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

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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 Na₂CO₃ produces the trans-amine-coordinated iridium carbamoyl complexes (TTP)Ir(NH₂R)[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 phosphate (P(OEt)₃), and dimethylphenylphosphine (PMe₂Ph) at 23 °C to afford the hexacoordinated carbamoyl complexes [(TTP)Ir(P(OEt)₃)]BF₄ (4a), [(TTP)Ir(PMe₂Ph)]BF₄ (6a), and [(TTP)Ir(NH₂Bn)]BF₄ (5a). The rate of this ligand displacement reaction is dependent on the nature of the amine and is second order in amine. Supportive kinetic studies involving the reaction of amines with trans-[M(CO)₄L₂]PF₆ (where M = Mn, Re and L = PPh₃, PMePh₂, PMe₂Ph) 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). 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)₂] as a catalyst, was observed.

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

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Supporting Information
proposed to involve the tungsten carbamoyl complex (CO)-
W[CO][NHBu(NH3R)2(NPh)] as an intermediate.8 This was
supported further by IR spectroscopic studies with stoichi-
ometric reactions of excess secondary and primary amines with
[(CO)2W(NPh)Cl]2, which produced formamides and 1,3-di-
substituted 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

\[
PdCl2[C(O)NHR] + X_2 \rightarrow PdCl2X_2 + RNCO
\]

\[
X = Cl, I
\]

(2)

Despite the diversity of metal carbamoyl complexes that exist,11−17 reports on the synthesis and isolation of met-
alloporphyrin carbamoyl complexes are rare. One example
involves the formation of the carbamoyl complex (TPP)Rh-
[C(O)NEt2] from the reaction of (TPP)Rh(CO)Cl with
LiNEt3 in HNEt3. Treatment of the Rh carbamoyl product with
HCl re-formed the starting chlorocarbonyl complex.18 In
addition, octaethyl- and tetraethylporphyrinato 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[N=C(NHR)2]]PF6 and [(TPP)Rh[CN(CNHR)2]]PF6 with
nucleophiles, such as methanol, to form the catonic rhodium
diaminocarbene species [(OEP)Rh=C(CNHR)2]PF6 and [(TPP)Rh=C(CNHR)2]PF6.19 Furthermore, Wayland and co-workers20 isolated pentacoordinate carbamoyl complexes of rhodium octaethylporphyrin, (OEP)Rh[C(O)NHR], by treating
[(OEP)Rh]+ with CO and primary amines (eq 3). In this
case, the reaction was proposed to proceed via a hydrox-
ynocarbene complex, [(OEP)Rh=C(CNHR)]+.

\[
\frac{1}{2}[(OEP)Rh]_2 + CO + \text{RNH}_2 \rightarrow 
\frac{1}{2}(OEP)RhC(O)NHR
\]

(3)

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

\section{RESULTS AND DISCUSSION}

\section{Reactions of (TPP)Ir(CO)Cl with Amines.} Generally,
carbonyl groups react with amines, to give carbamoyl ligands,
when \(\nu(CO)\) is greater than 2000 cm\(^{-1}\).5,6 The \(\nu(CO)\) value of
(TPP)Ir(CO)Cl (2056 cm\(^{-1}\))21 suggested that the carbonyl
ligand should be susceptible to nucleophilic attack. Thus,
treatment of THF solutions of (TPP)Ir(CO)Cl (1) with
primary amines, at 23 °C, immediately resulted in a color
change from red to brown. \(^1H\) NMR monitoring of the
reactions revealed that product formation was complete within
3 min. Amine-coordinated iridium carbamoyl complexes,
(TTP)Ir[NH(R)][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

\[\text{Na}_2\text{CO}_3, \text{workup resulted in some contamination with (TPP)Ir(CO)Cl, presumably due to reversion of the reaction. Similar observations were reported in the syntheses of the carbamoyl complexes cis-Mn(CNR)_2[C(O)NMe]-
(CO)_2(bipy) from fac-[Mn(CN)(CO)_2(bipy)]^+ and MeNH}_2.17\]

Formation of the carbamoyl complexes was readily followed
spectroscopically, as evidenced by the replacement of the \(^1H\) NMR \(\beta\)-pyrrole signal of (TPP)Ir(CO)Cl (1) with the \(\beta\)-pyrrole
signal of the corresponding carbamoyl products 2a−d. The \(^1H\) 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 (TPP)Ir[NH(Pr)_2][C(O)NHP(Pr)] (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 \(^1H\) NMR
experiments with added amine. When ∼1.5 equiv of benzyl-
amine was added to a C_6D_6 solution of 2a at 26 °C, the \(^1H\) 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.

\section{Ligand Replacement Reactions.} The lability of the
coordinated amine was further demonstrated by their ease of
substitution at 23 °C, by the ligands L = quinuclidine (1-
azacyclo[2.2.2]octane, ABCO), 1-methylimidazole (1-Melm),
thiethyl phosphate (P(OEt)_2), dimethylphenylphosphine
(PMe_2Ph), leading to the isolation of the complexes (TTP)-
Ir(L)[C(O)NHR] (3−6) (Scheme 3). Benzylamine in (TTP)-

\[\text{Scheme 2. Syntheses of Carbamoyl Complexes}
\]
CH2 proton signals (evidenced by 1H NMR signals of the carbamoyl NH (benzylcarbamoyl ligand remained bound to the metal center, as shifted up methyl and ring protons of the bound 1-MeIm, which are 1.63 (1H), 1.74 (1H), and 3.70 ppm (1H), assigned to the phosphite signal (Table 1). An analogous large up coupling. For example, in π earlier by Stulz and co-workers. In contrast, coordination of 1.34 and 2.00 ppm, respectively) of the compound (−C = 270.3 Hz), while a low-

Ligands in (TTP)Ir(L)[C(O)NHR] (L = P(OEt)3 (5a,b), PMe2Ph (6a−c))

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
complex & R & \(\delta_{\text{carbamoyl} \alpha-C}\) \\
\hline
5a & Bn & 162.72 (d, \(J_{\text{p-c}} = 270.3\) Hz) \\
5b & \textsuperscript{13}Bu & 162.73 (d, \(J_{\text{p-c}} = 267.3\) Hz) \\
6a & Bn & 163.87 (d, \(J_{\text{p-c}} = 184.2\) Hz) \\
6b & \textsuperscript{13}Bu & 163.87 (d, \(J_{\text{p-c}} = 182.7\) Hz) \\
6c & Pr & 163.39 (d, \(J_{\text{p-c}} = 184.2\) Hz) \\
\hline
\end{tabular}
\caption{13C NMR Data\textsuperscript{a} for the \(\alpha-C\) of the Carbamoyl Ligands in (TTP)Ir(L)[C(O)NHR] (L = P(OEt)\textsubscript{3} (5a,b), PMe\textsubscript{2}Ph (6a−c))}
\end{table}

Relative Binding Strengths of the Ligands. A series of substitution reactions to determine the relative binding affinities of the BnNH\textsubscript{2}, ABCO, 1-MeIm, and P(OEt)\textsubscript{3} ligands to the iridium center in the (TTP)Ir(L)[C(O)NHBn] complexes was monitored by 1H NMR (eq 4). Equilibrium constants determined for ligand exchange reactions in C\textsubscript{6}D\textsubscript{6} at 25 °C are given in Table 3.

<table>
<thead>
<tr>
<th>entry</th>
<th>L\textsubscript{1}</th>
<th>L\textsubscript{2}</th>
<th>K\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BnNH\textsubscript{2}</td>
<td>ABCO</td>
<td>9.4 ± 0.2</td>
</tr>
<tr>
<td>2</td>
<td>ABCO</td>
<td>BnNH\textsubscript{2}</td>
<td>0.11 ± 0.01</td>
</tr>
<tr>
<td>3</td>
<td>1-MeIm</td>
<td>BnNH\textsubscript{2}</td>
<td>0.06 ± 0.02</td>
</tr>
<tr>
<td>4</td>
<td>ABCO</td>
<td>1-MeIm</td>
<td>1.9 ± 0.1</td>
</tr>
<tr>
<td>5</td>
<td>1-MeIm</td>
<td>ABCO</td>
<td>0.58 ± 0.05</td>
</tr>
<tr>
<td>6</td>
<td>ABCO</td>
<td>P(OEt)\textsubscript{3}</td>
<td>14.4 ± 1.0</td>
</tr>
<tr>
<td>7</td>
<td>P(OEt)\textsubscript{3}</td>
<td>ABCO</td>
<td>0.07 ± 0.004</td>
</tr>
<tr>
<td>8</td>
<td>1-MeIm</td>
<td>P(OEt)\textsubscript{3}</td>
<td>5.7 ± 0.5</td>
</tr>
<tr>
<td>9</td>
<td>P(OEt)\textsubscript{3}</td>
<td>1-MeIm</td>
<td>0.18 ± 0.01</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reactions were carried out in C\textsubscript{6}D\textsubscript{6} in air, with 1,3,5-mesitylene as an internal standard, and monitored by \(^1H\) NMR (600 MHz).

The data in Table 3 show that P(OEt)\textsubscript{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.
binding of PMe6·Ph in comparison to P(OEt)3 is based on the observation that 5 equiv of P(OEt)3 failed to displace PMe6·Ph from the carbamoyl complex 6a at 23 °C. These results are in accord with the higher σ-donating ability of PMe6·Ph, 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, PCy3 (pKb 9.70, cone angle 170°),27 illustrates the importance of steric hindrance. When 1.5 equiv of PCy3 was added to a C6D6 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-Bu)3 (pKb 8.43, cone angle 136°),27 and PPh3 (pKb 2.73, cone angle 145°),27 readily displaced BnNH2 from complex 2a. Steric bulk also affects the binding of amines. This was apparent during an attempt to replace the benzylamine ligand (pKb 9.34; cone angle 106°)25,29 in complex 2a with Et3N (pKb 10.65; cone angle 150°)25,29 in C6D6 at 23 °C. Although Et3N is more basic than BnNH2, no reaction was observed, even after heating the reaction mixture to 90 °C for almost 9 h with 2 equiv of Et3N. However, when an excess of the more basic but less sterically hindered tertiary amine quinuclidine (pKb 11.00,30 cone angle 132°)25,29 was added at ambient temperature to a C6D6 solution of complex 2a, complete displacement of BnNH2 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)NHCH2Et2] complexes.

The molecular structure of (TTP)Ir(1-MeIm)[C(O)NHCH2Et2] (4a) was solved by single-crystal X-ray diffraction analysis (Figure 1). The benzyl group of the N-benzylcarbamoyl ligand [C(O)NHCH2Et2] 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(3) bond angle of 178.86(19)°. The C(53)–N(7) bond distance (1.355(8) Å) 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(CH2Me)3)] and that (1.34(1) Å)32 for the hexacoordinate ruthenium bis-carbamoyl complex [Ru(dppe)(CO)2(C(O)NHCH2Me)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–NMe2 in Ir(TTP)C(NMe2) (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(CH2Me)2).32

Reactions of the Carbamoyl Ligand with Electrophiles. Reactions with HBF4. 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 ligand24 (eq 5). When 2 equiv of HBF4·Et2O was added at 23 °C to benzene solutions of the amine-coordinated carbamoyl complexes (TTP)Ir(NH2R)[C(O)NHHR] (2a,b), the corresponding cationic amine-coordinated carbonyl complexes ((TTP)Ir(NH2R)(CO))BF4 (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)NHHR] (2–4) with HBF4.⁴

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 13C NMR resonance (Figure S33 Supporting Information). This is similar to the assignment for the carbonyl of [(TTP)Ir(CO)]BF4 (131.3 ppm) reported by Chan.34 Moreover, the parent ion peak (m/z 996.32TS) observed for [(TTP)Ir(NH2Bn)(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)]BF4/[(TTP)-Ir-C]+, described by Chan and co-workers.34 While a similar reaction between 2 equiv of HBF4·Et2O 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)]BF4 (8) (Scheme 4), the quinuclidine-coordinated carbamoyl complex (3a) reacted with acid (eq 6) to give the cationic benzylamine-coordinated carbonyl complex [(TTP)Ir(NH2Bn)(CO)]BF4 (7a), as the major porphyrin

Figure 1. Molecular structure of (TTP)Ir(1-MeIm)[C(O)NHCH2Et2] (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).
product (56%), by 1H NMR, with the coformation of a mixture of other unidentified porphyrin products. The formation of 7a, and not [(TTP)Ir(ABCO)(CO)]BF4, 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-Melm (4a) complexes, the ambient-temperature reactions between excess HBF4, Et2O (3–4 equiv) and each of the two PMe2Ph-coordinated carbamoyl complexes 6a,c resulted in loss of the entire carbamoyl ligand, as monitored by IR and NMR. The formation of [(TTP)Ir(PMe2Ph)]BF4 (9) was observed by 1H NMR in each case (eq 7). The appearance of 9 was manifested by a β-pyrrole proton signal at 8.83 ppm (in CD2Cl2) 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 CD2Cl2) were shifted upward 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 6a. When a C6D6 solution of 6a was treated with 2 equiv of HBF4,Et2O at 23 °C, the formation of [(TTP)IrP(OEt)3]BF4 (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).

The failure of the phosphate-coordinated complexes 6a,c to form the cationic carbonyl complex [(TTP)Ir(PMe2Ph)(CO)]BF4 is presumably due to the trans influence of the PMe2Ph ligand. In an analogous case, the trans effect of PPh3 was proposed as a reason for the failure to isolate phosphine-coordinated ruthenium(II) tetraarylporphyrinato carbonyl complexes of the form (PR3)2Ru(μ-Cl)(CO)(DPP), which were only observed in solution by IR spectroscopy.35 Similarly, the π acidity of P(OEt)3,36 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 BF4– is coordinating to the iridium metal center through a fluoride atom. Examples of metal ligation by weakly coordinating ligands such as BF4–, SbF6–, and PF6– have been studied by variable-temperature solution NMR experiments.36 A bound BF4 anion was established in mer-(cis-PMe3)(trans-NO)(CO)3W(μ-F)BF4 through a 31P NMR doublet at 192 K, as a result of 31P–1F coupling. When a CD2Cl2 solution of mer-(cis-PMe3)(trans-NO)(CO)3W(μ-F)BF4 was warmed to 262 K, the doublet 31P NMR signal became a pentet, due to exchange of the four fluorine atoms of the BF4– into the bridging position.36 However, solution 31P NMR spectra of [(TTP)Ir(PMe2Ph)]BF4 (9) acquired in CD2Cl2 at 223, 200, and 190 K revealed only a 31P NMR singlet peak at ∼39.61 ppm. This suggests that the BF4– 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 C6D6 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 1H 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(L)]I (eq 9). 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(PMe2Ph)(C(O)NHPr) (6c) with methyl iodide was identified as [i-PrNMe3]I. This characterization was accomplished by comparing the 1H NMR spectrum (in CD2O) and 13C NMR spectrum (in CDCl3) of the precipitate from the reaction mixture with that of an authentic sample of [i-PrNMe3]I (see Figures S69 and S70, Supporting Information), prepared by treating (i-Pr)NMe2 with 2-fold excess of methyl iodide at 23 °C. Similarly, [n-BuNMe3]I was the only ammonium salt produced from the treatment of (TTP)Ir(NH2Bu)[C(O)NHPr] (2b) with MeI. In the reaction of (TTP)Ir(NH2Bu)[C(O)NHPr] (2a) with 2 equiv of MeI, three ammonium salts were identified: [BnNMe3]I (66%), [BnNH3]I (25%), and [Me(Bn)NH2]I (9%). One-bond 13C–14N coupling was observed for the N–Me carbon atoms in the 13C NMR spectra of [BnNMe3]I, [n- Bu-NMe3]I, and [i-PrNMe3]I. Similar coupling in the 13C 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 iodide 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 C6D6 solution of the cationic
iridium carbyl complex [(TTP)Ir(NH2Bn)(CO)]BF4 (7a) with [Bu4N]I, for 3.5 h under reflux conditions resulted in a mixture that contained 63% [(TTP)Ir(NH2Bn)]I (11a), 36% (TTP)Ir(CO))31,33 and 1% (TTP)Ir(NH2Bn)[C(O)NHBn] (2a), as revealed by 1H NMR, rather than pure 11a.

**Reactions of [(TTP)Ir(L)]BF4 and [(TTP)Ir(L)CO]BF4 with Other Ligands. Reactions with [Bu4N]I.** Treatment of a CH2Cl2 solution of [(TTP)Ir(PMe2Ph)]BF4 (9) with ~2 equiv of [Bu4N]I at 23 °C for 8 min yielded the irido complex 13 in 69% isolated yield (eq 10). The 1H NMR spectrum (in CD2Cl2) was characterized by a singlet at 41.49 ppm, which is different from the 31P NMR signal (in C6D6) from the methyl protons of the coordinated PMe2Ph. These spectral properties matched those for the product of the reaction of MeI with (TTP)Ir(PMe2Ph)CO (6c) (eq 9).

An amine Ir phosphine complex, [(TTP)Ir(PMe2Ph)NH2Bn]BF4 (16), was prepared by treatment of a CH2Cl2 solution of phosphine complex 9 with NH2Bn. After the reaction mixture was stirred at 23 °C for 30 min, complex 16 was isolated in 90% yield (eq 11). The 31P NMR signal for [(TTP)Ir(PMe2Ph)NH2Bn]BF4 (16), which appeared at −41.49 ppm, was very similar to that of the starting complex [(TTP)Ir(PMe2Ph)]BF4 (9) (−41.28 ppm). However, the formulation of 16 was supported by the presence of a peak at m/z 1106.3899, corresponding to [16 − BF4]+, in the high-resolution mass spectrum. Moreover, the coordination of BnNH2 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 NH2 and CH2 protons, respectively. In addition, a doublet at −3.17 ppm (6H, CH2, Jp-H = 12 Hz) was assigned to the methyl protons of the PMe2Ph ligand.

**Reactions of [(TTP)Ir(PMe2Ph)]BF4 (9) with PMe2Ph.** The addition of 1.1 equiv of PMe2Ph to a CH2Cl2 solution of the mono-phosphine complex [(TTP)Ir(PMe2Ph)]BF4 (9) resulted in a rapid reaction. The most notable change in the 1H NMR spectrum, observed 10 min after initial addition of PMe2Ph, was the replacement of the 6-H methyl doublet of the mono-phosphine ligand at −2.75 ppm with a 12-H virtual triplet at −2.77 ppm assigned to the bis-phosphines in trans-[(TTP)Ir(PMe2Ph)2]BF4 (17). This virtual coupling is diagnostic of a trans arrangement of methylphosphines.40–44 Analogous rhodium and ruthenium porphyrinato bis-phosphine complexes have also been reported, including [DPAP]RhIII(TPP)] and (DPPA)RuII(DPP), where DPAP is diphenylidiphosphino)acetylene.23,35 The composition of complex 17 was confirmed further by the m/z peak at 1137.3752 for [17 − BF4]+ by HRMS. The 31P NMR signal (in CD2Cl2) 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 PMe2Ph ligands are colinear 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 (2.044–2.3927 Å).66–51 However, the iridium–phosphorus bonds in
complex 17 are both shorter than the Ir–P bond distance (2.537 Å) reported for the porphyrinic iridium phosphine complex (OEP)Ir(C6H4)(PPh3)4. This unusually long Ir–P bond length was attributed to the trans influence of the alkyl ligand and to steric repulsion between the bulky PPh3 ligand and the octaethylporphyrin ligand.

**CONCLUSIONS**

The reaction (Scheme 2) of (TTP)Ir(NO)Cl (1) with primary amines readily generates the amine-coordinated carbamoyl complexes (TTP)Ir(NH2R)[C(O)NHR] with HBF4 either at ambient conditions. A possible ligand and to steric repulsion between the bulky PPh3 ligand and the octaethylporphyrin ligand.

**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 of (TTP)Ir(CO)Cl (1) was prepared according to a literature procedure. Benzylamine and isopropylamine were distilled from CaH2 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. 1H and 13C NMR spectra were referenced to solvent resonance. 

**Scheme 2**

In a nitrogen-filled glovebag, a 20 mL round-bottomed flask was charged with (TTP)Ir(NO)(CO)(Cl) (1; 91 mg, 0.099 mmol), Na2CO3 (682 µL, 6.43 mmol, a 10 mM 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 N2 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 30 mL of hexanes, and 2a was obtained. Yield: 87% (95 mg, 0.086 mmol). Anal. Calcd for C63H54IrN6O+: C, 56.92; H, 3.88; N, 7.32. Found: C, 56.80; H, 3.92; N, 7.28. (TTP)Ir(NH2Bn)[C(O)NHBn] (2a).

**Scheme 3**

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 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 N2 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 30 mL of hexanes, and 2a was obtained. Yield: 87% (95 mg, 0.086 mmol). Anal. Calcd for C63H54IrN6O+: C, 56.92; H, 3.88; N, 7.32. Found: C, 56.80; H, 3.92; N, 7.28. (TTP)Ir(NH2Bn)[C(O)NHBn] (2a).

**Scheme 4**

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 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 N2 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 30 mL of hexanes, and 2a was obtained. Yield: 87% (95 mg, 0.086 mmol). Anal. Calcd for C63H54IrN6O+: C, 56.92; H, 3.88; N, 7.32. Found: C, 56.80; H, 3.92; N, 7.28. (TTP)Ir(NH2Bn)[C(O)NHBn] (2a).
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 hexane to a concentrated THF solution of the dried product, to afford complex 4a. Yield: 89% (74 mg, 0.069 mmol). Anal. Calcld for C60H51IrN7O+: C, 65.52; H, 4.81; N, 8.91. Found: C, 65.36; H, 4.67; N, 9.29. IR (NaCl, cm−1): 3420 (2.86), 2908 (3.02), 1720 (3.09), 1482 (3.32), 725 (3.40); IR (KBr, cm−1): 3420 (3.86), 2908 (3.29), 1720 (3.30), 1482 (3.32), 725 (3.35). 

In air, a 20 mL scintillation vial was charged with complex 2a (85 mg, 0.077 mmol), triethyl phosphate (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). IR (NaCl, cm−1): 3420 (3.02), 2920 (2.98), 1720 (2.98), 1482 (3.00), 725 (3.50); IR (KBr, cm−1): 3420 (3.32), 2920 (3.30), 1720 (3.32), 1482 (3.36), 725 (3.50). Anal. Calcld for C62H57IrN7O10P+: C, 69.85; H, 4.49; N, 5.95; P, 4.69. Found: C, 69.70; H, 4.63; N, 5.80; P, 4.83. 

In the glovebox, 0.65 mL of C6D6 was added excess hexane to a concentrated benzene solution of the dried 7a. Yield: 36% (18 mg, 0.017 mmol). Anal. Calcld for C64H55IrN5O4P+: C, 62.10; H, 4.19; N, 6.47. Found: C, 62.03; H, 4.10; N, 6.29. IR (KBr, cm−1): 3420 (2.86), 2920 (2.98), 1720 (2.98), 1482 (3.00), 725 (3.50); IR (KBr, cm−1): 3420 (3.32), 2920 (3.30), 1720 (3.32), 1482 (3.36), 725 (3.50). 

A nitrogen-fuilled glovebag, a 20 mL scintillation vial was charged with complex 6a (35 mg, 0.030 mmol), 6 mL of C6H6, and HBF4·EtOH (7.4 μL, 0.002 mmol). Recrystallization from CH3Cl2—hexanes afforded complex 8. Yield: 58% (19 mg, 0.018 mmol). IR (NaCl, cm−1): 3420 (3.02), 2920 (2.98), 1720 (2.98), 1482 (3.00), 725 (3.50); IR (KBr, cm−1): 3420 (3.29), 2920 (3.27), 1720 (3.27), 1482 (3.31), 725 (3.36). Anal. Calcld for C76H75IrN5O5P+: C, 74.02; H, 5.14; N, 4.41; P, 4.21. Found: C, 73.95; H, 5.07; N, 4.37; P, 4.19. 

A nitrogen-fuilled glovebag, a 20 mL scintillation vial was charged with complex 2a (53 mg, 0.031 mmol), 5 mL of C6H6, and HBF4·EtOH (7.4 μL, 0.002 mmol). Recrystallization from CH3Cl2—hexanes afforded complex 8. Yield: 89% (74 mg, 0.069 mmol). Anal. Calcld for C60H51IrN7O+: C, 65.52; H, 4.81; N, 8.91. Found: C, 65.36; H, 4.67; N, 9.29. H NMR (400 MHz, CDCl3): δ 0.19 (s, 1H, Im H), 0.97 (s, 1H, Im H), 2.19 (s, 3H, ImMe), 2.73 (s, 12H, −C6H4CH3), 4.96 (s, 1H, Im H), 7.62 (m, 8H, −C6H4CH3), 8.09 (m, 8H, −C6H4CH3), 9.06 (s, 8H, pyrrole H). IR (KBr, cm−1): 3420 (3.02), 2920 (2.98), 1720 (2.98), 1482 (3.00), 725 (3.50); IR (KBr, cm−1): 3420 (3.29), 2920 (3.27), 1720 (3.27), 1482 (3.31), 725 (3.36). Anal. Calcld for C80H80IrN7O10P+: C, 74.02; H, 5.14; N, 4.41; P, 4.21. Found: C, 73.95; H, 5.07; N, 4.37; P, 4.19.
under reduced pressure, followed by recrystallization of the residue.

$$\lambda$$

UV (C6H6): 312 (sh, 4.13), 333 (sh, 4.33), 385 (4.82), 439 (5.14), 545 (4.18), 582 nm (4.02). HRMS (+ESI): calcld for [M + 1]$$^+$$ [(C6H4H3InN2)]$$^+$$ m/z 999.3168; found m/z 999.3139.

*pmNMe4*+H. **HRM** (400 MHz, D2O): 1.38 (dt, 6H, CHMe2, J = 8 Hz, 4 Hz), 3.04 (s, 9H, NMe3), 3.64 (h, 1H, CH, J = 8 Hz). **13C** NMR (101 MHz, CDCl3): 175.0, 51.64 (t, J = 4.9 Hz, CH2), 67.81.

**(TTP)(PMePh2)(NH2Bn)**F6 (16). In air, a 20 mL scintillation vial was charged with complex 9 (30 mg, 0.028 mmol), benzyamine (7.5 µL, 0.068 mmol, 2.4 equiv), and 10 mL of C6H6. 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). **HR** NMR (400 MHz, CDCl3): δ = 3.42 (m, 2H, amine N–H), 2.77 (t, 12H, −C6H4CH2−), 0.94 (d, 8H, CH2), 8.73 (s, 8H, pyrrole H). **13C** NMR (151 MHz, CDCl3): 67.80 (d, J = 8 Hz, −C6H4−). UV–vis (CHCl3): $$\lambda_{max}$$ (log e) 419 (5.36), 528 (4.32), 561 nm (3.71). HRMS (+ESI): calcld for [M–BF4]$$^-$$ [(C6H4Ir2N2P2)$$^-$$] m/z 1106.3903; found m/z 1106.3899.

**General Procedure for the Determination of Equilibrium Constants.** Stock solutions of each carbamoyl complex (2a–5a) were made up in 5.0 mL of C6D6 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 C6D6. A single 5.0 mL C6D6 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, followed by 10 µL of C6D6, and the C6D6 was removed under reduced pressure. A known volume (typically 0.6 mL) of C6D6 was added to the solid carbamoyl complex, followed by either 10 µL of C6D6, or 20 µL of C6D6 of the internal standard solution. After analysis of the mixture by **1H** NMR, the actual molarity of the metal carbamoyl complex was calculated from its β-pyrole 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 **1H** 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 C6D6 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 reagents and products were determined by **1H** NMR analysis, monitored at 10–15 min intervals for each mixture.
X-ray Crystal Structure Determination of Complexes 4a and 17. X-ray-quality crystals of \([	ext{TPP}]\text{Ir(1-Melm)}[\text{C(O)NHBn}]\) (4a) and trans-\([\text{TPP}]\text{Ir(PMe}_3\text{Ph})_2\)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 plate like 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 o-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(eq) 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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