbamoyl compounds **2a−d** were notably broadened relative to all other signals (Figures S1, S5, S7, and S9, Supporting Information), suggesting that the amine ligand was labile. Cooling an NMR sample of **2a** (in $CDCl_3$) to 0 °C resulted in a sharpening of these signals (Figure S2, Supporting Information). Further evidence of this lability was demonstrated by ^{1}H NMR experiments with added amine. When ∼1.5 equiv of benzylamine was added to a C_6D_6 solution of **2a** at 26 °C, the ^{1}H NMR spectrum exhibited broad methylene signals for both the coordinated (−1.78 ppm) and free (3.55 ppm) amines. When the temperature of the NMR sample was increased to 45 °C, these signals coalesced into the baseline. Restoring the sample temperature to 26 °C produced the original spectrum, in which separate free and coordinated amine signals became visible again.

Ligand Replacement Reactions. The lability of the coordinated amines was further demonstrated by their ease of substitution at 23 °C, by the ligands L = quinuclidine (1-azabicyclo[2.2.2]octane, ABCO), 1-methylimidazole (1-MeIm), triethyl phosphite ($P(OEt)_3$), dimethylphenylphosphine (PMe_2Ph), leading to the isolation of the complexes (TTP)-Ir(L)[C(O)NHR] (**3−6**) (Scheme 3). Benzylamine in (TTP)-

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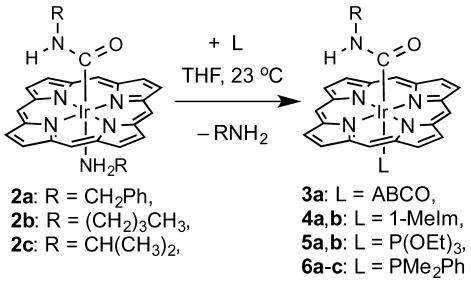
Scheme 3. Substitution of Amine Ligands in (TTP)Ir(NH_2R)[C(O)NHR][a]



[a]*meso*-tolyl groups are omitted.

Ir(NH_2Bn)[C(O)NHBn] (**2a**) was completely displaced by 1 equiv of 1-methylimidazole within 3 min. Coordination of the imidazole in (TTP)Ir(1-MeIm)[C(O)NHBn] (**4a**) was established by the appearance of sharp proton singlets at 0.43 (3H), 1.63 (1H), 1.74 (1H), and 3.70 ppm (1H), assigned to the methyl and ring protons of the bound 1-MeIm, which are shifted upfield from 2.51 (methyl protons), 6.26, 6.99, and 7.22 ppm (ring protons), respectively, in the free 1-MeIm. The *N*-benzylcarbamoyl ligand remained bound to the metal center, as evidenced by ^{1}H NMR signals of the carbamoyl NH (−1.13 ppm, t) and CH_2 (2.07 ppm, d) in complex **4a**, which were shifted downfield, in comparison with the carbamoyl NH and CH_2 proton signals (−1.34 and 2.00 ppm, respectively) of complex **2a**.

In complex **6a**, the ^{31}P NMR signal of PMe_2Ph shifted downfield from −46.61 to −41.23 ppm upon coordination to iridium (Table 1). A similar downfield shift in the ^{31}P NMR signal for phosphine ligand coordination to the rhodium tetraphenylporphyrin complex, $(DPAP)_2Rh^{III}TPP$, where DPAP is diphenyl(phenylethynyl)phosphine, was observed earlier by Stulz and co-workers.[23] In contrast, coordination of $P(OEt)_3$ to Ir in **5a,b** resulted in a large upfield shift of the phosphite signal (Table 1). An analogous large upfield shift in the compound (η-MeCp)$(CO)_2$Mn($P(OEt)_3$) was rationalized by metal d-electron back-donation to the π-acid $P(OEt)_3$ ligand.[24]

The ^{13}C chemical shifts for the α-C of the carbamoyl ligands were readily assigned in the $P(OEt)_3$ and PMe_2Ph complexes (**5a,b** and **6a−c**, respectively), due to two-bond ^{31}P−^{13}C coupling. For example, in **5a**, a low-field ^{13}C doublet appeared at 162.72 ppm ($^2J_{P-C}$ = 270.3 Hz), while a low-field ^{13}C doublet appeared at 163.87 ppm ($^2J_{P-C}$ = 184.2 Hz) for **6a** (Table 2).

Table 1. ^{31}P NMR Data[a] for $P(OEt)_3$ and PMe_2Ph as Free Ligands and Coordinated to Carbamoyl Complexes, (TTP)Ir(L)[C(O)NHR] (L = $P(OEt)_3$ (5a,b), PMe_2Ph (6a−c))

^{31}P (δ) free ligand	(TTP)Ir(L)[C(O)NHR]	^{31}P (δ) bound L
138.06 ($P(OEt)_3$)	R = Bn (**5a**)	72.06
	R = ^{n}Bu (**5b**)	72.88
−46.61 (PMe_2Ph)	R = Bn (**6a**)	−41.23
	R = ^{n}Bu (**6b**)	−41.32
	R = ^{i}Pr (**6c**)	−41.27

[a]With C_6D_6 solution of PPh_3 (^{31}P NMR δ −5.53 ppm) as an external standard.

Table 2. ^{13}C NMR Data[a] for the α-C of the Carbamoyl Ligands in (TTP)Ir(L)[C(O)NHR] (L = $P(OEt)_3$ (5a,b), PMe_2Ph (6a−c))

complex	R	δ carbamoyl α-C
5a	Bn	162.72 (d, $^2J_{P-C}$ = 270.3 Hz)
5b	^{n}Bu	162.73 (d, $^2J_{P-C}$ = 267.3 Hz)
6a	Bn	163.87 (d, $^2J_{P-C}$ = 184.2 Hz)
6b	^{n}Bu	163.87 (d, $^2J_{P-C}$ = 182.7 Hz)
6c	^{i}Pr	163.39 (d, $^2J_{P-C}$ = 184.2 Hz)

[a]In $CDCl_3$.

Relative Binding Strengths of the Ligands. A series of substitution reactions to determine the relative binding affinities of the $BnNH_2$, ABCO, 1-MeIm, and $P(OEt)_3$ ligands to the iridium center in the (TTP)Ir(L)[C(O)NHBn] complexes was monitored by ^{1}H NMR (eq 4). Equilibrium constants determined for ligand exchange reactions in C_6D_6 at 25 °C are given in Table 3.

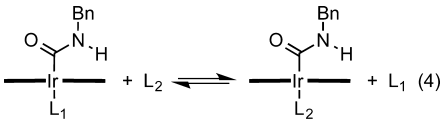


Table 3. Equilibrium Constants for Ligand Exchange Reactions Involving (TTP)Ir(L)[C(O)NHBn] at 25 °C (Eq 4)

entry	L_1	L_2	K^a
1	$BnNH_2$	ABCO	9.4 ± 0.2
2	ABCO	$BnNH_2$	0.11 ± 0.01
3	1-MeIm	$BnNH_2$	0.06 ± 0.02
4	ABCO	1-MeIm	1.9 ± 0.1
5	1-MeIm	ABCO	0.58 ± 0.05
6	ABCO	$P(OEt)_3$	14.4 ± 1.0
7	$P(OEt)_3$	ABCO	0.07 ± 0.004
8	1-MeIm	$P(OEt)_3$	5.7 ± 0.5
9	$P(OEt)_3$	1-MeIm	0.18 ± 0.01

[a]Reactions were carried out in C_6D_6 in air, with 1,3,5-mesitylene as an internal standard, and monitored by ^{1}H NMR (600 MHz).

The data in Table 3 show that $P(OEt)_3$ is more strongly bound to the iridium than 1-MeIm, on the basis of the values of the equilibrium constants shown in entries 8 and 9, and 1-MeIm is more strongly bound to the metal center than ABCO, as indicated by the equilibrium constants in entries 4 and 5.

In general, the more basic amines (conjugate acid pK_a values given in parentheses) *n*-butylamine (10.59), benzylamine (9.34), isopropylamine (10.63), and *tert*-butylamine (10.55)[25] were readily replaced by the less basic 1-MeIm (7.2),[26] $P(OEt)_3$ (3.31),[27] and PMe_2Ph (6.50).[27] Moreover, only 1 equiv of $P(OEt)_3$ or PMe_2Ph was required to completely displace 1-MeIm from the Ir carbamoyl complexes (TTP)Ir(1-MeIm)[C(O)NHR]. This indicates that factors other than the ligand basicity, such as π acidity and softness, influence ligand binding. Thus, the d^6 Ir(III) center, a soft acid[28] and electron-rich π-donor, prefers 1-methylimidazole and phosphorus ligands (soft bases) over amines (hard bases). Other studies (see below) indicate that the order of neutral ligand binding to (TTP)Ir(L)[C(O)NHBn] decreases in the order PMe_2Ph > $P(OEt)_3$ > 1-MeIm > ABCO > $BnNH_2$ ≫ Et_3N, PCy_3. The stronger

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binding of PMe_2Ph in comparison to $P(OEt)_3$ is based on the observation that 5 equiv of $P(OEt)_3$ failed to displace PMe_2Ph from the carbamoyl complex **6a** at 23 °C. These results are in accord with the higher σ-donating ability of PMe_2Ph, relative to $P(OEt)_3$.[24] In addition to electronic factors, steric hindrance also influences the binding of axial ligands to the iridium center. The reaction with tricyclohexylphosphine, PCy_3 (pK_a 9.70, cone angle 170°),[27] illustrates the importance of steric hindrance. When 1.5 equiv of PCy_3 was added to a C_6D_6 solution of **2a** at 23 °C, no reaction occurred after 12.5 h, as monitored by ^1H NMR. Other less basic and less sterically hindered tertiary phosphines, such as $P(n\text{-}Bu)_3$ (pK_a 8.43, cone angle 136°) and PPh_3 (pK_a 2.73, cone angle 145°),[27] readily displaced $BnNH_2$ from complex **2a**. Steric bulk also affects the binding of amines. This was apparent during an attempt to replace the benzylamine ligand (pK_a 9.34; cone angle 106°)[25,29] in complex **2a** with Et_3N (pK_a 10.65; cone angle 150°)[25,29] in C_6D_6, at 23 °C. Although Et_3N is more basic than $BnNH_2$, no reaction was observed, even after heating the reaction mixture to 90 °C for almost 9 h with 2 equiv of Et_3N. However, when an excess of the more basic but less sterically hindered tertiary amine quinuclidine (pK_a 11.0°,[30] cone angle 132°[29]) was added at ambient temperature to a C_6D_6 solution of complex **2a**, complete displacement of $BnNH_2$ was observed, affording complex **3a** in less than 7 min. All of these results indicate that both electronic and steric properties of the L ligand contribute to the overall trend in binding strengths in the (TTP)Ir(L)[C(O)NHBn] complexes.

The molecular structure for (TTP)Ir(1-MeIm)[C(O)NHBn] (**4a**) was solved by single-crystal X-ray diffraction analysis (Figure 1). The benzyl group of the *N*-benzylcarbamoyl ligand [C(O)NHBn] is anti to the iridium. The sum of the angles at the carbonyl carbon, C(53), is 360.0°, consistent with a trigonal-planar carbon atom. In addition, the *N*-benzylcarbamoyl and axial 1-MeIm ligands are collinear with a C(53)−Ir−N(5) bond angle of 178.86(19)°. The C(53)−N(7) bond distance (1.355(8) Å) of the carbamoyl ligand is similar to that of secondary organic amides, RC(O)NHR′ (1.334 Å),[31] and the C═O bond distance (1.217(7) Å) of the carbamoyl ligand is comparable to that of secondary organic amides (1.231 Å).[31] The C(53)−N(7) bond distance (1.355(8) Å) of the carbamoyl ligand is also analogous to that (1.341(5) Å)[20] reported for the pentacoordinate rhodium complex [(OEP)Rh[C(O)NH($C_6H_3Me_2$)] and that (1.34(1) Å)[32] for the hexacoordinate ruthenium bis-carbamoyl complex [Ru(dppe)$(CO)_2$[C(O)NHCHMe_2]$_2$. However, the Ir−N(5) bond distance of 2.208(5) Å in the 1-methylimidazole complex is longer than that reported for Ir−NMe_3 in Ir(TTP)Cl(NMe_3) (2.174(2) Å).[33] The Ir−C(53) length of 2.026(6) Å is comparable to the Ir−C length reported for the pentacoordinate Ir(TTP)[C(O)Ph] (2.038(12) Å)[34] but is longer than the Rh−C bond length (1.988(5) Å) in (OEP)Rh[C(O)NH($C_6H_3Me_2$)].[20]

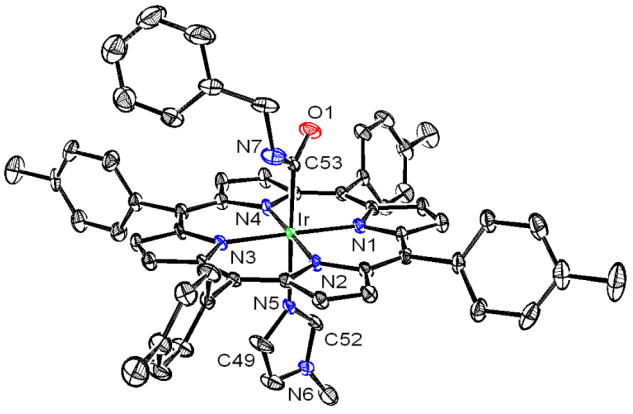
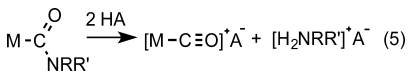


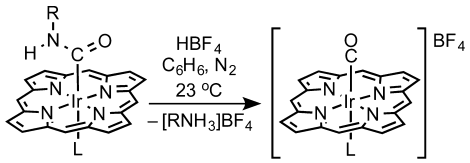
Figure 1. Molecular structure of (TTP)Ir(1-MeIm)[C(O)NHBn] (**4a**) with 30% probability ellipsoids. Selected bond distances (Å) and angles (deg): Ir−C(53) = 2.026(6), Ir−N(5) = 2.208(5), C(53)−O(1) = 1.217(7), C(53)−N(7) = 1.355(8); C(53)−Ir−N(5) = 178.86(19), N(3)−Ir−N(1) = 178.92(18), N(2)−Ir−N(4) = 178.44(18), O(1)−C(53)−N(7) = 119.0(6), O(1)−C(53)−Ir = 124.3(5), N(7)−C(53)−Ir = 116.7(4).

Reactions of the Carbamoyl Ligand with Electrophiles. *Reactions with HBF_4.* Metal carbamoyl complexes generally react with acids to form metal carbonyl complexes, a process that also serves as a supporting test for the presence of a carbamoyl ligand[4] (eq 5). When 2 equiv of $HBF_4{\cdot}Et_2O$ was



added at 23 °C to benzene solutions of the amine-coordinated carbamoyl complexes (TTP)Ir(NH_2R)[C(O)NHR] (**2a,b**), the corresponding cationic amine-coordinated carbonyl complexes [(TTP)Ir(NH_2R)(CO)]BF_4 (**7a,b**) were produced, as shown in Scheme 4. The carbonyl ligands of complexes **7a,b** exhibited CO stretching frequencies at 2075 and 2078 cm^{-1}, respectively.

Scheme 4. Reaction of Carbamoyl Complexes (TTP)Ir(L)[C(O)NHR] (2−4) with HBF_4[a]



2a-b
2a: L = RNH_2, R = Bn;
2b: L = RNH_2, R = *n*-Bu;
4a: L = 1-MeIm; R = Bn

7-8
7a: L = $BnNH_2$,
7b: L = *n*-$BuNH_2$,
8: L = 1-MeIm

[a] *meso*-tolyl groups are omitted.

The characterization of complex **7a** was representative of these new cationic carbonyl compounds. A low-intensity peak at 138.96 ppm was assigned as the carbonyl ^{13}C NMR resonance (Figure S33 Supporting Information). This is similar to the assignment for the carbonyl of [(TTP)Ir(CO)]BF_4 (131.3 ppm) reported by Chan.[34] Moreover, the parent ion peak (*m*/*z* 996.3275) observed by HRMS for [(TTP)Ir(NH_2Bn)(CO)]$^+$ and satisfactory elemental analysis provided confirmation of the composition and purity of complex **7a**. This represents the second account of a cationic iridium porphyrinato carbonyl complex. The first report was for an inseparable mixture of cations, [(TTP)Ir(CO)]BF_4/[(TTP)Ir]BF_4, described by Chan and co-workers.[34] While a similar reaction between 2 equiv of $HBF_4{\cdot}Et_2O$ and the 1-MeIm-coordinated carbamoyl complex (**4a**) led to the formation of the cationic 1-MeIm-coordinated carbonyl complex [(TTP)Ir(1-MeIm)(CO)]BF_4 (**8**) (Scheme 4), the quinuclidine-coordinated carbamoyl complex (**3a**) reacted with acid (eq 6) to give the cationic benzylamine-coordinated carbonyl complex [(TTP)Ir(NH_2Bn)(CO)]BF_4 (**7a**), as the major porphyrin

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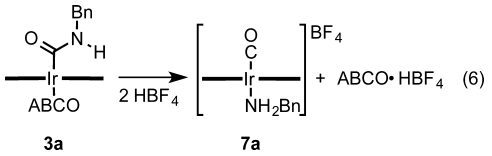
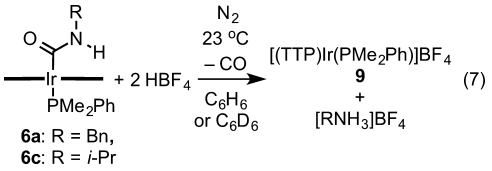


3a 7a

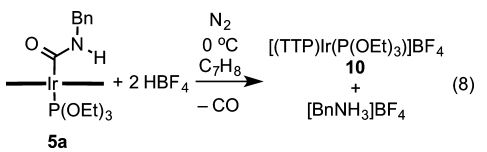
product (56%, by ^{1}H NMR), with the coformation of a mixture of other unidentified porphyrin products. The formation of **7a**, and not [(TTP)Ir(ABCO)(CO)]BF_4, is in accord with the higher basicity of quinuclidine in comparison with benzylamine and its thermodynamic preference for the ammonium form.

In contrast to the reactions of the amine (**2a**,**b**) and 1-MeIm (**4a**) complexes, the ambient-temperature reactions between excess HBF_4·Et_2O (3−4 equiv) and each of the two PMe_2Ph-coordinated carbamoyl complexes **6a**,**c** resulted in loss of the entire carbamoyl ligand, as monitored by IR and NMR. The formation of [(TTP)Ir(PMe_2Ph)]BF_4 (**9**) was observed by ^{1}H NMR in each case (eq 7). The appearance of **9** was manifested



6a: R = Bn,
6c: R = *i*-Pr

by a *β*-pyrrole proton signal at 8.83 ppm (in C_6D_6) and the upfield shift of the methyl resonance of the phosphine ligand from −2.66 ppm in the carbamoyl complex **6a** to −3.23 ppm in **9**. Moreover, the *ortho* and *meta* aryl proton signals of the phosphine ligand (in C_6D_6) were shifted upfield from 4.07 (2H) and 6.34 (2H) ppm in **6a** to 3.57 (2H) and 6.13 (2H) ppm in **9**, respectively. Temperature was an important factor in the protonolysis of the $P(OEt)_3$-coordinated carbamoyl complex **5a**. When a C_6D_6 solution of **5a** was treated with 2 equiv of HBF_4·Et_2O, at 23 °C, the formation of [(TTP)IrP-$(OEt)_3$]BF_4 (**10**) was accompanied by two other unidentified porphyrin products (5.5% and 11.5%), neither of which contained a CO ligand, as revealed by IR analysis. However, when the same reaction was carried out in toluene at 0 °C, complex **10** was formed as the only porphyrin product (eq 8).

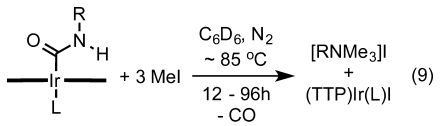


5a

The failure of the phosphine-coordinated complexes **6a**,**c** to form the cationic carbonyl complex [(TTP)Ir(PMe_2Ph)(CO)]-BF_4 is presumably due to the trans influence of the PMe_2Ph ligand. In an analogous case, the trans effect of PPh_3 was proposed as a reason for the failure to isolate phosphine-coordinated ruthenium(II) tetraarylporphyrinato carbonyl complexes of the form $(PR_3)Ru^{II}(CO)(DPP)$, which were only observed in solution by IR spectroscopy.[35] Similarly, the *π* acidity of $P(OEt)_3$[24] may have contributed to the dissociation of the CO ligand (eq 8).

It is not clear whether complexes **9** and **10** are pentacoordinate with a noncoordinating counteranion or whether the BF_4^- is coordinating to the iridium metal center through a fluoride atom. Examples of metal ligation by weakly coordinating ligands such as BF_4^-, SbF_6^-, and PF_6^- have been studied by variable-temperature solution NMR experiments.[36,37] A bound BF_4 anion was established in *mer*-(*cis*-PMe_3)(*trans*-NO)$(CO)_3W(\mu$-F)BF_3 through a ^{31}P NMR doublet at 192 K, as a result of ^{31}P−^{19}F coupling. When a CD_2Cl_2 solution of *mer*-(*cis*-PMe_3)(*trans*-NO)$(CO)_3W(\mu$-F)BF_3 was warmed to 262 K, the doublet ^{31}P NMR signal became a pentet, due to exchange of the four fluorine atoms of the BF_4^- into the bridging position.[36] However, solution ^{31}P NMR spectra of [(TTP)Ir(PMe_2Ph)]BF_4 (**9**) acquired in CD_2Cl_2 at 223, 200, and 190 K revealed only a ^{31}P NMR singlet peak at −39.61 ppm. This suggests that the BF_4^- anion is not coordinated to the metal center in complex **9** or is rapidly dissociating on the NMR time scale.

Reactions with Methyl Iodide. When a C_6D_6 solution of a carbamoyl complex (**2a**−**d**, **4a**, **5b**, or **6c**) was heated to ∼85 °C with 3−6 equiv of MeI for 12−96 h, the iodo complex (TTP)Ir(L)I was produced as the main porphyrin product with purities ranging from 88 to 94% (eq 9), as identified by ^{1}H



2a: L = RNH_2, R = Bn; **11a**: L = $BnNH_2$,
2b: L = RNH_2, R = *n*-Bu; **11b**: L = *n*-$BuNH_2$,
2c: L = RNH_2, R = *i*-Pr; **11c**: L = *i*-$PrNH_2$,
2d; L = RNH_2, R = *t*-Bu; **11d**: L = *t*-$BuNH_2$,
4a: L = 1-MeIm; R = Bn; **12**: L = 1-MeIm,
5b: L = $P(OEt)_3$; R = *n*-Bu; **13**: L = $P(OEt)_3$,
6c: L = PMe_2Ph; R = *i*-Pr **14**: L = PMe_2Ph

NMR. For example, the *β*-pyrrole signal of the *tert*-butylamine-coordinated carbamoyl complex **2d** at 8.88 ppm was replaced by a new resonance at 8.94 ppm, upon formation of the iodo complex (TTP)Ir(NH_2Bu^t)I (**11d**). In addition, the complete loss of the proton resonances for the *tert*-butylcarbamoyl ligand was observed. Of the amine carbamoyl complexes (**2a**−**d**), the *n*-butyl analogue (**2b**) reacted with MeI the fastest (12 h), an indication that a less sterically bulky carbamoyl substituent increases the reaction rate.

In the reactions of **2a**,**b** and **6c** with MeI, ammonium iodide coproducts were detected in the precipitate from the reaction mixtures. For example, the only ammonium salt produced from the reaction of (TTP)Ir(PMe_2Ph)[C(O)NH^iPr] (**6c**) with methyl iodide was identified as [*i*-$PrNMe_3$]I. This characterization was accomplished by comparing the ^{1}H NMR spectrum (in D_2O) and ^{13}C NMR spectrum (in $CDCl_3$) of the precipitate from the reaction mixture with that of an authentic sample of [*i*-$PrNMe_3$]I (see Figures S69 and S70, Supporting Information), prepared by treating (*i*-Pr)NMe_2 with a 2-fold excess of methyl iodide at 23 °C. Similarly, [*n*-$BuNMe_3$]I was the only ammonium salt produced from the treatment of (TTP)Ir($NH_2{}^nBu$)[C(O)NH^nBu] (**2b**) with MeI. In the reaction of (TTP)Ir(NH_2Bn)[C(O)NHBn] (**2a**) with 2 equiv of MeI, three ammonium salts were identified: [$BnNMe_3$]I (66%), [$BnNH_3$]I (25%), and [$Me(Bn)NH_2$]I (9%). One-bond ^{13}C−^{14}N coupling was observed for the N−Me carbon atoms in the ^{13}C NMR spectra of [$BnNMe_3$]I, [*n*-$BuNMe_3$]I, and [*i*-$PrNMe_3$]I. Similar coupling in the ^{13}C NMR spectra of quaternary ammonium halide salts was reported earlier.[38,39] Increasing the scale of reaction 9, up to 3-fold, failed to provide cleanly isolable iodo products. However, complexes **13** and **14** were conveniently synthesized by an independent method (vide infra). Although the formation of the (TTP)Ir-(L)I complexes could proceed via a transient [(TTP)Ir(L)-CO]$^+$ intermediate, treatment of a C_6D_6 solution of the cationic

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iridium carbonyl complex $[(TTP)Ir(NH_2Bn)(CO)]BF_4$ (**7a**) with $[Bu_4N]I$, for 3.5 h under reflux conditions resulted in a mixture that contained 63% $(TTP)Ir(NH_2Bn)I$ (**11a**), 36% $(TTP)Ir(CO)I$,[33] and 1% $(TTP)Ir(NH_2Bn)[C(O)NHBn]$ (**2a**), as revealed by ^1H NMR, rather than pure **11a**.

Reactions of $[(TTP)Ir(L)]BF_4$ and $[(TTP)Ir(L)CO]BF_4$ with Other Ligands. *Reactions with [Bu₄N]I.* Treatment of a CH_2Cl_2 solution of $[(TTP)Ir(PMe_2Ph)]BF_4$ (**9**) with ~2 equiv of $[Bu_4N]I$ at 23 °C for 8 min yielded the iodo complex **14** in 69% isolated yield (eq 10). The ^1H NMR spectrum (in C_6D_6)

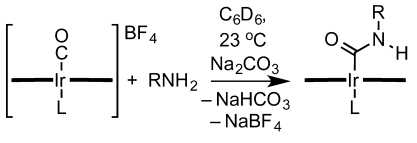
$$[Bu_4N]I + [(TTP)Ir(L)]BF_4 \xrightarrow[23\ ^oC]{C_6D_6 \text{ or } CH_2Cl_2} [Bu_4N]BF_4 + (TTP)Ir(L)I \quad (10)$$

9: L = PMe_2Ph, **10**: L = $P(OEt)_3$ — **14**: L = PMe_2Ph, **13**: L = $P(OEt)_3$,

of $(TTP)Ir(PMe_2Ph)I$ (**14**) exhibited a β-pyrrole proton resonance at 8.84 ppm and a doublet peak at −3.06 ppm for the methyl protons of the coordinated PMe_2Ph. These spectral properties matched those for the product of the reaction of MeI with $(TTP)Ir(PMe_2Ph)[C(O)NHPr^i]$ (**6c**) (eq 9). In addition, the ^{31}P NMR signal for $(TTP)Ir(PMe_2Ph)I$ (**14**) appeared at −43.55 ppm, which is different from the ^{31}P NMR signal (−41.28 ppm) for $[(TTP)Ir(PMe_2Ph)]BF_4$ (**9**). Similarly, a 2.2 mg scale synthesis of the $P(OEt)_3$ analogue (**13**) was carried out by treating a C_6D_6 solution of $[(TTP)Ir(P(OEt)_3)]BF_4$ (**10**) with ~3 equiv of $[Bu_4N]I$ (eq 10). The formation of $(TTP)Ir[P(OEt)_3]I$ (**13**) (43.5% isolated yield) was observed by ^1H NMR, as evidenced by the shifts of the CH_3 and CH_2 ^1H NMR signals (in C_6D_6) from −0.53 and 0.55 ppm to −0.38 and 0.70 ppm, respectively, in going from reactant **10** to product **13**. The ^{31}P NMR signal of the reactant **10** at 35.16 ppm was also replaced by a signal at −0.01 ppm upon formation of the product **13**. An independent synthesis was carried out by treating a benzene solution of $[(TTP)Ir(P(OEt)_3)(NH_2Bn)]BF_4$ (**15**) with 5 equiv of $[Bu_4N]I$, resulting in a 49% isolated yield of $(TTP)Ir[P(OEt)_3]I$ (**13**).

Reactions of $[(TTP)Ir(L)CO]BF_4$ and $[(TTP)Ir(L)]BF_4$ with Primary Amines. The cationic CO complexes could be used in alternative syntheses of carbamoyl compounds. When C_6D_6 solutions of each of the cationic CO complexes **7a** and **8** were treated with 1 equiv of $BnNH_2$, in the presence of Na_2CO_3, the carbamoyl complexes **2a** and **4a** were formed quantitatively (Scheme 5).

Scheme 5. Reactions of $[(TTP)Ir(L)CO]BF_4$ (L = $BnNH_2$ (7a), 1-MeIm (8)) with Primary Amines RNH_2



7a: L = $BnNH_2$, **8**: L = 1-MeIm — **2a**: L = $BnNH_2$, R = Bn; **4a**: L = 1-MeIm, R = Bn

An amine Ir phosphine complex, $[(TTP)Ir(PMe_2Ph)(NH_2Bn)]BF_4$ (**16**), was prepared by treatment of a C_6H_6 solution of phosphine complex **9** with $BnNH_2$. After the reaction mixture was stirred at 23 °C for 30 min, complex **16** was isolated in 90% yield (eq 11). The ^{31}P NMR signal for $[(TTP)Ir(PMe_2Ph)(NH_2Bn)]BF_4$ (**16**), which appeared at −41.49 ppm, was very similar to that of the starting complex $[(TTP)Ir(PMe_2Ph)]BF_4$ (**9**) (−41.28 ppm). However, the

$$BnNH_2 + [(TTP)Ir(PMe_2Ph)]BF_4 \xrightarrow[23\ ^oC]{C_6H_6} [(TTP)Ir(NH_2Bn)(PMe_2Ph)]BF_4 \quad (11)$$

9 — **16**

formulation of **16** was supported by the presence of a peak at m/z 1106.3899, corresponding to $[\mathbf{16} - BF_4]^+$, in the high-resolution mass spectrum. Moreover, the coordination of $BnNH_2$ in complex **16** was established by ^1H NMR spectroscopy, with the appearance of upfield multiplet signals at −3.42 (2H) and −1.72 (2H) ppm, assigned to the NH_2 and CH_2 protons, respectively. In addition, a doublet at −3.17 ppm (6H, CH_3, $^2J_{P-H}$ = 12 Hz) was assigned to the methyl protons of the PMe_2Ph ligand.

Reactions of $[(TTP)Ir(PMe_2Ph)]BF_4$ (9) with PMe_2Ph. The addition of 1.1 equiv of PMe_2Ph to a $CDCl_3$ solution of the monophosphine complex $[(TTP)Ir(PMe_2Ph)]BF_4$ (**9**) resulted in a rapid reaction. The most notable change in the ^1H NMR spectrum, observed 10 min after initial addition of PMe_2Ph, was the replacement of the 6-H methyl doublet of the monophosphine ligand at −2.75 ppm with a 12-H virtual triplet at −2.77 ppm assigned to the bis-phosphines in *trans*-$[(TTP)Ir(PMe_2Ph)_2]BF_4$ (**17**). This virtual coupling is diagnostic of a *trans* arrangement of methylphosphines.[40−44] The apparent J_{P-H} value measured for **17** was 4.0 Hz and is similar to the values for the coupling constants in *trans*-$PdI_2(PMe_2Ph)_2$ (4.4 Hz), and for the *trans*-PMe_2Ph ligands in $IrCl_3(PMe_2Ph)_3$ (4.5 Hz).[45] Analogous rhodium and ruthenium porphyrinato bis-phosphine complexes have also been reported, including $[(DPAP)_2Rh^{III}(TPP)]I$ and $(DPPA)_2Ru^{II}(DPP)$, where DPAP is diphenyl(phenylethynyl)phosphine and DPPA is bis-(diphenylphosphino)acetylene.[23,35] The composition of complex **17** was confirmed further by the m/z peak at 1137.3752 for $[\mathbf{17} - BF_4]^+$ by HRMS. The ^{31}P NMR signal (in C_6D_6) for **17** (−32.35 ppm) was also markedly different from that for **9** (−41.28 ppm).

The molecular structure of **17** was confirmed by single-crystal X-ray diffraction (Figure 2). The two axial PMe_2Ph ligands are collinear with a P(1)−Ir−P(2) bond angle of 179.20(11)°. The iridium−phosphorus bond distances of Ir−P(1) = 2.354(3) Å and Ir−P(2) = 2.348(3) Å are comparable to the Ir−P distances reported for nonporphyrinic mono-, bis-, tris-, and tetrakis-phosphino iridium complexes (2.2044−2.3927 Å).[46−51] However, the iridium−phosphorus bonds in

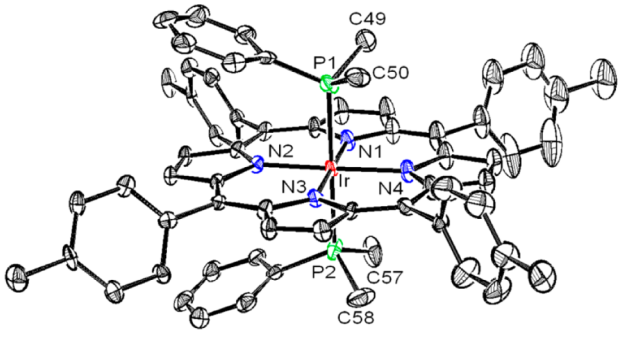


Figure 2. Molecular structure of *trans*-$[(TTP)Ir(PMe_2Ph)_2]BF_4$ (**17**) with 30% probability ellipsoids. Selected bond distances (Å) and angles (deg): Ir−P(1) = 2.354(3), Ir−P(2) = 2.348(3); P(1)−C(49) = 1.783(13), P(1)−C(50) = 1.800(12), P(1)−C(51) = 1.794(12), P(2)−C(57) = 1.822(13), P(2)−C(58) = 1.805(13), P(2)−C(59) = 1.808(12); P(1)−Ir−P(2) = 179.20(11).

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complex **17** are both shorter than the Ir−P bond distance (2.537 Å) reported for the porphyrinic iridium phosphine complex (OEP)Ir(C_3H_7)(PPh_3).[52] This unusually long Ir−P bond length was attributed to the trans influence of the alkyl ligand and to steric repulsion between the bulky PPh_3 ligand and the octaethylporphyrin ligand.

■ CONCLUSIONS

The reaction (Scheme 2) of (TTP)Ir(CO)Cl (**1**) with primary amines readily generates the amine-coordinated carbamoyl complexes (TTP)Ir(NH_2R)[C(O)NHR] (**2a−d**) under ambient conditions. A possible first step in the mechanism of this reaction is amine attack on the CO ligand to give a carbamoyl group (eq 1); such a reaction is expected, on the basis of the high CO stretching frequency (2056 cm^{-1}) in **1**. Also supporting this step is the known reaction[33] of **1** with O−NMe_3 to give (TTP)Ir(Cl)(NMe_3) and CO_2, which presumably involves nucleophilic attack of O−NMe_3 on the CO ligand in **1**. This is a reaction typical of O−NMe_3 with CO ligands in a variety of metal carbonyl complexes.[53−55] Following carbamoyl ligand formation in the first step, the Cl^- ligand could be rapidly substituted by an amine to give the (TTP)Ir(NH_2R)-[C(O)NHR] product. Although this mechanism for the reactions of **1** with amines is entirely plausible, it is not possible to exclude an alternate pathway in which the first step involves amine substitution of the Cl^- ligand to give the cationic (TTP)Ir(NH_2R)$(CO)^+$, which would be expected to react rapidly with amine to give the final carbamoyl product **2**.

The amine ligand in **2** is labile on the NMR time scale at 23 °C, allowing substitution with a variety of ligands. This has led to the preparation of phosphine-, phosphite-, 1-MeIm-, and ABCO-coordinated (TTP)Ir(L)[C(O)NHR] carbamoyl complexes. Equilibrium studies of ligand displacement reactions of these complexes show that the binding affinities of the L ligands decrease in the order PMe_2Ph > $P(OEt)_3$ > 1-MeIm > ABCO > $BnNH_2$ ≫ Et_3N, PCy_3. Reactions of these carbamoyl complexes (TTP)Ir(L)[C(O)NHR] with HBF_4 either at room temperature (for L = RNH_2, 1-MeIm (Scheme 4) and L = PMe_2Ph (eq 7)) or at 0 °C (for L = $P(OEt)_3$) (eq 8) give products that depend on the nature of the axial L ligand. When this ligand is an amine (**2a,b**, **4a**), the reactions produce cationic Ir carbonyl complexes of the form [(TTP)Ir(L)-(CO)]BF_4 (**7a,b**, **8**). With complexes containing phosphite (**5a**) or phosphine (**6a,c**) ligands, treatment with HBF_4 results in complete loss of the carbamoyl ligand and production of complexes **9** and **10** ([(TTP)Ir(L)]BF_4, L = PMe_2Ph, $P(OEt)_3$), respectively. Reactions of MeI with all of the carbamoyl complexes require a higher temperature (85 °C) and afford the neutral iodo complexes (TTP)Ir(L)I (**11a−d**, **12−14**), regardless of the L ligand. All of these results demonstrate that carbamoyl complexes of Ir(III) porphyrin complexes are easily formed and show a broad range of reactivity.

■ EXPERIMENTAL SECTION

All manipulations were performed under a dry nitrogen atmosphere in a glovebag or glovebox or using Schlenk techniques, except where otherwise stated. Ir(TTP)Cl(CO) (**1**) was prepared according to a literature procedure.[56] Benzylamine and isopropylamine were distilled from CaH_2 and stored over 4 Å molecular sieves prior to use. Dimethylphenylphosphine was stored in an inert-atmosphere glovebox. Tetrahydrofuran and toluene were deoxygenated and dried by passage through columns of reduced copper and alumina, respectively. All other chemicals were reagent grade and were used without further purification. NMR spectra were collected using Varian VXR 300 MHz, Varian VXR 400 MHz, Bruker DRX 400 MHz, Varian MR 400 MHz, and Bruker AVIII 600 MHz spectrometers. IR spectra were acquired in the solid state on NaCl plates, using a Bruker IFS66 V FTIR instrument. ^{1}H NMR peak positions were referenced against residual proton resonances of deuterated solvents (δ (ppm): $CDCl_3$, 7.26; C_6D_6, 7.15; D_2O, 4.79), while ^{13}C NMR peaks were referenced to $CDCl_3$ (δ 77.36 ppm). When multiple porphyrin products were obtained in NMR-tube reactions, the purity of the major product was determined by the ratio of its β-pyrrole proton area to that of the total β-pyrrole integration. A solution of PPh_3 in C_6D_6 (^{31}P NMR: δ −5.53 ppm) was used as an external standard during ^{31}P NMR data collection.

(TTP)Ir(NH_2Bn)[C(O)NHBn] (2a). In a nitrogen-filled glovebag, a 100 mL round-bottomed flask was charged with (TTP)Ir(CO)(Cl) (**1**; 91 mg, 0.099 mmol), Na_2CO_3 (682 mg, 6.43 mmol), a stir bar, and 30 mL of THF. Benzylamine (610 μL, 5.6 mmol, 57 equiv) was added by syringe into the flask, the flask was capped with a rubber septum, and the mixture was stirred under N_2 for 6 h. The reaction mixture was then opened to air, and solids were removed via filtration. Solvent and excess benzylamine were removed under reduced pressure. The residue was washed with 60 mL of hexanes, and **2a** was obtained. Yield: 87% (95 mg, 0.086 mmol). Anal. Calcd for $C_{63}H_{53}IrN_6O\cdot 0.7H_2O$: C, 67.87; H, 4.91; N, 7.54. Found: C, 67.90; H, 4.74; N, 7.37. ^{1}H NMR (299 K, 300 MHz, C_6D_6): δ −5.14 (br, 2H, NH_2), −1.78 (br, 2H, amine CH_2), −1.34 (t, 1H, J = 6 Hz, carbamoyl N*H*), 0.41 (s, 1.40H, H_2O), 2.00 (d, 2H, J = 6 Hz, carbamoyl CH_2), 2.38 (s, 12H, -C_6H_4-CH_3), 4.52 (br, 2H, amine *o-H*), 5.27 (d, 2H, J = 6 Hz, carbamoyl *o-H*), 6.22 (br, 2H, amine *m-H*), 6.39 (br, 1H, amine *p-H*), 6.79 (m, 3H, carbamoyl *m,p-H*), 7.21 (dd, 4H, J = 6 Hz, 3 Hz, -C_6H_4-CH_3), 7.28 (dd, 4H, J = 6 Hz, 3 Hz, -C_6H_4-CH_3), 7.94 (dd, 4H, J = 6 Hz, 3 Hz, -C_6H_4-CH_3), 8.15 (dd, 4H, J = 9 Hz, 3 Hz, -C_6H_4-CH_3), 8.91 (s, 8H, pyrrole-*H*). ^{1}H NMR (273 K, 400 MHz, $CDCl_3$): δ −5.01 (t, 2H, J = 8 Hz, NH_2), −2.00 (t, 2H, J = 8 Hz, amine CH_2), −1.83 (t, 1H, J = 8 Hz, carbamoyl N*H*), 1.76 (d, 2H, J = 8 Hz, carbamoyl CH_2), 2.68 (s, 12H, −$C_6H_4CH_3$), 5.03 (d, 2H, 8 Hz amine *o-H*), 5.17 (d, 2H, J = 8 Hz, carbamoyl *o-H*), 6.52 (t, 2H, J = 8 Hz, amine *m-H*), 6.65 (t, 1H, J = 8 Hz, amine *p-H*), 6.83 (t, 2 H, J = 8 Hz, carbamoyl *m-H*), 6.93 (t, 1 H, J = 8 Hz, carbamoyl *p-H*), 7.49 (dd, 8H, J = 16 Hz, 8 Hz, −$C_6H_4CH_3$), 7.85 (dd, 4H, J = 8 Hz, 4 Hz, -C_6H_4-CH_3), 7.99 (dd, 4H, J = 8 Hz, 4 Hz, -C_6H_4-CH_3), 8.62 (s, 8H, pyrrole-*H*). ^{13}C NMR (151 MHz, $CDCl_3$): δ 21.87, 40.36, 41.64 (low intensity peak assigned by 2D HSQC), 122.91, 125.89, 126.03, 127.17, 127.47, 127.82, 127.84, 128.30, 128.60, 128.92, 131.83, 133.82, 134.68, 137.40, 139.19, 139.56, 142.80, 143.64 (CO Carbon). UV−vis (C_6H_6): λ_{max} (log ε) 414 (5.24), 521 nm (4.21). HRMS (+ESI): calcd for $[MH]^+$ $(C_{63}H_{54}IrN_6O)^+$ m/z 1103.3988; found m/z 1103.3921.

(TTP)Ir(ABCO)[C(O)NHBn] (3a). In a nitrogen-filled glovebag, a 20 mL scintillation vial was charged with complex **2a** (71 mg, 0.064 mmol), quinuclidine (ABCO; 112 mg, 1.0 mmol, 15.6 equiv), and 10 mL of C_6H_6. After the mixture was stirred at 23 °C for 20 min, volatile materials were removed under reduced pressure and the residues were washed with 50 mL of hexanes to remove free benzylamine. Additional treatment under reduced pressure at 85 °C for 2.5 days was needed to remove excess quinuclidine, affording complex **3a**. Yield: 52% (37 mg, 0.034 mmol). ^{1}H NMR (400 MHz, C_6D_6): δ −2.73 (br t, 6H, J = 8 Hz, ABCO NCH_2), −1.56 (t, 1H, J = 8 Hz, carbamoyl N*H*), −0.8 (br, 6H, ABCO CCH_2), −0.27 (br, 1H, ABCO C*H*), 1.90 (d, 2H, J = 8 Hz, carbamoyl CH_2), 2.37 (s, 12H, −$C_6H_4CH_3$), 5.22 (d, 2H, J = 8 Hz, carbamoyl *o-H*), 6.77 (m, 3H, carbamoyl *m/p-H*), 7.20 (d, 4H, J = 8 Hz, −$C_6H_4CH_3$), 7.32 (d, 4H, J = 8 Hz, −$C_6H_4CH_3$), 7.92 (dd, 4H, J = 8 Hz, 4 Hz, −$C_6H_4CH_3$), 8.20 (dd, 4H, J = 8 Hz, 4 Hz, −$C_6H_4CH_3$), 8.87 (s, 8H, pyrrole *H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 17.94, 21.87, 24.20, 40.47, 43.73, 123.26, 125.89, 126.00, 127.36, 127.80, 127.83, 131.79, 134.00, 134.41, 137.37, 137.68, 139.26, 139.36, 142.78. UV−vis (C_6H_6): λ_{max} (log ε) 415 (5.19), 519 nm (4.19). HRMS (+ESI): calcd for $[MH]^+$ $(C_{63}H_{58}IrN_6O)^+$ m/z 1107.4301; found m/z 1107.4299.

(TTP)Ir(1-MeIm)[C(O)NHBn] (4a). In air, a 20 mL scintillation vial was charged with complex **2a** (85 mg, 0.077 mmol), 1-

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methylimidazole (40 μL, 0.50 mmol, 6.5 equiv), and 15 mL of THF. After the solution was stirred at 23 °C for 1 h, volatile materials were removed under reduced pressure. Recrystallization was then done by adding hexanes to a concentrated THF solution of the dried product, to afford complex **4a**. Yield: 89% (74 mg, 0.069 mmol). Anal. Calcd for $C_{60}H_{50}IrN_7O{\cdot}1.25H_2O$: C, 65.52; H, 4.81; N, 8.91. Found: C, 65.36; H, 4.35; N, 8.63. ^{1}H NMR (300 MHz, C_6D_6): δ −1.13 (t, 1H, *J* = 6 Hz, carbamoyl N*H*), 0.40 (s, 1.40H, H_2O peak), 0.43 (s, 3H; 1-MeIm *Me*), 1.63 (s, 1H, 1-MeIm aryl *H*), 1.74 (s, 1H, 1-MeIm aryl *H*), 2.07 (d, 2H, *J* = 6 Hz, carbamoyl CH_2), 2.35 (s, 12H, $-C_6H_4CH_3$), 3.70 (s, 1H, 1-MeIm aryl *H*), 5.32 (d, 2H, *J* = 3 Hz, carbamoyl *o-H*), 6.79 (m, 3H, carbamoyl *m/p-H*), 7.22 (d, 4H, *J* = 9 Hz, $-C_6H_4CH_3$), 7.25 (d, 4H, *J* = 9 Hz, $-C_6H_4CH_3$), 7.98 (d, 4H, *J* = 9 Hz, $-C_6H_4CH_3$), 8.13 (d, 4H, *J* = 9 Hz, $-C_6H_4CH_3$), 8.91 (s, 8H, pyrrole-*H*). ^{13}C NMR (151 MHz, $CDCl_3$): δ 21.76, 32.93, 39.99, 117.76, 122.60, 122.98, 125.63, 125.92, 127.15, 127.60, 127.67, 131.35, 131.62, 133.74, 134.55, 137.06, 139.39, 139.78, 142.48, 146.83 (CO carbon). UV−vis (C_6H_6): λ_{max} (log ε) 416 (5.23), 523 nm (4.22). HRMS (+ESI): calcd for $[MH]^+$ $(C_{60}H_{51}IrN_7O)^+$ *m/z* 1078.3784; found *m/z* 1078.3780.

(TTP)IrP(OEt)$_3$[C(O)NHBn] (5a). In air, a 20 mL scintillation vial was charged with complex **2a** (85 mg, 0.077 mmol), triethyl phosphite (70 μL, 0.40 mmol, 5.2 equiv), and 15 mL of THF. After the solution was stirred at 23 °C for 40 min, volatile materials were removed under reduced pressure. After washing with hexanes and further drying under reduced pressure, **5a** was obtained. Yield: 46% (42 mg, 0.036 mmol). ^{1}H NMR (400 MHz, C_6D_6): δ −1.48 (t, 1H, *J* = 8 Hz, carbamoyl N*H*), −0.18 (t, 9H, *J* = 8 Hz, PCH_2Me), 0.85 (p, 6H, *J* = 8 Hz, PCH_2), 1.93 (d, 2H, *J* = 8 Hz, carbamoyl CH_2), 2.38 (s, 12H, $-C_6H_4$-CH_3), 5.18 (d, 2H, *J* = 8 Hz, carbamoyl *o-H*), 6.77 (m, 3H, carbamoyl *m,p-H*), 7.21 (d, 4H, *J* = 8 Hz, $-C_6H_4CH_3$), 7.33 (d, 4H, *J* = 8 Hz, $-C_6H_4CH_3$), 7.96 (dd, 4H, *J* = 8 Hz, 4 Hz, $-C_6H_4CH_3$), 8.20 (dd, 4H, *J* = 8 Hz, 4 Hz, $-C_6H_4CH_3$), 8.93 (s, 8H, pyrrole *H*). ^{13}C NMR (151 MHz, $CDCl_3$): δ 15.50 (d, *J* = 4.5 Hz), 21.77, 39.32 (d, *J* = 4.5 Hz), 56.66 (d, *J* = 4.5 Hz), 122.25, 125.64, 125.94, 127.17, 127.59, 127.65, 131.36, 133.89, 134.60, 137.07, 139.56, 139.61, 142.28, 162.72 ($^2J_{P-C}$ = 270.3 Hz, CO Carbon). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ 72.06 ppm. UV−vis (C_6H_6): λ_{max} (log ε) 396 (5.07), 429 (4.75), 546 (3.96), 593 nm (3.80). HRMS (+ESI): calcd for $[MH]^+$ $(C_{62}H_{60}IrN_5O_4P)^+$ *m/z* 1162.4012; found *m/z* 1162.4009.

(TTP)Ir(PMe$_2$Ph)[C(O)NHBn] (6a). In a glovebox, a 20 mL scintillation vial was charged with complex **2a** (101 mg, 0.091 mmol), dimethylphenylphosphine (70 μL, 0.49 mmol, 5.4 equiv), and 15 mL of THF. After the solution was stirred at 23 °C for 30 min, volatile materials were removed under reduced pressure. After washing with hexanes and further drying under reduced pressure, **6a** was obtained. Yield: 45% (46 mg, 0.041 mmol). Anal. Calcd for $C_{64}H_{55}IrN_5OP{\cdot}2.5H_2O$: C, 65.23; H, 5.13; N, 5.94. Found: C, 65.05; H, 4.82; N, 5.78. ^{1}H NMR (400 MHz, C_6D_6): δ −2.66 (d, 6H, *J* = 8 Hz, P*Me*), −1.38 (t, 1H, *J* = 8 Hz, carbamoyl N*H*), 0.44 (s, 5H, H_2O), 1.97 (d, 2H, *J* = 8 Hz, carbamoyl CH_2), 2.40 (s, 12H, $-C_6H_4CH_3$), 4.07 (t, 2H, *J* = 8 Hz, *o*-PPh), 5.20 (d, 2H, *J* = 8 Hz, carbamoyl *o-H*), 6.34 (t, 2H, *J* = 8 Hz, *m*-PPh), 6.58 (t, 1H, *J* = 8 Hz, *p*-PPh), 6.76 (m, 3H, carbamoyl *m/p-H*), 7.20 (d, 4H, *J* = 8 Hz, $-C_6H_4CH_3$), 7.37 (d, 4H, *J* = 8 Hz, $-C_6H_4CH_3$), 7.92 (d, 4H, *J* = 8 Hz, $-C_6H_4CH_3$), 8.02 (d, 4H, *J* = 8 Hz, $-C_6H_4CH_3$), 8.80 (s, 8H, pyrrole *H*). ^{13}C NMR (151 MHz, $CDCl_3$): δ 5.34 (d, *J* = 18.1 Hz), 21.87, 39.62, 122.37, 125.75, 126.05, 126.41 (d, *J* = 10.6 Hz), 127.18 (d, *J* = 7.6 Hz), 127.24, 127.70, 127.76, 127.81, 130.94 (d, *J* = 30.2 Hz), 131.60, 133.97, 134.67, 137.26, 139.37, 139.80, 142.19, 163.87 (d, $^2J_{P-C}$ = 184.2 Hz, CO carbon). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ −41.23 ppm. UV−vis (C_6H_6): λ_{max} (log ε) 398 (5.09), 419 (4.80), 440 (4.62), 548 (3.86), 601 nm (3.81). HRMS (+APCI): calcd for $[MH]^+$ $(C_{64}H_{56}IrN_5OP)^+$ *m/z* 1134.3852; found *m/z* 1134.3852.

[(TTP)Ir(CO)(NH$_2$Bn)]BF$_4$ (7a). In a nitrogen-filled glovebag, a 20 mL scintillation vial was charged with complex **2a** (51 mg, 0.047 mmol), 6 mL of C_6H_6, and $HBF_4{\cdot}Et_2O$ (11 μL, 0.092 mmol, 2 equiv). After the solution was stirred at 23 °C for 20 min, the reddish porphyrin product solution was separated, via vacuum filtration, from the insoluble precipitate. Thereafter, volatile materials were removed from the filtrate under reduced pressure. After recrystallization of the porphyrin product by adding excess hexanes to a concentrated benzene solution of the dried product, **7a** was obtained. Yield: 36% (18 mg, 0.017 mmol). Anal. Calcd for $C_{56}H_{45}BF_4IrN_5O$: C, 62.10; H, 4.19; N, 6.47. Found: C, 62.03; H, 4.10; N, 6.29. ^{1}H NMR (400 MHz, C_6D_6): δ −2.98 (br, 2H, amine NH_2), −1.89 (t, 2H, *J* = 8 Hz, amine CH_2), 2.41 (s, 12H, $-C_6H_4CH_3$), 4.76 (d, 2H, *J* = 8 Hz, amine *o-H*), 6.25 (t, 2H, *J* = 8 Hz, amine *m-H*), 6.39 (t, 1H, *J* = 8 Hz, amine *p-H*), 7.25 (d, 4H, *J* = 8 Hz, $-C_6H_4CH_3$), 7.34 (d, 4H, 8 Hz, $-C_6H_4CH_3$), 7.92 (d, 4H, *J* = 8 Hz,$-C_6H_4CH_3$), 8.37 (d, 4H, *J* = 8 Hz, $-C_6H_4CH_3$), 9.09 (s, 8H, pyrrole *H*). ^{13}C NMR (151 MHz, $CDCl_3$): δ 21.84, 40.52, 123.03, 125.77, 127.43, 127.80, 127.99, 128.40, 132.92, 133.08, 134.12, 134.98, 137.55, 138.48, 138.96 (CO Carbon), 141.63. IR (NaCl, cm^{-1}): ν(C≡O) 2078 (s). UV−vis (C_6H_6): λ_{max} (log ε) 420 (5.33), 529 (4.33), 564 nm (3.73). HRMS (+ESI): calcd for $[M - BF_4]^+$ $([C_{56}H_{45}IrN_5O]^+)$ *m/z* 996.3253; found *m/z* 996.3275.

[(TTP)Ir(CO)(1-MeIm)]BF$_4$ (8). This compound was prepared similarly to **7a**, using complex **4a** (33 mg, 0.031 mmol), 5 mL of C_6H_6, and $HBF_4{\cdot}Et_2O$ (7.4 μL, 0.062 mmol, 2 equiv). Recrystallization from CH_2Cl_2−hexanes afforded complex **8**. Yield: 58% (19 mg, 0.018 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.19 (s, 1H, Im *H*), 0.97 (s, 1H, Im *H*), 2.19 (s, 3H, Im*Me*), 2.73 (s, 12H, $-C_6H_4CH_3$), 4.96 (s, 1H, Im-*H*), 7.62 (m, 8H, $-C_6H_4CH_3$), 8.09 (m, 8H,$-C_6H_4CH_3$), 9.06 (s, 8H, pyrrole *H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.91, 34.13, 119.00, 120.33, 123.21, 128.13, 128.49, 129.95, 133.04, 134.38, 134.81, 137.42, 138.85, 139.65 (CO carbon), 141.52. IR (NaCl, cm^{-1}): ν(C≡O) 2079 (s). UV−vis (CH_2Cl_2): λ_{max} (log ε): 416 (5.61), 528 (4.39), 564 nm (3.75) . HRMS (+ESI): calcd for $[M - BF_4]^+$ $([C_{53}H_{42}IrN_6O]^+)$ *m/z* 971.3049; found *m/z* 971.3050.

[(TTP)Ir(PMe$_2$Ph)]BF$_4$ (9). In a nitrogen-filled glovebag, a 20 mL scintillation vial was charged with complex **6a** (35 mg, 0.030 mmol), 6 mL of C_6H_6, and $HBF_4{\cdot}Et_2O$ (14.5 μL, 0.12 mmol, 4 equiv). After it was stirred at 23 °C for 20 min, the reaction mixture was decanted, to separate it from the precipitates. Volatile materials were then removed from the mother liquor under reduced pressure. Recrystallization by adding excess hexanes to a concentrated benzene solution of the dried product afforded the product **9**. Yield: 81% (27 mg, 0.024 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ −2.75 (d, 6H, *J* = 12 Hz, P*Me*), 2.71 (s, 12H, $-C_6H_4CH_3$), 3.84 (m, 2H, *o*-PPh), 6.53 (t, 2H, *J* = 8 Hz, *m*-PPh), 6.96 (t, 1H, *J* = 8 Hz, *p*-PPh), 7.57 (t, 8H, *J* = 8 Hz, $-C_6H_4CH_3$), 7.91 (d, 4H, *J* = 8 Hz, $-C_6H_4CH_3$), 8.12 (d, 4H, *J* = 8 Hz, $-C_6H_4CH_3$), 8.78 (s, 8H, pyrrole *H*). ^{13}C NMR (151 MHz, $CDCl_3$): δ 5.05 (d, *J* = 45.3 Hz), 21.90, 123.41, 125.90 (d, *J* = 7.6 Hz), 127.58, 127.71 (d, *J* = 12.1 Hz), 128.45, 130.43, 132.44, 133.64, 135.03, 138.17, 138.26, 142.27. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ −41.28 ppm. UV−vis (CH_2Cl_2): λ_{max} (log ε) 414 (5.38), 520 (4.41), 551 nm (3.66). HRMS (+ESI): calcd for $[M - BF_4]^+$ $([C_{56}H_{47}IrN_4P]^+)$ *m/z* 999.3168; found *m/z* 999.3141.

[(TTP)IrP(OEt)$_3$]BF$_4$ (10). A nitrogen-purged 5 mL round-bottomed flask containing a 1 mL toluene solution of complex **5a** (2.7 mg, 0.0023 mmol) at 0 °C was charged with 0.8 μL of $HBF_4{\cdot}Et_2O$. While the solution was stirred at 0 °C for 3 min, the reaction mixture quickly changed from brown-black to bright red. After volatile materials were removed under reduced pressure, the residues were washed with hexane and further dried under reduced pressure to afford **10** (88%, 2.2 mg, 0.0020 mmol). ^{1}H NMR (400 MHz, C_6D_6): δ −0.53 (t, 9H, *J* = 8 Hz, PCH_2−*Me*), 0.55 (p, 6H, *J* = 8 Hz, PCH_2), 2.42 (s, 12H, $-C_6H_4CH_3$), 7.31 (d, 4H, 8 Hz, $-C_6H_4CH_3$), 7.36 (d, 4H, 8 Hz, $-C_6H_4CH_3$), 8.05 (d, 4H, *J* = 8 Hz, $-C_6H_4CH_3$), 8.30 (d, 4H, *J* = 8 Hz, $-C_6H_4CH_3$), 8.98 (s, 8H, pyrrole *H*). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ 35.16 ppm (s). HRMS (+ESI): calcd for $[M - BF_4]^+$ $([C_{54}H_{51}IrN_4O_3P]^+)$ *m/z* 1027.3328; found *m/z* 1027.3326.

(TTP)Ir(NH$_2$Bn)I (11a). In the glovebox, 0.65 mL of C_6D_6 was added to an NMR tube containing **2a** (6 mg, 0.0056 mmol). This was followed by the addition of 11 μL (0.011 mmol, 2 equiv) of a C_6D_6 stock solution containing 0.11 mM of MeI. The NMR tube was sealed with a rubber septum and heated to 85 °C for 72 h, while the reaction was monitored by ^{1}H NMR spectroscopy for the consumption of **2a**. The reaction mixture was filtered through Celite to remove insoluble precipitates. Removal of volatile components from the filtrate under reduced pressure yielded **11a** (61%, 3.8 mg, 0.0035 mmol, 92%

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purity). ^{1}H NMR (300 MHz, C_6D_6): δ −4.87 (t, 2H, J = 6 Hz, NH_2), −2.32 (t, 2H, J = 9 Hz, CH_2), 2.38 (s, 12H, −$C_6H_4CH_3$), 4.21 (d, 2H, J = 6 Hz, amine *o-H*), 6.05 (t, 2H, J = 6 Hz, amine *m-H*), 6.28 (t, 1H, J = 6 Hz, amine *p-H*), 7.20 (d, 4H, J = 9 Hz,−$C_6H_4CH_3$), 7.30 (d, 4H, J = 9 Hz, −$C_6H_4CH_3$), 8.02 (d, 4H, J = 9 Hz, −$C_6H_4CH_3$), 8.16 (d, 4H, J = 9 Hz, −$C_6H_4CH_3$), 8.96 (s, 8H, pyrrole *H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.89, 42.68, 122.95, 126.31, 127.48, 128.00, 128.11, 128.54, 132.32, 133.74, 134.37, 135.05, 137.62, 139.09, 142.89. UV−vis (C_6H_6): λ_{max} (log ε): 418 (5.42), 528 (4.27), 562nm (3.65). HRMS (+ESI): calcd for $[M + H]^+$ ($[C_{55}H_{46}IrN_5I]^+$) m/z 1096.2427; found m/z 1096.2448.

[BnNMe$_3$]I. ^{1}H NMR (400 MHz, D_2O): δ 3.08 (s, 9H, N-*Me*), 4.48 (s, 2H, CH_2), 7.53−7.59 (m, 5H, C_6H_5). ^{13}C NMR (101 MHz, $CDCl_3$): 53.29 (t, $^1J_{C-N}$ = 4 Hz), 69.31 (t, $^1J_{C-N}$ = 2 Hz), 127.42, 129.70, 131.37, 133.44. HRMS (+ESI): calcd for $[M - I]^+$ ($[C_{10}H_{16}N]^+$) m/z 150.1283; found m/z 150.1281.

(TTP)Ir(1-MeIm)I (12). In a glovebox, a 20 mL scintillation vial was charged with **4a** (27 mg, 0.025 mmol), 5 mL of C_6H_6, and MeI (3.4 μL, 0.055 mmol, 2.2 equiv). After the contents of the vial were refluxed at 80 °C for 36 h, the solution was vacuum-filtered through Celite on a fritted funnel. After removal of volatile components from the filtrate under reduced pressure, followed by recrystallization of the residue from C_6H_6−hexanes, **12** was obtained in 88% purity, as determined by ^{1}H NMR. Yield: 61% (16 mg, 0.015 mmol). ^{1}H NMR (400 MHz, C_6D_6): δ 0.16 (s, 3H, 1-MeIm *Me*), 1.14 (t, 1H, J = 4 Hz, 1-MeIm aryl *H*), 1.28 (t, 1H, J = 4 Hz, 1-MeIm aryl *H*), 2.35 (s, 12H, −$C_6H_4CH_3$), 3.39 (t, 1H, J = 4 Hz, 1-MeIm aryl *H*), 7.19 (dd, 4H, J = 8 Hz, 4 Hz, −$C_6H_4CH_3$), 7.27 (d, 4H, J = 8 Hz, 4 Hz, −$C_6H_4CH_3$), 8.06 (dd, 4H, J = 8 Hz, 4 Hz, −$C_6H_4CH_3$), 8.17 (dd, 4H, J = 8 Hz, 4 Hz,−$C_6H_4CH_3$), 8.97 (s, 8H, pyrrole *H*). ^{13}C NMR (151 MHz, $CDCl_3$): δ 21.88, 33.67, 117.61, 122.25, 122.72, 127.25, 127.86, 130.45, 131.86, 133.76, 135.02, 137.36, 139.44, 142.62. UV−vis (C_6H_6): λ_{max} (log ε) 420 (5.38), 528 (4.27), 563 nm (3.71). HRMS (+ESI): calcd for $[M]^{\cdot+}$ ($[C_{52}H_{42}IrN_6I]^+$) m/z 1070.2145; found m/z 1070.2162.

(TTP)Ir[P(OEt)$_3$]I (13). In air, a 20 mL scintillation vial was charged with 28 mg of crude (~60% pure) compound **15** (0.013 mmol), 6 mL of benzene, and 24.5 mg (0.065 mmol, 5 equiv) of $[Bu_4N]I$. The mixture was then stirred at 23 °C for 30 h. The *n*-butylammonium salts were extracted from the organic layer, using water. After the volatile components were removed under reduced pressure, followed by a hexane wash, complex **13** was obtained. Yield: 49% (8 mg, 0.0065 mmol). ^{1}H NMR (400 MHz, C_6D_6): δ −0.38 (t, 9H, J = 8 Hz, PCH_2Me), 0.70 (p, 6H, J = 8 Hz, PCH_2), 2.38 (s, 12H, −$C_6H_4CH_3$), 7.19 (d, 4H, J = 8 Hz, −$C_6H_4CH_3$), 7.36 (d, 4H, J = 8 Hz, −$C_6H_4CH_3$), 8.03 (dd, 4H, J = 8 Hz, 4 Hz,−$C_6H_4CH_3$), 8.19 (dd, 4H, J = 8 Hz, 4 Hz, −$C_6H_4CH_3$), 8.99 (s, 8H, pyrrole *H*). ^{13}C NMR (151 MHz, $CDCl_3$): δ 15.22 (d, J = 6.0 Hz), 21.87, 59.39 (d, J = 7.6 Hz), 122.80, 127.29, 127.96, 131.67, 133.75, 135.17, 137.45, 139.56, 142.29. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ −0.01 ppm. UV−vis (CH_2Cl_2): λ_{max} nm (log ε) 370 (4.55), 433 (5.17), 539 (4.20), 576 (3.89). HRMS (+ESI): calcd for $[M - I]^+$ ($[C_{54}H_{51}IrN_4O_3P]^+$) m/z 1027.3328; found m/z 1027.3302.

(TTP)Ir(PMe$_2$Ph)I (14). In air, a 20 mL scintillation vial was charged with complex **9** (34 mg, 0.031 mmol), $[Bu_4N]I$ (23.1 mg, 0.061 mmol, 2 equiv), and CH_2Cl_2 (5 mL). After the mixture was stirred at 23 °C for 8 min, the *n*-butylammonium salts were extracted from the organic phase using water. Volatile components were then removed from the organic phase under reduced pressure. After washing with hexanes and drying under reduced pressure, complex **14** was obtained. Yield: 69% (24 mg, 0.021 mmol) Anal. Calcd for $C_{56}H_{47}IrN_4PI\cdot0.12C_6H_{14}$: C, 59.95; H, 4.32; N, 4.93. Found: C, 60.25; H, 4.16; N, 4.79. ^{1}H NMR (400 MHz, C_6D_6): δ −3.06 (d, 6H, J = 8 Hz, P*Me*), 0.89 (t, 0.73H, C_6H_{14}), 1.24 (m, 0.96H, C_6H_{14}), 2.40 (s, 12H, −$C_6H_4CH_3$), 3.86 (m, 2H, PPh *o-H*), 6.23 (td, 2H, J = 8 Hz, 4 Hz, PPh *m-H*), 6.57 (m, 1H, PPh-p*H*), 7.18 (d, 4H, J = 8 Hz, −$C_6H_4CH_3$), 7.39 (d, 4H, J = 8 Hz, −$C_6H_4CH_3$), 7.95 (dd, 4H, J = 8 Hz, 4 Hz, −$C_6H_4CH_3$), 8.04 (dd, 4H, J = 8 Hz, 4 Hz, −$C_6H_4CH_3$), 8.84 (s, 8H, pyrrole *H*). ^{13}C NMR (151 MHz, $CDCl_3$): δ 3.69 (d, J = 37.8 Hz), 21.88, 122.93, 125.27 (d, J = 55.9 Hz), 126.36 (d, J = 9.1 Hz), 127.27, 127.42 (d, J = 9.1 Hz), 127.95, 129.55, 131.93, 133.66, 135.15, 137.52, 139.20, 142.05. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ −43.55 ppm. UV−vis (C_6H_6): λ_{max} (log ε) 385 (4.82), 439 (5.14), 545 (4.18), 582 nm (4.02). HRMS (+ESI): calcd for $[M - I]^+$ ($[C_{56}H_{47}IrN_4P]^+$) m/z 999.3168; found m/z 999.3139.

[i-PrNMe$_3$]I. ^{1}H NMR (400 MHz, D_2O): 1.38 (dt, 6H, CH*Me*, J = 8 Hz, 4 Hz)), 3.04 (s, 9H, N*Me*), 3.64 (h, 1H, C*H*, J = 8 Hz). ^{13}C NMR (101 MHz, $CDCl_3$): 17.50, 51.64 (t, $^1J_{C-N}$ = 4 Hz), 67.81.

[(TTP)Ir(PMe$_2$Ph)(NH$_2$Bn)]BF$_4$ (16). In air, a 20 mL scintillation vial was charged with complex **9** (30 mg, 0.028 mmol), benzylamine (7.5 μL, 0.068 mmol, 2.4 equiv), and 10 mL of C_6H_6. After the mixture was stirred at 23 °C for 30 min, volatile materials were removed under reduced pressure. Recrystallization of the residues from THF−hexanes afforded complex **16** (90%, 30 mg, 0.025 mmol). ^{1}H NMR (400 MHz, C_6D_6): δ −3.42 (m, 2H, amine NH_2), −3.17 (d, 6H, J = 12 Hz, P*Me*), −1.72 (m, 2H, amine CH_2), 2.44 (s, 12H, −$C_6H_4CH_3$), 3.64 (m, 2H, PPh *o-H*), 4.89 (d, 2H, J = 8 Hz, amine *o-H*), 6.17 (t, 2H, J = 8 Hz, PPh *m-H*), 6.25 (t, 2H, J = 8 Hz, amine *m-H*), 6.37 (t, 1H, J = 8 Hz, PPh *p-H*), 6.51 (t, 1H, J = 8 Hz, amine *p-H*), 7.32 (d, 4H, J = 8 Hz, −$C_6H_4CH_3$), 7.41 (d, 4H, J = 8 Hz, −$C_6H_4CH_3$), 7.95 (dd, 4H, J = 8 Hz, 4 Hz, −$C_6H_4CH_3$), 8.34 (dd, 4H, J = 8 Hz, 4 Hz, −$C_6H_4CH_3$), 8.86 (s, 8H, pyrrole *H*). ^{13}C NMR (151 MHz, $CDCl_3$): δ 4.90 (d, J = 42.3 Hz), 21.92, 41.37, 123.18, 125.15 (d, J = 58.9 Hz), 125.96, 126.06 (d, J = 9.1 Hz), 127.32, 127.71 (d, J = 10.6 Hz), 127.78, 128.13, 128.38, 130.00, 132.76, 133.97, 134.91, 135.15, 138.03, 138.29, 142.19. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ −41.49 ppm. UV−vis (C_6H_6): λ_{max} (log ε) 419 (5.36), 528 (4.32), 561 nm (3.71). HRMS (+ESI): calcd for $[M - BF_4]^+$ ($[C_{63}H_{56}IrN_5P]^+$) m/z 1106.3903; found m/z 1106.3899.

***trans*-[(TTP)Ir(PMe$_2$Ph)$_2$]BF$_4$ (17).** In a glovebox, an NMR tube was charged with 20 mg (0.0185 mmol) of **9**, 1.0 mL of $CDCl_3$, and 2.9 μL (0.020 mmol, 1.1 equiv) of PMe_2Ph. Analysis, by ^{1}H NMR, after 6.5 h showed quantitative formation of **17**. After the volatile components were removed under reduced pressure, compound **17** was obtained. Yield: 80% (18 mg, 0.015 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ −2.77 (t, 12H, J = 4 Hz, P*Me*), 2.73 (s, 12H, −$C_6H_4CH_3$), 3.82 (m, 4H, *o*-PPh), 6.51 (t, 4H, J = 8 Hz, *m*-PPh), 6.91 (t, 2H, J = 8 Hz, *p*-PPh), 7.60 (d, 8H, J = 8 Hz, −$C_6H_4CH_3$), 7.87 (d, 8H, J = 8 Hz, −$C_6H_4CH_3$), 8.73 (s, 8H, pyrrole *H*). ^{13}C NMR (151 MHz, $CDCl_3$): δ 4.20 (t, J = 16.6 Hz), 21.89, 123.23, 125.34 (t, J = 24.2 Hz), 126.35 (t, J = 4.5 Hz), 127.80 (t, J = 4.5 Hz), 128.22, 129.86, 132.92, 134.33, 137.63, 138.66, 141.92. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ −32.35 ppm. UV−vis (CH_2Cl_2): λ_{max} (log ε): 312 (sh, 4.13), 333 (sh, 4.33), 356 (4.50), 432 (5.21), 541 (4.14), 578 nm (4.09). HRMS (+ESI): calcd for $[M - BF_4]^+$ ($[C_{64}H_{58}IrN_4P_2]^+$) m/z 1137.3766; found m/z 1137.3752.

General Procedure for the Determination of Equilibrium Constants. Stock solutions of each carbamoyl complex (**2a**−**5a**) were made up in 5.0 mL of C_6H_6, with concentrations ranging between 3.9 and 6.4 mM. Additional stock solutions of the free ligands were made up in 5.0 mL of C_6D_6. A single 5.0 mL C_6D_6 stock solution (91.7 mM) of mesitylene was used for the internal standard in all the reactions. A known volume of the carbamoyl complex solution was added to an NMR tube equipped with a high-vacuum Teflon stopcock, and the C_6H_6 was removed under reduced pressure. A known volume (typically 0.6 mL) of C_6D_6 was added to the solid carbamoyl complex, followed by either 10 μL (0.92 μmol) or 20 μL (1.83 μmol) of the internal standard solution. After analysis of the mixture by ^{1}H NMR, the actual molarity of the metal carbamoyl complex was calculated from its β-pyrrole peak integration versus the mesitylene aliphatic proton peak integration. The actual molarity of the stock solution of each free ligand was similarly determined by the ^{1}H NMR analysis of a mixture of a known volume of the ligand and internal standard. For the equilibrium measurements, a fresh volume of the free ligand solution was transferred by syringe into the NMR tube containing a C_6D_6 solution of both the complex and the internal standard. Each reaction was then monitored by NMR, over a period of up to 1 h (note that the reaction of **5a** with quinuclidine took 10 h to reach equilibrium). Concentrations of reactants and products were determined by ^{1}H NMR analysis, monitored at 10−15 min intervals for each mixture.

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X-ray Crystal Structure Determination of Complexes 4a and 17. X-ray-quality crystals of (TTP)Ir(1-MeIm)[C(O)NHBn] (**4a**) and *trans*-[(TTP)Ir(PMe_2Ph)$_2$]BF_4 (**17**) were obtained by layering a saturated THF solution of the complex with hexanes and allowing the hexane to slowly diffuse into the THF solution at −21 °C over a period of 24 h (for **4a**) and 10 days (for **17**).

A red needlelike single crystal of **4a** and brown platelike crystal of **17** were selected under the microscope and covered with PARATONE oil. The samples were mounted in a Bruker APEX2 diffractometer under a stream of cold nitrogen. Full sphere X-ray intensity data were measured to a resolution of 0.71 Å (0.5° width ω-scan, 15 s per frame, Mo Kα radiation. λ = 0.71073 Å, graphite monochromator). The frames were integrated using a narrow-frame algorithm. Data were corrected for absorption effects using the multiscan method.[57,58] Structures were solved by direct methods. All non-hydrogen atoms were refined in a full-matrix anisotropic approximation based on F^2. All expected hydrogen atoms were placed on calculated positions and were refined in an isotropic approximation using a "riding" model. The U_{iso}(H) values were set at 1.2−1.5 times the U_{eq} value of the carrier atom. All calculations were performed using the APEX II software suite.[59]

One molecule of **4a** and three THF solvent molecules were found in the asymmetric unit of the triclinic cell. Although additional THF molecules may partially occupy observed voids, attempts to apply SQUEEZE were not able to improve the refinement significantly. Thus, the original data set was used for final results. Similarity constraints on geometrical parameters and on displacement parameters were used to treat solvent molecules.

Three chemically equivalent but crystallographically nonequivalent molecules were observed in the structure refinement of **17**. One molecule, two halves of the same molecule lying on an inversion center, two BF_4^- counterions (one of them disordered by two equivalent positions), and two solvent THF molecules were found in the asymmetric unit of the triclinic cell. Similarity constraints on geometrical parameters and on displacement parameters were used to obtain a reasonable molecular geometry and displacement coefficients for the atoms of the BF_4^- counterions and THF solvent molecules.

■ ASSOCIATED CONTENT

Supporting Information

Text, figures, tables, and CIF files giving preparative details, ^{1}H, ^{13}C, ^{31}P and 2-D NMR spectra for compounds **2**−**17**, and single-crystal X-ray structural refinement data for compounds **4a** and **17**. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC files 977996−977997 also contain 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.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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