Bis-Cyclometalated Iridium Complexes with Chelating Dicarbene Ancillary Ligands

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ABSTRACT: In this work, we report that covalent postsynthetic modification can be used for the preparation of a class of bis-cyclometalated iridium complexes featuring Chugaev-type chelating dicarbene ligands. Bis-cyclometalated iridium complexes with electron-deficient aryl isocyanide ancillary ligands react with hydrazine to form neutral dicarbene complexes. The neutral iridium carbene complexes have a basic site that can be protonated by strong acid, permitting access to complexes in two protonation states and allowing an additional layer of control over the key properties. These new Chugaev-type iridium complexes exhibit blue phosphorescence at both room temperature and 77 K. Compared to their bis-isocyanide precursors, the electrochemical and photophysical properties of these new complexes are substantially perturbed, demonstrating the concept that the electronic structure and excited state dynamics are dependent on the protonation state of the dicarbene ancillary ligand, and we note an ~2-fold increase in emission quantum yield when the ancillary ligand is protonated. This study demonstrates that ligand-based reactivity can be an alternative method for elaborating the structures of bis-cyclometalated iridium complexes and gives access to structures not readily obtainable by other means.

INTRODUCTION

Cyclometalated iridium(III) complexes are one of the most extensively studied classes of molecules for optoelectronic applications, such as organic light-emitting diodes (OLEDs),1,2 light-emitting electrochemical cells (LECs),3 and luminescent sensors.4 The favorable emission properties exhibited by most of these complexes, namely their relatively short phosphorescence lifetimes and high quantum yields, are attributed to the highly efficient spin–orbit coupling induced by the heavy Ir(III) center. Heteroleptic bis-cyclometalated iridium complexes, where either one bidentate or two monodentate ancillary ligands occupy the remaining two coordination sites, have been attracting considerable interest in recent years. The ancillary ligand(s) offer another means of controlling the key electrochemical and photophysical properties, motivating studies on a variety of ancillary structures with diverse structural and electronic properties.5–9

Because of the substitutional inertness of octahedral Ir(III), most synthetic preparations for installing ancillary ligands require forcing reaction conditions with high temperatures, long reaction times, and/or harsh reagents. As an example relevant to the present work, many recent studies on bis-cyclometalated iridium complexes utilize N-heterocyclic carbenes (NHCs) as ancillary ligands, which is a promising strategy for preparing complexes with efficient blue phosphorescence. NHCs10–13 are one of the most well-known ligand types due to their attractive features such as strong $\sigma$-donating character and high chemical and thermal stability.14–17 A common synthetic route for NHC-containing complexes is transmetalation, most often from silver(I).18–20 Thus, almost all examples of bis-cyclometalated Ir(III) complexes containing carbene ancillary ligands involve in situ generation of silver carbenes via reaction of imidazolium precursors with Ag$_2$O followed by transfer of the carbene(s) to chloro-bridged Ir dimers. These reactions require high temperature (95–120 °C) and long reaction times (12–36 h).21–23 However, this NHC transmetalation strategy is not general across all structure types and can result in bimetallic complexes when chelating bis-NHC ligand precursors are used.21–23 Because of these limitations, only a limited number of Ir(III) complexes bearing bidentate carbene ancillary ligands have been reported.

An alternative approach is to use postsynthetic modification to provide access to ancillary ligand structures not obtainable via traditional synthetic routes. Our group has previously shown that postsynthetic modification via Lewis acid–base interactions can modulate the properties of platinum diimine chromophores in a rapid and systematic way,24 and here we demonstrate that covalent postsynthetic modification can be used to install new ancillary ligands onto bis-cyclometalated iridium complexes and alter key properties. This method relies on the inherent reactivity of coordinated ligands, a phenom-
enon that has been studied for many decades but is not commonly applied to the design of new cyclometalated iridium complexes. It is known that electrophilic-coordinated isocyanides can react with hydrazine to form bidentate “Chugaev-type” acyclic dianimocarbene (ADC) chelate complexes. ADCs have similar structural, electronic, and steric properties as NHCs, but they are relatively free from geometric constraints, which results in variable N–Carbone–N carbene bond angles and electron-donating ability. Chugaev-type chelating ADCs were discovered as early as 1915 and fully characterized in 1970, although they have received little attention in recent years. All of the published work on Chugaev-type carbene species involves square planar Pt, with electron-donating ability.29 Chugaev-type chelating ADCs and electron-rich aryl isocyanide ligands react smoothly with hydrazine to form chelated dicarbene complexes. The electrochemical and photophysical properties of these new complexes are substantially altered relative to their bis-isocyanide precursors.

We also demonstrate that the Chugaev-type complexes described here can be isolated in two protonation states. The emission wavelengths and dynamics are altered when the ADC is protonated at the backbone nitrogen, providing an additional layer of control over the photophysical properties. This work demonstrates a conceptual advance in the design of new bis-cyclometalated iridium phosphors, where inherent ligand-based reactivity can be leveraged to give rise to new structures that cannot be prepared using typical synthetic approaches.

## RESULTS AND DISCUSSION

**Synthesis.** The syntheses begin with bis-cyclometalated bis(aryl isocyanide) iridium(III) complexes, [Ir(F2ppy)2(CNAr)2]PF6 (1a–1c; F2ppy = 2-(2,4-difluorophenyl)pyridine). These precursors are readily obtained by the reaction of the chloro-bridged Ir dimer, [Ir(F2ppy)3(μ-Cl)]2+, in dichloromethane with 2 equiv of silver hexafluorophosphate (AgPF6) followed by addition of 4 equiv of aryl isocyanide. The complexes differ with respect to the identity of the isocyanide ancillary ligand, 4-trifluoromethylphenyl isocyanide (CNAr+CF3) for 1a, 3,5-bis(trifluoromethyl)phenyl isocyanide (CNAr3,5-CF3) for 1b, and 4-nitrophenyl isocyanide (CNArNO2) for 1c. We have utilized this route to prepare previously described complexes 1b and 1c as well as a series of related complexes with other isocyanide ancillary ligands.43

Addition of excess hydrazine hydrate to dichloromethane solutions of complexes 1a–1c at room temperature results in chelative addition of hydrazine to the coordinated isocyanides, affording neutral “Chugaev-type” carbene complexes (2a–2c) in 88–90% yield (Scheme 1). In contrast, analogues of 1a–1c with electron-rich aryl isocyanide ligands, such as 2,6-dimethylphenylisocyanide and 4-methoxyphenylisocyanide, do not react cleanly with hydrazine, suggesting that the electron-withdrawing NO2 or CF3 groups are required to enhance the electrophilicity of the isocyanides and promote reactivity. In addition to the expected signals arising from the F2ppy ligands and the substituted aryl groups, 1H NMR spectra of 2a–2c exhibit two broad N–H signals in a 1:2 ratio, one in the range of δ 9.46–9.94 ppm and the other between δ 6.39 and 7.50 ppm. Given that the “backbone” chelate-ring N–H bonds of the Chugaev-type carbene ligand are known to be more acidic than the exterior N–H bonds,33,40 the downfield chemical shifts are assigned to the internal N–H groups (shown in blue in Scheme 1), whereas the upfield chemical shifts correspond to terminal N–H groups outside the chelate ring (red in Scheme 1). The aromatic region of the 1H NMR spectra and the 19F NMR spectra show one set of resonances for the two F2ppy ligands and the two substituted aryl rings, suggesting C2-symmetric structures that arise from rapid N–H tautomerization as previously observed for palladium and platinum analogues.55,56 Treatment of dichloromethane solutions of 2a–2c with one equivalent of HBF4 immediately affords cationic dicarbene complexes 3a–3c in 78–94% isolated yield.

1H NMR spectra display two broad N–H signals in a 1:1 ratio, and 19F NMR signals from the BF4− counteranion are observed, confirming that protonation of the interior nitrogen atom occurs.

**IR Spectroscopy.** Infrared (IR) spectra of isocyanide precursors 1a–1c evince the electrophilic nature of the coordinated isocyanides, and spectra of the hydrazine insertion products 2a–2c and 3a–3c further confirm the structure of the products. In general, a positive value of Δν = ν(C=N)coord − ν(C=N)free, i.e., a hypsochromic shift in the C≡N stretching frequency, indicates electrophilic character of the isocyanide carbon atom and susceptibility to nucleophilic attack.25,44 IR data for all complexes and free isocyanide ligands are included in Table S1. The IR spectra of complexes 1a–1c reveal the presence of two strong ν(C≡N) stretching vibrations in the range of 2197–2156 cm−1, whereas ν(C=N) stretching bands of the free isocyanide ligands are located between 2148 and 2129 cm−1. The resulting positive value of Δν (∼40 cm−1 for 1a, ∼68 cm−1 for 1b, and ∼51 cm−1 for 1c) on going from the...
free isocyanide ligand to the coordinated isocyanide ligand confirms the electrophilic character of the isocyanide carbon atom and activation for reaction with nucleophiles. Conversion of complexes 1a−1c into 2a−2c/3a−3c results in disappearance of the two strong v(C≡N) stretching bands as well as emergence of weak bands at 3262−3405 cm⁻¹ corresponding to v(N−H) stretching.

**Crystal Structures.** The molecular structures of 2a, 2c, 3a, and 3c were ascertained by single-crystal X-ray diffraction and are consistent with the NMR spectra described above. Crystallographic data and selected bond lengths and angles are reported in Tables S2−S4. As shown in Figures 1 and 2, all complexes have distorted octahedral coordination geometries about the Ir center with two cyclometalated F₂ppy ligands and one chelating carbene ligand. In all cases, the F₂ppy nitrogen atoms are in a trans orientation relative to each other. The carbene bite angles (C−Ir−C) of all complexes span a narrow range of 75.48(15)−79.08(16)°, which is smaller than those of methylene-bridged bis-NHC Ir complexes (∼85°)

In all of the structures, the N−H hydrogen atoms were located in the difference map and refined isotropically. The hydrogen atoms are localized in the structures of 2a and 2c, resulting in an asymmetric chelating dicarbene and suggesting that the N−H proton does not tautomerize at low temperature (123 ± 2 K) in the solid state. The most notable differences between the structures of the neutral (2a and 2c) and protonated (3a and 3c) forms involve the Ir−Ccarbene bond lengths. In the case of complexes 2a and 2c, bond lengths between Ir and Ccarbene are unequal, 2.046(3) (2a) and 2.039(4) Å for the bond adjacent to the protonated backbone nitrogen, and 2.068(3) (2a) and 2.079(4) Å, for the Ir−Ccarbene bond closest to the unprotonated backbone nitrogen. In contrast, protonated dicarbene complexes 3a and 3c exhibit two nearly identical Ir−Ccarbene bond lengths that differ by not more than 0.015(4) Å.

**Electrochemistry.** The electrochemical properties of the complexes were investigated by cyclic voltammetry (CV) experiments (Figures S1−S3), and the results for the dicarbene complexes are summarized in Table 1. Much like the parent isocyanide complexes in related NHC complexes (2.120(1)−2.104(1) Å), indicating a slightly stronger interaction between the ADC and the metal center.

In all the structures, the N−H hydrogen atoms were located in the difference map and refined isotropically. The hydrogen atoms are localized in the structures of 2a and 2c, resulting in an asymmetric chelating dicarbene and suggesting that the N−H proton does not tautomerize at low temperature (123 ± 2 K) in the solid state. The most notable differences between the structures of the neutral (2a and 2c) and protonated (3a and 3c) forms involve the Ir−Ccarbene bond lengths. In the case of complexes 2a and 2c, bond lengths between Ir and Ccarbene are unequal, 2.046(3) (2a) and 2.039(4) (2c) Å for the bond adjacent to the protonated backbone nitrogen, and 2.068(3) (2a) and 2.079(4) (2c) Å, for the Ir−Ccarbene bond closest to the unprotonated backbone nitrogen. In contrast, protonated dicarbene complexes 3a and 3c exhibit two nearly identical Ir−Ccarbene bond lengths that differ by not more than 0.015(4) Å.

**Figure 1.** X-ray crystal structures of 2a and 3a. Ellipsoids are shown at the 50% probability level with carbon-bound hydrogen atoms and solvent molecules omitted.

**Figure 2.** X-ray crystal structures of 2c and 3c. Ellipsoids are shown at the 50% probability level with carbon-bound hydrogen atoms and solvent molecules omitted.
potentials of the complexes are relatively invariant, occurring at 0.98–1.10 V and depending on the substituents of the dicarbene’s aryl groups. These potentials are quite similar to the observed oxidation potentials for a series of cyclometalated Ir(III) complexes containing NHC ancillary ligands, which also occur in the region of 0.97–1.10 V.\textsuperscript{10,13} Therefore, we suggest that the first oxidation is a primarily metal-centered Ir\textsuperscript{IV}/Ir\textsuperscript{III} couple. Compared to bis(aryl isocyanide)Ir(III) complexes (1a–1c), Ir complexes bearing chelated carbene (2a–3c) are 500–600 mV easier to oxidize, indicating destabilization of the (HOMO) levels when the isocyanide ancillary ligands are converted into a dicarbene chelating ligand.

All NO\textsubscript{2}-containing complexes (2c and 3c) exhibit the first reduction potentials at comparatively positive potentials of −1.87 (2c) and −1.86 V (3c), which are likely attributed to a nitrophenyl-centered reduction.

The remaining reduction potentials of the complexes lie between −2.47 and −2.78 V, suggesting that reduction involves population of a π* orbital in either C=\textsuperscript{N} ligand or carbene ancillary ligand. Compared to complexes 1a–1c, significant cathodic shifts in the reduction potentials of the dicarbene complexes are also observed, indicating destabilized LUMO levels.

**Photophysical Properties.** The UV–vis absorption spectra of complexes 2a–3c, obtained in CH\textsubscript{2}Cl\textsubscript{2} solutions at room temperature, are shown in Figure 3, and the data are summarized in Table 2. All complexes exhibit strong absorption bands (ε \textasciitilde 26–80 \times 10\textsuperscript{3} M\textsuperscript{−1} cm\textsuperscript{−1}) in the spectral region below 340 nm, which are attributed to the spin-allowed ligand-centered π-π* transitions (1LC) involving the F\textsubscript{2}ppy ligands.

In contrast to complexes 1a–1c, where charge transfer (CT) absorption bands occur below 350 nm (Figure S4), complexes 2a–3c display absorption bands tailing into the visible region. The weak, lowest-energy absorption bands extending from 340 to 460 nm can be tentatively assigned as both singlet and triplet metal-to-ligand charge transfer (MLCT) transitions that are consistent with previously reported experimental and DFT calculation results of Ir(III) carbene complexes,\textsuperscript{10,11,13} though other charge-transfer transitions in this region of the spectrum are also possible.

All of the complexes except NO\textsubscript{2}-containing complexes (2c and 3c) are luminescent at both room temperature and low temperature, showing that luminescence is preserved in complexes with Chugaev-type dicarbene ancillary ligands. Table 2 summarizes the steady-state and time-resolved emission data, and Figure 4 shows overlaid room temperature and low temperature emission spectra of 2a and 3a as representative examples. Figures S5–S10 show individual emission spectra for all of complexes 1a, 1b, 2a, 2b, 3a, and 3b. Complexes 2a and 2b exhibit broad, blue phosphorescence at room temperature in CH\textsubscript{2}Cl\textsubscript{2} solution with emission maxima (λ\textsubscript{max}) at 474 and 473 nm and quantum yields (Φ) of 0.044 and 0.010, respectively. The excitation spectra (Figures S11 and S12) of complexes 2a and 2b are well-matched to the absorption spectra, indicating that phosphorescence originates from the corresponding Ir complexes. When cooled to 77 K, the emission spectra of 2a and 2b show well-defined vibronic structure with rigidochromic blue shifts in λ\textsubscript{max} of 28 nm (∼1330 cm\textsuperscript{−1}). This significant temperature dependence on the emission profile may indicate that the dicarbene introduces a thermally accessible excited state, which is populated at room temperature but not at 77 K, though we note that many other cyclometalated iridium complexes exhibit significant rigidochromism,\textsuperscript{6,7,47} so this phenomenon is not unique to these complexes. The spectra of complexes 2a and 2b are nearly identical to one another at both room temperature and 77 K, demonstrating that changing the substitution pattern on the ancillary ligand has little effect on the nature of the lowest excited state. Time-resolved emission data were also obtained at room temperature, and complexes 2a and 2b exhibit biexponential decays with lifetimes in the range of 0.42–0.63 μs. These observed biexponential decays might arise from two different emitting excited states or originate from different triplet sublevels within same excited state.\textsuperscript{48,50} The poorly resolved vibronic structure in the room temperature spectrum and large rigidochromic shifts upon cooling suggest that one of the emitting states has significant charge-transfer character, although the nature of this state (metal-to-ligand charge transfer vs interligand charge transfer) remains unclear. On the basis of the experimentally obtained quantum yields and lifetimes, the radiative (k\textsubscript{r}) and nonradiative (k\textsubscript{nr}) decay constants were calculated. The k\textsubscript{r} values are 7.0 (2a) and 2.4 (2b) \times 10\textsuperscript{4} s\textsuperscript{−1}, whereas k\textsubscript{nr} values are substantially larger with values of 1.5 (2a) and 2.4 (2b) \times 10\textsuperscript{6} s\textsuperscript{−1}.

To obtain a better understanding of the photophysics of 2a and 2b, we compared the emission properties to bis-(aryl isocyanide) iridium(III) complexes (1a and 1b, see Table S6 and Figures S5 and S6). Complexes 1a and 1b show small rigidochromic shifts of ∼5 nm (∼262 cm\textsuperscript{−1}) when cooled to low temperature and significantly longer lifetimes of ∼52 μs, indicating that the lowest excited state is a predominantly F\textsubscript{2}ppy-centered LC state with very minimal contributions from MLCT states. In sharp contrast, complexes

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**Table 1. Summary of Electrochemical Data**

<table>
<thead>
<tr>
<th>compound</th>
<th>E\textsuperscript{ox} (V)</th>
<th>E\textsuperscript{red} (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>0.98, 1.19, 1.46</td>
<td>2.47, −2.78</td>
</tr>
<tr>
<td>2b</td>
<td>1.02, 1.18, 1.32</td>
<td>−2.76</td>
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<tr>
<td>2c</td>
<td>1.05, 1.24, 1.51</td>
<td>−1.87\textsuperscript{b}, −2.60</td>
</tr>
<tr>
<td>3a</td>
<td>1.00, 1.18, 1.46</td>
<td>−2.54, −2.74</td>
</tr>
<tr>
<td>3b</td>
<td>1.07, 1.26, 1.52</td>
<td>−2.70</td>
</tr>
<tr>
<td>3c</td>
<td>1.10, 1.28, 1.53</td>
<td>−1.86\textsuperscript{b}, −2.64</td>
</tr>
</tbody>
</table>

\textsuperscript{b}Measured in 0.1 M NBu\textsubscript{4}PF\textsubscript{6} acetonitrile solution with a scan rate of 0.1 V/s. All potentials are reported relative to Fc\textsuperscript{+}/Fc. \textsuperscript{a}NO\textsubscript{2}-centered quasi-reversible reduction.

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**Figure 3.** Overlaid UV-vis absorption spectra of 2a–3c in CH\textsubscript{2}Cl\textsubscript{2}. Data were collected in 1 nm intervals; the symbols on the lines are to aid visualization of the overlaid data.
The improved quantum yields ($\Phi_{\text{em}}$) occur at 442 nm with well-resolved vibronic structure and changes in the room-temperature emission spectra. The room-temperature emission proflife times, and increased dynamics of the excited states in addition to perturbing the excited-state dicarbene ancillary ligands have subtle impacts on the energies.

Data was collected in 1 nm intervals; the symbols on the lines are to aid visualization of the overlaid data.

2a and 2b exhibit more significant rigidochromic shifts with much shorter lifetimes of less than 1 µs. The $k_e$ values are increased relative to 1a and 1b, but an even greater increase in $k_{nr}$ values result in lower quantum yields for 2a and 2b. Large rigidochromic shifts, less-resolved emission profiles, shorter lifetimes, and increased $k_{nr}$ values in complexes 2a and 2b suggest that they may have more pronounced MLCT character in the lowest excited state, which arise from the destabilized Ir-$\pi$ orbital (HOMO) brought on by substituting isocyanide.

Protonation of complexes 2a and 2b leads to substantial changes in the room-temperature emission spectra. The room-temperature emission maxima in protonated complexes 3a and 3b occur at 442 nm with well-resolved vibronic structure and improved quantum yields ($\Phi = 0.078$ and 0.023, respectively) relative to those of the neutral precursors. The ~2-fold increase in quantum yields is caused by subtle augmentation of $k_e$ and slight depression of $k_{nr}$ in each case. The excitation spectra (Figures S13 and S14) of complexes 3a and 3b are well-matched with the absorption spectra. In contrast to 2a and 2b, complexes 3a and 3b display low-temperature emission spectra almost identical to the room-temperature spectra, indicating substantial LC character in the lowest excited states, minor contributions from MLCT states, and no thermally accessible excited states at higher temperature. Moreover, vibronic spacing between successive maxima (1393 cm$^{-1}$ at room temperature and 1509 cm$^{-1}$ at low temperature) is nearly identical to that of complexes 1a and 1b (∼1368 cm$^{-1}$ at room temperature, 1536 cm$^{-1}$ at low temperature),51,52 and these further support that the lowest emitting excited state has substantial contribution from F$_2$ppy-localized LC states with almost no contributions from MLCT states. Finally, comparison of the 77 K spectra of neutral 2a/2b with protonated 3a/3b indicates an ~400 cm$^{-1}$ blue shift in the emission energies upon protonation, indicating that the protonation state of the dicarbene ancillary ligand subtly affects the excited-state energies in addition to strongly perturbing the nature and dynamics of the excited state. There are other examples of complexes with basic functional groups that undergo substantial changes in their emission spectra and/or quantum yields upon protonation, where protonation often results in a change in the relative energies of charge-transfer and ligand-centered states,51,52 including one example featuring dicarbene ligands akin to those presented here.53 We think an analogous mechanism is responsible for the change in room-temperature emission profile and quantum yields upon protonation of the dicarbene backbone.

## CONCLUSIONS

In this work, we have demonstrated that postsynthetic covalent modification can be used to install new ancillary ligand structures on bis-cyclometalated iridium complexes. Leveraging the electrophilic reactivity of coordinated isocyanides toward hydrazine, which has been demonstrated on a number of square planar complexes, we have accessed octahedral bis-cyclometalated iridium(III) complexes with ancillary Chugaev-type chelating dicarbene ligands. We show that the electrochemical and photophysical properties are significantly perturbed upon converting the isocyanides into carbene, further demonstrating the concept that the electronic structure and excited-state dynamics can be controlled by ancillary ligand modification. In addition, these dicarbene ancillary ligands have a basic site that can be protonated, giving another means by which to control the electronic structures and optical properties. In ongoing work, we are preparing bis-cyclometalated iridium Chugaev-type complexes with other cyclometalating ligands, which allows emission color tuning and better understanding of the interplay between LC and MLCT states in these complexes, and substituted hydrazines can give access to more elaborate

Table 2. Photophysical Properties

<table>
<thead>
<tr>
<th>complex</th>
<th>absorbance $a$ $\lambda_{\text{nm}}$ (ε $\times 10^{3}$ M$^{-1}$ cm$^{-1}$)</th>
<th>emission $b$ $\lambda_{\text{nm}}$/nm</th>
<th>CH$_2$Cl$_2$ at 298 K</th>
<th>CH$_2$Cl$_2$/toluene at 77 K</th>
<th>quantum yield ($\Phi_{\text{em}}$)</th>
<th>lifetime ($\mu$s)</th>
<th>($k_e^{\text{nr}}/k_{nr}^{\text{nr}}$) $\times 10^3$/s$^{-1}$</th>
<th>($k_e^{\text{nr}}/k_{nr}^{\text{nr}}$) $\times 10^3$/s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>256(61), 303(32), 361(13)</td>
<td>453(sh), 474, 498(sh)</td>
<td>446, 477</td>
<td>0.044</td>
<td>0.63$^3$</td>
<td>7.0/15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2b</td>
<td>254(59), 304(29), 362(9.2)</td>
<td>449(sh), 473, 495(sh)</td>
<td>445, 475</td>
<td>0.010</td>
<td>0.42$^3$</td>
<td>2.4/24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2c</td>
<td>253(54), 305(26), 393(23)</td>
<td>c</td>
<td>c</td>
<td>c</td>
<td>c</td>
<td>c</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>248(61), 301(33), 357(7.3)</td>
<td>442, 471</td>
<td>438, 469</td>
<td>0.078</td>
<td>0.97</td>
<td>8.0/9.5</td>
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<tr>
<td>3b</td>
<td>248(80), 302(38), 356(11)</td>
<td>442, 471</td>
<td>438, 469</td>
<td>0.023</td>
<td>0.42</td>
<td>5.5/23</td>
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<tr>
<td>3c</td>
<td>245(65), 313(43), 339(30)</td>
<td>c</td>
<td>c</td>
<td>c</td>
<td>c</td>
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$^a$Recorded in CH$_2$Cl$_2$. $^b$recorded in CH$_2$Cl$_2$/toluene. 2969 DOI: 10.1021/acs.organomet.7b00428 Organometallics 2017, 36, 2963–2972
dicarbene structures. We also envision that other nucleophiles could react with coordinated isocyanides in bis-cyclometalated iridium complexes, which would lead to a much more diverse range of structures. Motivated by the work presented here, we are currently pursuing all of these aforementioned avenues as we continue to use nontraditional synthetic approaches to generate a wide range of ancillary ligand structures in bis-cyclometalated iridium complexes.

**EXPERIMENTAL SECTION**

Materials. Reactions were performed in ambient condition unless otherwise stated. Dry solvents were obtained from a Grubb Solvent Purification System and degassed with argon. Starting materials and reagents, unless otherwise specified, were obtained from commercial sources and used without further purification. Previously reported bis-cyclometalated bis(aryl isocyanide)iridium(III) complexes 1b and 1c were synthesized in a nitrogen-filled glovebox by the reaction of the chloro-bridged Ir dimer, [Ir(C^N)2(μ-Cl)]2, in dichloromethane with 2 equiv of silver hexafluorophosphate (AgPF6) followed by addition of 4 equiv of aryl isocyanide.1

Physical Methods. 1H and 19F NMR spectra were recorded at room temperature using a JEOL ECA-500 or ECA-600 NMR spectrometer. UV–vis absorption spectra were recorded in dichloromethane in screw-capped 1 cm quartz cuvettes using an Agilent Carey 8454 UV–vis spectrophotometer. Steady-state emission and excitation spectra were recorded using a Horiba FluoroMax-4 spectrofluorometer. To exclude air, samples for emission spectra were prepared in a nitrogen-filled glovebox using dry, deoxygenated solvents. Samples for room-temperature emission were housed in 1 cm quartz cuvettes with septum-sealed screw caps, and samples for low-temperature emission were contained in a custom quartz EPR tube with high-vacuum valve and immersed in liquid nitrogen using a finger Dewar.

General Procedure for the Preparation of Dicarbene Complexes 2a–2c. The complex [Ir(F2ppy)2(CNAr)]PF6 (1a–1c) was dissolved in a minimum amount of CH2Cl2 and combined with excess NH4PF6 to remove residual water. The volume of the resulting solution was decreased and the product was precipitated by adding hexane or pentane before drying under vacuum. The resulting crude product was purified either by column chromatography or by recrystallization from CH2Cl2/hexane to give a bright yellow solid.

In the glovebox, 1 equiv of HBF4·EtOH was added to a stirring CH2Cl2 solution of Ir(F2ppy)2(CNAr)PF6 (2a–2c). The solvent was removed under vacuum, and the crude product was dissolved in a minimum amount of THF and precipitated from...
pentane. Pale yellow product was obtained after recrystallization from THF/pentane or CH2Cl2/hexane.

\[[\text{Ir}(Fppy)_2(\text{C}_{12}N_4\text{H}_2\text{Ar}^\text{3,5}\text{-NO}_2)_2]\text{BF}_4(3\text{a})\]. Prepared by the general procedure, using 55 mg of \(\text{Ir}(\text{F}2\text{ppy})_2(\text{C}_2\text{N}_4\text{H}_3(\text{Ar}_4\text{-NO}_2)_2)\) according to the general procedure. Yield: 17 mg, 78%. 

1H NMR (600 MHz, CD3CN): \(\delta\) 7.91 (s, 2H), 7.85 (d, \(J = 5.4 \text{ Hz}, 2\text{H}\)), 7.35 (m, 2H), 6.53 (m, 2H), 6.35 (d, \(J = 8.4 \text{ Hz}, 2\text{H}\)), 2.42 (t, \(J = 6.8 \text{ Hz}, 2\text{H}\)). 19F NMR (565 MHz, CD3CN): \(\delta\) = 110.61 (t, \(J = 7.1 \text{ Hz}, 2\text{F}\)), −110.44 (t, \(J = 7.3 \text{ Hz}, 2\text{F}\)), −110.39 (t, \(J = 7.2 \text{ Hz}, 2\text{F}\)).

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00428.

Crystallographic summary, IR spectral data, UV–vis absorption spectra of 1a−1c, emission spectra of 1a and 1b, individual emission and excitation spectra of 2a, 2b, 3a, 3b, the cyclic voltammograms of 1a−3c, NMR spectra of all new complexes, and crystallographic data in CIF format (PDF)

Accession Codes
CCDC 1555006−1555009 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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