Deep blue

Cyano-Isocyanide Iridium(III) Complexes with Pure Blue Phosphorescence

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characterized by NMR, mass spectrometry, infrared spectroscopy, and, for five of the compounds, by X-ray crystallography. Cyclic voltammetry establishes that these compounds have large HOMO– LUMO gaps. The mixed cyano-isocyanide compounds are weakly luminescent in solution, but they phosphoresce with moderate to good efficiency when doped into poly(methyl methacrylate) films, with Commission Internationale de L'Eclairage coordinates that indicate deep blue emission for five of the six compounds. The photophysical studies show that the photoluminescence quantum yields are greatly enhanced in the cyano complexes relative to the chloride precursors, affirming the benefit of strong-field ancillary ligands in the design of blue-phosphorescent complexes. Density functional theory calculations confirm that this enhancement arises from a significant destabilization of the higher-energy ligand-field states in the cyanide complexes relative to the chloride precursors.

INTRODUCTION

Phosphorescent iridium complexes have long been used as dopants in organic light-emitting diodes (OLEDs), due to their ability to significantly increase device efficiency. The heavy iridium center results in strong spin-orbit coupling (SOC), enabling fast singlet-to-triplet intersystem crossing in the excited-state manifold. Mixing of these states partially removes the spin-forbidden nature of the T_1 to ground-state radiative relaxation, which results in efficient phosphorescent emission with a short radiative decay time. Cyclometalated iridium complexes have become a particularly prominent class of phosphorescent compounds, exhibiting many desirable attributes which include high photoluminescence quantum yields, relatively short μ s lifetimes, good stability, and facile tuning of the photoluminescence properties via ligand alteration. One of the first breakthroughs in blue-light emitting iridium complexes for OLEDS is the complex FIrpic, which includes 2-(2,4difluorophenyl)pyridine cyclometalating ligands and an ancillary picolinate ligand. This complex showed an electroluminescence peak wavelength of 475 nm with Commission Internationale de L'Eclairage (CIE) coordinates of (x = 0.16, y= 0.29), representing sky-blue emission.¹ For typical color display applications, a much deeper blue color is needed, motivating the discovery of high-efficiency blue molecular phosphors,²⁻¹⁴ which remains a significant challenge in this

cyanide ancillary ligand onto a chloride precursor and are

area of research. A blue-emitting dopant for OLED displays ideally must have CIE coordinates of (x = 0.14, y = 0.08) to meet the National Television Standards Committee standard and be suitable for realistic color displays with wide color gamuts.

Sky blue to blue

The stability and efficiency of blue phosphors are, in most cases, significantly poorer than their green and red counterparts, presenting a significant fundamental challenge that must be overcome with improved molecular design. One key deactivation mechanism is that the emissive state is in proximity to one or more nonemissive metal-centered d-d states, making the phosphorescence prone to quenching and resulting in ligand-loss degradation pathways.^{15–17} As a result, there is a significant reduction of the emission efficiency and photostability of blue-emitting complexes, the latter not only causing shorter device lifetimes but also poor color stability. Attaining blue phosphors with high quantum yields and better

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stability for OLEDs thus requires innovative synthetic pathways and molecular designs. The energy level of the emissive excited state, and thus the luminescence color, is primarily determined by the structure and substituents of the cyclometalating ligand. An effective molecular design strategy for blue-phosphorescent iridium complexes is to use cyclometalating ligands with large HOMO-LUMO gaps, and those derived from aryl-triazoles (1,2,4-triazoles in particular) and Naryl-substituted N-heterocyclic carbenes (NHCs) fit this criterion and have been employed in several studies.^{10,18-24} These 1,2,4-triazole and NHC-based cyclometalating ligands have been used primarily in homoleptic tris-cyclometalated iridium complexes, which have emerged as promising blue-phosphorescent materials.²⁵⁻³⁴ The HOMO of these complexes is delocalized, typically involving significant contribution from an Ir-centered $d\pi$ orbital and the phenyl rings of the cyclometalating ligand, while the LUMO is mainly localized on the triazolyl or imidazolyl moiety. The lowest energy triplet excited state (T_1) that gives rise to the phosphorescent emission involves both ligand-centered (³LC or ${}^{3}\pi \rightarrow \pi^{*}$) and metal-to-ligand charge-transfer (³MLCT or ³ $d \rightarrow \pi^*$) character. The phosphorescence energy can be modified by substituents on the cyclometalating ligand, and in most cases it will increase in energy with electron-withdrawing groups on the phenyl ring or electron-donating groups on the Nheterocycle.

Reports of heteroleptic complexes with 1,2,4-triazole or NHC cyclometalating ligands are rare,^{35–38} despite the potential advantage of these compounds using the ancillary ligand(s) to tune the luminescence color, improve the stability, and/or impart additional functionality. Employing a strong σ donor as an ancillary ligand would destabilize the ligand-field d-d excited states that are populated as a common nonradiative deactivation, which we have recently shown in a series of complexes partnering a strong σ -donor acyclic diamino carbene (ADC) ancillary ligand with two cyclometalated NHCs, producing blue phosphors with good color purity and quantum yields.³⁸ Another heteroleptic design we have investigated is cationic bis-cyclometalated complexes with two aryl isocyanide ancillary ligands. Aryl isocyanides are strong-field ligands, both good σ -donors π -acceptors, imparting larger HOMO-LUMO energy gaps primarily by stabilization of the HOMO, and they are particularly effective at supporting efficient phosphorescence in the blue to green regions of the spectrum.^{35,39-41} The cationic nature of these bis-isocyanide compounds will make them less appealing for many optoelectronic applications, where charge-neutral, volatile molecules capable of thermal deposition are preferred.⁴² In this work we describe six blue-phosphorescent heteroleptic complexes of the type $Ir(C^Y)_2(CNAr)(CN)$, where C^Y is a 1,2,4-triazole or NHC-based cyclometalating ligand. These compounds have many of the same advantages imparted by strong-field ancillary ligands but are charge neutral. The mixed cyano-isocyanide ancillary ligand set was previously used in a series of sky-blue to blue-green iridium phosphors,⁴³ and we show in this work that this design is likewise effective for compounds which emit in the deep-blue region. These compounds are prepared via a simple and general route, substituting the chloride in $Ir(C^Y)_2(CNAr)(Cl)$ precursors for the stronger σ -donor cyanide. In contrast to the strongly luminescent cyanide complexes, the chloride precursors are minimally luminescent, further underscoring the importance of strong σ -donor ligands in blue-phosphorescent complexes. The photophysical properties of these compounds are described in detail, with both steady-state and time-resolved measurements in solution and in solid polymer films. Several of the conclusions from the photophysical analysis are supported and further elaborated by density functional theory (DFT) computations. Taken together, the results show that these mixed cyano-isocyanide compounds represent a promising design for efficient and stable deep blue-phosphorescent organometallics.

EXPERIMENTAL SECTION

Materials. Reactions were performed in air unless specified otherwise. Solvents for reactions and photophysical measurements were dried using a Grubbs solvent purification system and deoxygenated with argon. Starting materials and reagents obtained commercially were used as received. Chloro-bridged Ir dimers, $[Ir(C^{Y})_2(\mu$ -Cl)]_2 (C^Y = cyclometalating ligand), and 4-trifluor-omethylphenyl isocyanide (CNAr^{4-CF3}) were prepared as described previously.^{33,44,45} The freshly synthesized CNAr^{4-CF3} ligand was immediately used for the next step, and measured amounts of this ligand are approximate given its propensity to decompose.

ligand are approximate given its propensity to decompose. Physical Methods. ¹H and ¹⁹F NMR spectra were recorded at room temperature using a JEOL ECA-400, ECA-500, or ECA-600 NMR spectrometer. The static nanoESI-MS experiments were carried out using a Thermo Exactive mass spectrometer and operated in positive ionization mode, with a spray voltage of 1.5 kV. Infrared (IR) spectra were measured using a Thermo Nicolet Avatar FT-IR spectrometer with diamond ATR. UV-vis absorption spectra were measured in dichloromethane, with samples housed in 1 cm quartz cuvettes sealed with a screw cap and septum. An Agilent Carey 8454 UV-vis spectrophotometer was used to acquire UV-vis absorption spectra. Steady-state photoluminescence and excitation spectra were recorded with a Horiba FluoroMax-4 spectrofluorometer. Samples for emission measurements were prepared in a glovebox using dry, deoxygenated solvents, and poly(methyl methacrylate) (PMMA) film samples were stored under nitrogen until the measurements were made. Samples for low-temperature emission were contained in a quartz EPR tube fitted with a high-vacuum Teflon valve and cooled in liquid nitrogen using a finger Dewar. Emission quantum yields were measured via a relative method, using quinine sulfate in 0.05 M sulfuric acid as the standard. This standard has a fluorescence quantum yield ($\Phi_{\rm E}$) of 0.52.⁴⁶ The quantum yields of PMMA thinfilm samples were measured with a Spectralon-coated integrating sphere attached to a Horiba FluoroMax-4 spectrofluorometer. Photoluminescence lifetimes were recorded on a Horiba DeltaFlex time-correlated single-photon counting Lifetime System using 330 nm pulsed LED excitation. Cyclic voltammetry (CV) experiments were measured with a CH Instruments 602E potentiostat in a nitrogenfilled glovebox. CV experiments used a 3 mm diameter glassy-carbon working electrode, Pt wire counter electrode, and silver wire pseudoreference electrode. Samples for CV experiments were dissolved in acetonitrile with 0.1 M TBAPF₆ as a supporting electrolyte, and voltammograms were recorded at a scan rate of 0.1 V/s. Ferrocene was added to the solution as an internal reference, and potentials quoted in this paper are all referenced to the ferrocene/ ferrocenium couple. NMR spectra (see Figures S3-S26 in the Supporting Information) provide evidence for bulk purity of all isolated compounds.

PMMA Film Preparation. PMMA (98 mg, 35 kDa) was dissolved in dichloromethane (1.0 mL) in a glovebox at room temperature. Then, the iridium complex (2 mg, 2 wt %) was added with stirring to form a homogeneous solution, which was drop-coated onto a quartz substrate and dried at room temperature overnight.

X-ray Crystallography Details. Single crystals were grown by layering CH₂Cl₂, CHCl₃, or ethyl acetate solutions with hexane, pentane, or diethyl ether. Crystals were mounted on Mitegen loops, and diffraction data were collected at 123(2) K with a Bruker Apex II three-circle diffractometer, using MoK α radiation ($\lambda = 0.71073$ Å).

The data were processed and refined within the instrument's APEXII software. Structures were solved in SHELXT using intrinsic phasing methods and refined in the program SHELXL. Hydrogen atoms were placed in calculated positions using standard riding models and refined isotropically. All non-hydrogen atoms were refined anisotropically. The structures of 2a, 2b, and 5b all contained a heavily disordered solvent electron density that could not be satisfactorily modeled. For these structures, the SQUEEZE function in PLATON was used. The structures of all ptz complexes (1a, 1b, 2a, 2b, and 4b) all contained one or more disordered propyl groups. The structure of 2a additionally included a rotational disorder of the 2,6dimethylphenyl ring, and 4b had rotational disorder in three of the CF₃ groups. The structure of 1b included solvent electron density that was best modeled as a disordered 2-butanone molecule, likely originating from an impurity in the ethyl acetate crystallization solvent. The 1,2 and 1,3 distances of all disordered parts were fixed with distance restraints (SADI), and rigid-bond restraints (SIMU and DELU) were used for the ellipsoid parameters. The structure of 1b gave rise to a level B checkCIF error caused by a large residual electron density peak near the disordered propyl group. Attempts to resolve this electron density by altering the disorder model were unsuccessful. The structure of 2b produced a level B checkCIF error for low C-C bond precision, which we believe arises due to the presence of three disordered propyl groups (the structure has three crystallographically independent molecules) and does not indicate any serious problems with the structure.

Computational Details. Inputs for all computations were generated from crystal structure atomic coordinates with the appropriate truncations. Gas-phase computations for the ground states of model complexes 2a', 2b', and 4b' were performed at the B3LYP-D3 level, with 6-311G(d,p) basis set for nonmetal atoms and SDD basis set containing an effective core potential for Ir. Triplet excited states were optimized in the gas phase using the UB3LYP-D3 functional and the same basis sets. Optimization of the ${}^{3}(d-d)$ states in 2a' and 2b' was performed by elongating the X⁻ ligand (Cl⁻ in 2a', CN⁻ in 2b'). Excitation energies and orbital compositions for the T₁ states were based on the optimized T₁ geometry and used the TD-M06-2X functional with the same atomic basis sets. Orbital composition analysis was performed by Multiwfn.⁴⁸

General Procedure for the Synthesis of $Ir(C^Y)_2(CNAr)(CI)$ (1a–6a). Precursor complexes were synthesized following a procedure adapted from reported literature.³⁸ The chloro-bridged Ir dimer $[Ir(C^Y)_2(\mu-CI)]_2$ (C^AY = F₂ptz, CF₃ptz, (CF₃)₂ptz, pCF₃pmi, or mCF₃pmi) in CH₂Cl₂ was combined with 2,6-dimethylphenyl isocyanide (CNAr^{dmp}) or 4-trifluoromethylphenyl isocyanide (CNAr^{4-CF₃}) (2 equiv). The resulting mixture was stirred at room temperature overnight. The reaction mixture was filtered, and the filtrate volume was reduced before adding hexane or diethyl ether to precipitate the product. The collected solid was dried under vacuum and purified either via a second precipitation or by column chromatography on silica gel using CH₂Cl₂/hexane as eluent. The final isolated products appeared as white or yellow solids.

Ir(*F*₂*p*tz)₂(*CNAr*^{*dmp*})(*CI*) (*1a*). Prepared by the general procedure, using [Ir(F₂ptz)₂(μ -Cl)]₂ (500 mg, 0.357 mmol) and 2,6dimethylphenyl isocyanide (94 mg, 0.72 mmol). The product was purified by precipitation from CH₂Cl₂/hexane to give a light brown solid. Yield: 559 mg, 94%. ¹H NMR (400 MHz, CDCl₃) δ: 7.15 (t, *J* = 7.6 Hz, 1H, ArH), 7.05 (d, *J* = 7.8 Hz, 2H, ArH), 6.47–6.36 (m, 2H, ArH), 6.02 (dd, *J* = 8.5, 2.1 Hz, 1H, ArH), 5.80 (dd, *J* = 8.0, 2.1 Hz, 1H, ArH), 4.35 (d, *J* = 7.2 Hz, 3H, NCH₃), 4.31 (d, *J* = 7.6 Hz, 3H, NCH₃), 3.33–3.26 (m, 2H, CCH₂CH₂CH₃), 2.94–2.86 (m, 2H, CCH₂CH₂CH₃), 1.01 (t, *J* = 7.3 Hz, 3H, CCH₂CH₂CH₃), 0.88–0.80 (m, 3H, CCH₂CH₂CH₃). ¹⁹F NMR (376 MHz, CDCl₃) δ: -103.04 to -103.24 (m, 1F, ArF), -103.25 to -103.41 (m, 1F, ArF), -105.95 (q, *J* = 9.0 Hz, 1F, ArF), -106.26 (q, *J* = 8.7 Hz, 1F, ArF). FT-IR (cm⁻¹): 2147 ($\bar{\nu}_{CN}$).

 $Ir(CF_3ptz)_2(CNAr^{dmp})(CI)$ (2a). Prepared by the general procedure using $[Ir(CF_3ptz)_2(\mu-CI)]_2$ (1.00 g, 0.654 mmol) and 2,6-dimethylphenyl isocyanide (171 mg, 1.30 mmol). The product was

purified by precipitation to form pale yellow powder, which was dried in vacuo. Yield: 1.05 g, 90%. ¹H NMR (400 MHz, CDCl₃) δ : 7.67 (d, J = 10.1 Hz, 2H, ArH), 7.17–7.03 (m, 5H, ArH), 6.70 (d, J = 8.2 Hz, 1H, ArH), 6.51 (d, J = 7.8 Hz, 1H, ArH), 4.36 (s, 3H, NCH₃), 4.31 (s, 3H, NCH₃), 3.41–3.25 (m, 2H, CCH₂CH₂CH₃), 2.97–2.89 (m, 2H, CCH₂CH₂CH₃), 2.13 (s, 6H, ArCH₃), 1.99–1.83 (m, 4H, CCH₂CH₂CH₃), 0.94 (dt, J = 76.9, 7.3 Hz, 6H, CCH₂CH₂CH₃). ¹⁹F NMR (376 MHz, CDCl₃) δ : –62.06 (s, 3F, CF₃), –62.12 (s, 3F, CF₃). FT-IR (cm⁻¹): 2127 ($\tilde{\nu}_{CN}$).

I(*CF*₃*ptz*)₂(*CN*)*A*^{*A*-*CF*₃})(*CI*) (*3a*). Prepared by the general procedure using [Ir(CF₃*ptz*)₂(*μ*-CI)]₂ (664 mg, 0.434 mmol) and 4-trifluor-omethylphenyl isocyanide (~149 mg, 0.868 mmol, 2 equiv). The product was purified by column chromatography on silica gel to obtain a pale-yellow solid, which was dried in vacuo. Yield: 565 mg, 70%. ¹H NMR (400 MHz, CDCl₃) δ: 7.66 (d, *J* = 10.5 Hz, 4H, ArH), 7.41 (d, *J* = 8.2 Hz, 2H, ArH), 7.17 (d, *J* = 7.3 Hz, 1H, ArH), 6.44 (d, *J* = 8.2 Hz, 1H, ArH), 6.64 (d, *J* = 7.8 Hz, 1H, ArH), 6.44 (d, *J* = 8.2 Hz, 1H, ArH), 6.64 (d, *J* = 7.8 Hz, 1H, ArH), 6.44 (d, *J* = 8.2 Hz, 1H, ArH), 1.37 (s, 3H, NCH₃), 4.31 (s, 3H, NCH₃), 3.56–3.39 (m, 1H, CCH₂CH₂CH₃), 3.24–3.08 (m, 1H, CCH₂CH₂CH₃), 2.95 (dd, *J* = 17.6, 8.0 Hz, 2H, CCH₂CH₂CH₃), 2.11–1.75 (m, 4H, CCH₂CH₂CH₃), 1.03 (t, *J* = 7.3 Hz, 3H, CCH₂CH₂CH₃), 0.99–0.89 (m, 3H, CCH₂CH₂CH₃). ¹⁹F NMR (376 MHz, CDCl₃) δ: -62.04 (s, 3F, CF₃), -62.17 (s, 3F, CF₃), -62.83 (s, 3F, CNArCF₃). FT-IR (cm⁻¹): 2118 ($\tilde{\nu}_{CN}$).

Ir((*CF*₃)₂*ptz*)₂(*CNAr*^{4-*CF*₃)(*CI*) (*4a*). Prepared by the general procedure using [Ir((*CF*₃)₂*ptz*)₂(μ -*Cl*)]₂ (520 mg, 0.289 mmol) and 4-trifluoromethylphenyl isocyanide (~99 mg, 0.58 mmol, 2 equiv). The product was purified by precipitation to obtain a yellow powder, which was dried in vacuo. Yield: 265 mg, 43%. ¹H NMR (600 MHz, CDCl₃) δ : 7.84 (d, *J* = 12.4 Hz, 2H, ArH), 7.69 (d, *J* = 7.6 Hz, 2H, ArH), 7.63 (s, 1H, ArH), 7.59 (s, 1H, ArH), 7.35 (d, *J* = 7.6 Hz, 2H, ArH), 4.32 (s, 3H, NCH₃), 4.28 (s, 3H, NCH₃), 3.64 (t, *J* = 6.9 Hz, 1H, CCH₂CH₂CH₃), 3.13 (t, *J* = 6.9 Hz, 1H, CCH₂CH₂CH₃), 3.04 (t, *J* = 8.2 Hz, 1H, CCH₂CH₂CH₃), 2.80 (t, *J* = 7.6 Hz, 1H, CCH₂CH₂CH₃), 2.01 (s, 1H, CCH₂CH₂CH₃), 1.94 (d, *J* = 6.9 Hz, 2H, CCH₂CH₂CH₃), 1.85 (t, *J* = 6.9 Hz, 1H, CCH₂CH₂CH₃), 1.05 (t, *J* = 7.2 Hz, 3H, CCH₂CH₂CH₃), 0.88 (t, *J* = 7.2 Hz, 3H, CCH₂CH₂CH₃), 0.88 (t, *J* = 7.2 Hz, 3H, CCH₂CH₂CH₃), 0.88 (t, *J* = 7.2 Hz, 3H, CCH₂CH₂CH₃), -60.16 (s, 3F, CF₃), -62.55 (s, 3F, CF₃), -62.63 (s, 3F, CF₃), -62.93 (s, 3F, CNArCF₃). FT-IR (cm⁻¹): 2154 ($\tilde{\nu}_{CN}$).}

Ir(*p*C*F*₃*pmi*)₂(*CNAr*^{dmp})(*CI*) (*5a*). The reaction was performed with [Ir(pCF₃*pmi*)₂(*μ*-CI)]₂ (266 mg, 0.196 mmol) and 2,6-dimethylphenyl isocyanide (52 mg, 0.40 mmol) according to the general procedure. The crude product was purified by precipitation from hexane to afford a light brown solid. Yield: 265 mg, 84%. ¹H NMR (400 MHz, CDCl₃) δ: 7.60 (s, 1H, ArH), 7.52 (s, 1H), 7.27 (s, 1H, ArH), 7.22 (d, *J* = 13.3 Hz, 2H, ArH), 7.10 (t, *J* = 7.6 Hz, 2H, ArH), 7.01 (d, *J* = 7.3 Hz, 2H, ArH), 6.91 (d, *J* = 7.8 Hz, 1H, ArH), 6.80 (d, *J* = 7.3 Hz, 1H, ArH), 6.56 (q, *J* = 7.9 Hz, 2H, ArH), 4.42 (s, 3H, NCH₃), 4.20 (d, *J* = 15.6 Hz, 3H, NCH₃), 2.11 (s, 6H, ArCH₃). ¹⁹F NMR (376 MHz, CDCl₃) δ: -61.62 (s, 3F, CF₃), -61.73 (s, 3F, CF₃). FT-IR (cm⁻¹): 2121 ($\tilde{\nu}_{CN}$).

Ir(*m*CF₃*pmi*)₂(*CNAr*^{*dmp*})(*CI*) (*Ga*). The reaction was performed with [Ir(mCF₃*pmi*)₂(*μ*-CI)]₂ (280 mg, 0.206 mmol) and 2,6-dimethylphenyl isocyanide (54 mg, 0.41 mmol) according to the general procedure. The crude product was purified by precipitation and dried under vacuo to obtain a white powder. Yield: 157 mg, 47%. ¹H NMR (600 MHz, CDCl₃) δ: 7.59 (s, 1H, ArH), 7.50 (s, 1H, ArH), 7.21 (s, 1H, ArH), 7.14 (s, 2H, ArH), 7.10 (d, *J* = 7.6 Hz, 4H, ArH), 7.01 (d, *J* = 7.6 Hz, 2H, ArH), 6.67 (s, 1H, ArH), 6.60 (s, 1H, ArH), 4.42 (s, 3H, NCH₃), 4.17 (s, 3H, NCH₃), 2.09 (s, 6H, ArCH₃). ¹⁹F NMR (565 MHz, CDCl₃) δ: -61.58 (s, 3F, CF₃), -61.68 (s, 3F, CF₃). FT-IR (cm⁻¹): 2123 ($\tilde{\nu}_{CN}$).

General Procedure for the Synthesis of $Ir(C^Y)_2(CNAr)(CN)$ (1b-6b). The synthesis of cyano-isocyanide complexes was carried out using a modified literature procedure.⁴³ The monochloride $Ir(C^Y)_2(CNAr)(Cl)$ (1a-6a), 1.3 equiv of AgCF₃CO₂, and MeOH were added to a round-bottom flask equipped with a Dimroth condenser. The mixture was stirred at 50 °C for 0.5 h. After the formed precipitate was removed by filtration, 1.9 equiv of NaCN pubs.acs.org/IC

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Scheme 1. Synthesis of Cyano-Isocyanide Complexes 1b-6b



dissolved in deionized water was added, and the mixture was heated to reflux for another 0.5 h while stirring. The volume of the cooled mixture was reduced to less than half, resulting in precipitation of the desired product, which was collected by filtration and carefully washed with MeOH. The crude product was dissolved in CH₂Cl₂ and purified by filtration over silica gel. After washing with CH₂Cl₂, the product was eluted using CH₂Cl₂/MeOH (95:5 v/v). If further purification was necessary, recrystallization from CH₂Cl₂/hexane or CHCl₃/hexane or precipitation from CH₂Cl₂/hexane was used. All products were dried thoroughly under vacuum.

 $Ir(F_2ptz)_2(CNAr^{dmp})(CN)$ (1b). Prepared following the general procedure described above, using $Ir(F_2ptz)_2(CNAr^{dmp})(Cl)$ (1a) (250 mg, 0.301 mmol) and AgCF₃CO₂ (97 mg, 0.44 mmol) in 25 mL of MeOH. After the AgCl precipitate was removed, NaCN (32 mg, 0.65 mmol) dissolved in 5 mL of distilled water was added to the filtrate. Yield: 107 mg, 43%. ¹H NMR (500 MHz, CD₂Cl₂) δ: 7.14 (t, J = 7.7 Hz, 1H, ArH), 7.05 (d, J = 7.4 Hz, 2H, ArH), 6.45 (t, J = 10.3Hz, 2H, ArH), 6.02 (d, J = 7.4 Hz, 1H, ArH), 5.83 (d, J = 8.0 Hz, 1H, ArH), 4.29 (d, J = 6.5 Hz, 3H, NCH₃), 4.28 (d, J = 7.5 Hz, 3H, NCH3) (Note: the previous two peaks overlapped and form an apparent triplet), 3.23-3.18 (m, 1H, CCH₂CH₂CH₃), 3.13-3.07 (m, 1H, CCH₂CH₂CH₃), 2.81 (m, J = 22.6, 7.4 Hz, 2H, CCH₂CH₂CH₃), 2.13 (s, 6H, ArCH₃), 1.89-1.78 (m, 4H, CCH₂CH₂CH₃), 1.03 (t, J = 7.2 Hz, 3H, $CCH_2CH_2CH_3$), 0.80 (t, I = 7.4 Hz, 3H, CCH₂CH₂CH₃). ¹⁹F NMR (470 MHz, CD₂Cl₂) δ : -102.97 to -103.07 (m, 1F, ArF), -103.17 to -103.26 (m, 1F, ArF), -106.95 (q, J = 8.9 Hz, 1F, ArF), -107.11 (q, J = 8.6 Hz, 1F, ArF). FT-IR $(cm^{-1}): 2145 (\tilde{\nu}_{CN}), 2123 (\tilde{\nu}_{CN}). HRMS-ESI (m/z): [M + H]^+ calcd$ for $C_{34}H_{33}F_4IrN_8$, 823.24718; found, 823.25049. $Ir(CF_3ptz)_2(CNAr^{dmp})(CN)$ (**2b**). Following the general procedure

Ir(*CF*₃*ptz*)₂(*CNAr*^{*dnip*})(*CN*) (**2b**). Following the general procedure described above, Ir(CF₃*ptz*)₂(CNAr^{*dnip*})(Cl) (**2a**) (250 mg, 0.279 mmol) was allowed to react with AgCF₃CO₂ (80 mg, 0.36 mmol) in 21 mL of MeOH. After the precipitate was removed, NaCN (26 mg, 0.53 mmol) dissolved in 4 mL of deionized water was added to the filtrate. Yield: 124 mg, 50%. ¹H NMR (600 MHz, CD₂Cl₂) δ: 7.73 (s, 1H, ArH), 7.70 (s, 1H, ArH), 7.15–7.10 (m, 3H, ArH), 7.03 (d, *J* = 7.6 Hz, 2H, ArH), 6.71 (d, *J* = 8.2 Hz, 1H, ArH), 6.54 (d, *J* = 7.6 Hz, 1H, ArH), 4.29 (s, 3H, NCH₃), 4.28 (s, 3H, NCH₃), 3.26–3.10 (m, 2H, CCH₂CH₂CH₃), 2.89–2.79 (m, 2H, CCH₂CH₂CH₃), 2.08 (s, 6H, ArCH₃), 1.97–1.89 (m, 4H, CCH₂CH₂CH₃), 1.04 (t, *J* = 7.2 Hz, 3H, CCH₂CH₂CH₃), 0.82 (t, *J* = 7.2 Hz, 3H, CCH₂CH₂CH₃). ¹⁹F NMR (565 MHz, CD₂Cl₂) δ: -62.35 (s, 3F, CF₃), -62.39 (s, 3F, CF₃). FT-IR (cm⁻¹): 2145 ($\tilde{\nu}_{CN}$), 2120 ($\tilde{\nu}_{CN}$). HRMS-ESI (*m*/*z*): [M + H]⁺ calcd for C₃₆H₃₅F₆IrN₈, 887.25964; found, 887.26196. *Ir*(*CF₃ptz*)₂(*CNAr*^{4-*CF*₃)(*CN*) (**3b**). Following the general procedure}

 $Ir(CF_3ptz)_2(CNAr^{4-CF_3})(CN)$ (**3b**). Following the general procedure described above, $Ir(CF_3ptz)_2(CNAr^{4-CF_3})(Cl)$ (**3a**) (55 mg, 0.059 mmol) was allowed to react with AgCF₃CO₂ (18 mg, 0.081 mmol) in

4 mL of MeOH. This step was performed in a nitrogen atmosphere using Schlenk techniques. After the AgCl precipitate was removed, NaCN (5 mg, 0.1 mmol) dissolved in 1 mL of deionized water was added to the filtrate. Yield: 15 mg, 27%. ¹H NMR (600 MHz, CD₂Cl₂) &: 7.72 (d, *J* = 5.5 Hz, 2H, ArH), 7.66 (d, *J* = 8.2 Hz, 2H, ArH), 7.37 (s, 1H, ArH), 7.35 (s, 1H, ArH), 7.15 (d, *J* = 7.6 Hz, 1H, ArH), 7.13 (d, *J* = 7.6 Hz, 1H, ArH), 6.65 (d, *J* = 8.2 Hz, 1H, ArH), 6.48 (d, *J* = 8.2 Hz, 1H, ArH), 4.30 (s, 3H, NCH₃), 4.29 (s, 3H, NCH₃), 3.30–3.25 (m, 1H, CCH₂CH₂CH₃), 3.10–3.05 (m, 1H, CCH₂CH₂CH₃), 1.97–1.83 (m, 4H, CCH₂CH₂CH₃), 1.05 (t, *J* = 7.2 Hz, 3H, CCH₂CH₂CH₃), 0.92 (t, *J* = 7.6 Hz, 3H, CCH₂CH₂CH₃), ¹⁹F NMR (565 MHz, CD₂Cl₂) &: -62.37 (s, 3F, CF₃), -62.40 (s, 3F, CF₃), -63.26 (s, 3F, CNArCF₃). FT-IR (cm⁻¹): 2143 ($\tilde{\nu}_{CN}$), 2120 ($\tilde{\nu}_{CN}$). HRMS-ESI (*m*/*z*): [M + H]⁺ calcd for C₃₃H₃₀F₉IrN₈, 927.21572; found, 927.21570. *Ir*((*CF₃)*₂ptz)₂(*CNAr*^{4-CF₃)(*CN*) (**4b**). Following the general procedure}

described above, Ir((CF₃)₂ptz)₂(CNAr^{4-CF₃})(Cl) (4a) (226 mg, 0.211 mmol) was allowed to react with AgCF₃CO₂ (60 mg, 0.27 mmol) in 16 mL of MeOH. After the precipitate was removed, NaCN (20 mg, 0.41 mmol) dissolved in 3 mL of deionized water was added to the filtrate. Recrystallization of the crude product from CHCl₃/hexane resulted in a colorless solid. Yield: 100 mg, 45%. ¹H NMR (400 MHz, CDCl₃) δ : 7.84 (s, 1H, ArH), 7.81 (s, 1H, ArH), 7.72 (s, 1H, ArH), 7.70 (s, 1H, ArH), 7.63 (s, 2H, ArH), 7.36 (s, 1H, ArH), 7.33 (s, 1H, ArH), 4.28 (s, J = 5.5 Hz, 3H, NCH₃), 4.27 (s, J = 5.5 Hz, 3H, NCH₃), 3.60-3.52 (m, 1H, CCH₂CH₂CH₃), 3.24-3.16 (m, 1H, CCH₂CH₂CH₃), 3.03-2.95 (m, 1H, CCH₂CH₂CH₃), 2.82-2.74 (m, 1H, CCH₂CH₂CH₃), 2.12–2.05 (m, 1H, CCH₂CH₂CH₃), 2.02–1.91 (m, 3H, $CCH_2CH_2CH_3$), 1.12 (t, J = 7.3 Hz, 3H, $CCH_2CH_2CH_3$), 0.90 (t, J = 7.3 Hz, 3H, $CCH_2CH_2CH_3$). ¹⁹F NMR (376 MHz, $CDCl_3$) δ : -59.89 (s, 3F, CF₃), -60.70 (s, 3F, CF₃), -62.57 (s, 3F, CF₃), -62.61 (s, 3F, CF₃), -62.94 (s, 3F, CNArCF₃). FT-IR (cm⁻¹): 2166 ($\tilde{\nu}_{CN}$), 2127 ($\tilde{\nu}_{CN}$). HRMS-ESI (m/z): [M + H]⁺ calcd for C37H28F15IrN8, 1063.19049; found, 1063.19080.

Ir(*pCF*₃*pmi*)₂(*CNAr*^{dmp})(*CN*) (*5b*). Following the general procedure described above, Ir(pCF₃pmi)₂(CNAr^{dmp})(CI) (5a) (149 mg, 0.184 mmol) was allowed to react with AgCF₃CO₂ (51 mg, 0.23 mmol) in 13 mL of MeOH. After the AgCl precipitate was removed, NaCN (17 mg, 0.35 mmol) dissolved in 3 mL of deionized water was added to the filtrate. Precipitation of the crude product from CH₂Cl₂/hexane resulted in a colorless powder. Yield: 96 mg, 65%. ¹H NMR (600 MHz, CD₂Cl₂) δ: 7.60 (d, *J* = 2.1 Hz, 1H, ArH), 7.59 (d, *J* = 1.4 Hz, 1H, ArH), 7.33 (s, 1H, ArH), 7.31 (s, 1H, ArH), 7.09 (t, *J* = 7.6 Hz, 1H, ArH), 7.00 (d, *J* = 7.6 Hz, 2H, ArH), 6.88 (d, *J* = 7.6 Hz, 1H, ArH), 6.53 (d, *J* = 7.6 Hz, 1H, ArH), 4.33 (s, 3H, NCH₃), 4.08 (s, 3H, NCH₃), 2.06



Figure 1. Molecular structures of 1b, 2b, and 4b-6b from single-crystal X-ray diffraction. Ellipsoids are shown at the 50% probability level with hydrogen atoms and solvent molecules omitted.

(s, 6H, ArCH₃). ¹⁹F NMR (565 MHz, CD₂Cl₂) δ : -61.97 (s, 3F, CF₃), -61.99 (s, 3F, CF₃). FT-IR (cm⁻¹): 2137 ($\tilde{\nu}_{CN}$), 2108 ($\tilde{\nu}_{CN}$). HRMS-ESI (*m*/*z*): [M + H]⁺ calcd for C₃₂H₂₅F₆IrN₆, 801.17524; found, 801.17511.

Ir(*m*CF₃*pmi*)₂(*CNAr*^{dmp})(*CN*) (*6b*). Following the general procedure described above, Ir(mCF₃pmi)₂(CNAr^{dmp})(CI) (*6a*) (157 mg, 0.194 mmol) was allowed to react with AgCF₃CO₂ (55 mg, 0.25 mmol) in 14 mL of MeOH. This first step was performed in a nitrogen atmosphere using Schlenk techniques. After the AgCl precipitate was removed, NaCN (18 mg, 0.37 mmol) dissolved in 3 mL of deionized water was added to the filtrate. Recrystallization of the crude product from CHCl₃/hexane resulted in a colorless powder. Yield: 68 mg, 45%. ¹H NMR (400 MHz, CDCl₃) δ: 7.57 (s, 1H, ArH), 7.53 (s, 1H, ArH), 7.19 (s, 1H, ArH), 7.15–7.08 (m, 6H, ArH), 7.00 (d, *J* = 7.3 Hz, 2H, ArH), 6.74 (s, 1H, ArH), 6.53 (s, 1H, ArH), 4.37 (s, 3H, NCH₃), 4.08 (s, 3H, NCH₃), 2.06 (s, 6H, ArCH₃). ¹⁹F NMR (376 MHz, CDCl₃) δ: -61.60 (s, 3F, CF₃), -61.64 (s, 3F, CF₃). FT-IR (cm⁻¹): 2127 ($\tilde{\nu}_{CN}$), 2106 ($\tilde{\nu}_{CN}$). HRMS-ESI (*m*/*z*): [M + H]⁺ calcd for C₃₂H₂₃F₆IrN₆, 801.17524; found, 801.17389.

RESULTS AND DISCUSSION

Synthesis. The six neutral bis-cyclometalated iridium cvano-isocvanide complexes described in this work were prepared as outlined in Scheme 1, following a procedure previously reported for related compounds with substituted 2phenylpyridine cyclometalating ligands.⁴³ In this reaction, the precursor monoisocyanide, monochloride complex Ir- $(C^Y)_2(CNAr)(Cl)$ (1a-6a) is combined with 1.3 equiv of AgCF₃CO₂ in methanol, and the mixture is stirred for 0.5 h at 50 °C. After filtering to remove AgCl, the filtrate is refluxed with an aqueous solution containing 1.9 equiv of NaCN for 0.5 h. Concentration of the reaction solution precipitates the crude product, which is collected and purified by elution of a CH₂Cl₂ solution through a short plug of silica and in some cases additionally by recrystallization. The six compounds combine five different cyclometalating ligands and two different aryl isocyanides. Three 5-aryl-1,2,4-triazole cyclometalating ligands,

 F_2 ptz, CF₃ptz, and (CF₃)₂ptz, with varying substituents on the aryl ring are included, along with the 1-methyl-3-aryl-imidazol-2-ylidine (NHC) cyclometalating ligands pCF₃pmi and mCF₃pmi. The two isocyanides are 2,6-dimethylphenyl isocyanide (CNAr^{dmp}), which is available commercially and stable as a free ligand, and 4-trifluoromethylphenyl isocyanide (CNAr^{4-CF₃}), which is not very stable and must be coordinated to iridium immediately after preparation. The identity and purity of all six complexes were ascertained by high-resolution mass spectrometry and ¹H and ¹⁹F NMR spectroscopy. NMR spectroscopy is consistent with the compounds belonging to the C_1 point group, with each cyclometalating ligand residing in a unique chemical environment. Infrared spectroscopy data for C=N stretching bands were also collected to further differentiate the target compounds (1b-6b) from their precursor chloride complexes (1a-6a). For the precursor complexes, we clearly observe a single absorption band in the C≡N stretching region attributed to the isocyanide, while for the cyano-isocyanide complexes, we observe two bands in the same region.

X-ray Crystal Structures. Single-crystal X-ray diffraction validates the molecular structures of five of the mixed cyanoisocyanide complexes. All structure refinement data are summarized in the Supporting Information, Tables S1–S4. The structures are shown in Figure 1, with hydrogen atoms and solvate molecules omitted. The triazole rings in 1b–4b and the NHCs in 5b and 6b are arranged in a trans disposition. The isocyanide C \equiv N internuclear distances and C \equiv N– C(aryl) angles vary little, indicating that these values are not greatly influenced by the identity of the C^Y ligand. The isocyanide C \equiv N bond distances are short (\leq 1.17 Å) and the angles near-linear (\geq 163°), suggesting that π backbonding into the isocyanide is minor. For all 5 complexes, the C \equiv N internuclear distance for the cyanide ligand is \approx 1.15 Å. Crystal structures of two of the chloride precursors, 1a and 2a, were also obtained and are shown in Figures S1 and S2 of the Supporting Information. Comparing the chloride precursors to the cyanide counterparts, one slight difference is in the $Ir-C_{aryl}$ bond distance trans to the X⁻ ligand (Cl⁻ in 1a/2a, CN⁻ in 1b/2b). This distance is on average ca. 0.04 Å longer in the cyanide complexes than in the chloride complexes, suggesting a stronger trans influence of cyanide compared to chloride.

Electrochemistry. Figure 2 shows cyclic voltammograms of complexes **1b**–**6b**, with the data summarized in Table 1. All



Figure 2. Cyclic voltammograms of complexes 1b-6b, recorded in MeCN with 0.1 TBAPF₆ supporting electrolyte. A glassy carbon working electrode, platinum wire counter electrode, and silver wire pseudoreference electrode were used. Potentials are referenced to an internal standard of ferrocene. Separate anodic (black) and cathodic (red) traces were recorded. In 1b-4b, these are plotted on the same scale, and in 5b-6b, there are no peaks in the cathodic scan so only the anodic (oxidation) sweep is shown.

redox waves in these compounds are irreversible, which is typically the case for cyclometalated iridium complexes with isocyanide ancillary ligands.^{35,39,40} NHC-based complexes **5b**

Table 1. Cyclic Voltammetry Data for Complexes 1b-6b

	$(E \text{ vs FcH}^+/\text{FcH})$ (V)				
	E _{p,a}	$E_{\rm p,c}$			
1b	1.39	-2.66, -2.82			
2b	1.35	-2.64			
3b	1.38	-2.43, -2.66			
4b	1.76	-2.33, -2.42			
5b	1.20	N.D. ^a			
6b	1.17	N.D. ^a			

^aNo cathodic peaks observed within the solvent window.

and **6b** are particularly difficult to reduce, and sweeping cathodically, there are no clear reduction waves, out to about -2.8 V vs the ferrocenium/ferrocene (FcH⁺/FcH) couple. This shows that the LUMO energies in the NHC compounds are higher in energy than those of the aryl-triazole iridium complexes, which have clearly resolved albeit irreversible first reduction waves in the range of -2.33 (4b) to -2.65 (1b) V. The potentials of these reduction waves in 1b-4b are dependent on the substituent pattern of the cyclometalating ligand, consistent with a LUMO that is primarily localized on the cyclometalating ligand. As a specific comparison, we consider the potentials of 3b and 4b, which differ by the number of CF_3 groups on the ptz ligand. In complex 3b, the CF₃ptz cyclometalating ligand has a single CF₃ group, and it is reduced with a peak potential of -2.43 V. In complex 4b, each C^N ligand has two CF₃ groups, and the corresponding reduction potential is anodically shifted (more positive) by 100 mV. The influence of the second CF_3 group in 4b is even more pronounced when comparing the formal Ir^{IV}/Ir^{III} potentials of 3b and 4b, consistent with the HOMO having significant contribution from the cyclometalated aryls. In 3b, the peak anodic (oxidation) potential is observed at 1.38 V in 3b, shifting to 1.76 V in 4b. The electronic differences between the triazole and NHC-based cyclometalating ligands are apparent when comparing the formal Ir^{IV}/Ir^{III} redox waves of complexes 1b-2b and 5b-6b. All four complexes have the 2,6dimethylphenyl isocyanide and cyano ancillary ligands. Complexes 1b and 2b, which have aryl-triazole C^N ligands, have anodic peak potentials that occur at 1.39 and 1.35 V, respectively. These potentials cathodically shift by at least 150 mV when switching to NHC-based C^C: ligands for complexes 5b and 6b. For complexes 2b and 3b, which both have the trifluoromethylated aryl-triazole-based cyclometalating ligand CF₃ptz, the peripheral substitution of the isocyanide has very little effect on the HOMO energy as indicated by similar anodic potentials (1.35 and 1.38 V, respectively), although the reduction potential is over 210 mV more positive in 3b where the isocyanide is CNAr^{4-CF₃}. The large separation between the reduction and oxidation potentials suggests large HOMO-LUMO gaps of at least 3.8 eV in each case, which makes it possible for the compounds to have deep-blue phosphorescence.

Photophysics. Overlaid UV-vis absorption spectra of complexes 1a-6a and 1b-6b are shown in Figure 3. Absorption spectra for precursor chloride complexes 1a-6a are shown in black solid lines and spectra for the cyanoisocyanide complexes 1b-6b are shown in red dashed lines. In all cases, the low-energy absorption bands of the cyanoisocyanide complexes are blue-shifted relative to their precursor chloride complexes. These low-energy bands are assigned as metal-to-ligand charge-transfer (MLCT) bands involving the $d\pi$ HOMO and the C^Y-centered LUMO. Replacing a π -donating chloride with a π -accepting cyanide ligand stabilizes the HOMO and other nearby $d\pi$ orbitals, resulting in a larger HOMO-LUMO gap and a blue-shift of the low-energy bands. As a result, the MLCT bands for these compounds occur in the UV region. In complexes 1b-6b, all absorption is in the UV region, tailing to baseline by 380 nm and resulting in a colorless appearance for bulk solids and solutions of these compounds. In the UV region, there is strong absorption assigned to $\pi
ightarrow \pi^*$ transitions on the ligands along with lower-energy shoulders that depend on the identity of the cyclometalating ligand.



Figure 3. Overlaid UV-vis absorption spectra of complexes 1a-6a and 1b-6b. UV-vis absorption spectra of monoisocyanide monochloride complexes (black solid line) and cyano-isocyanide complexes (red dashed line) were recorded in CH_2Cl_2 at room temperature.

The photoluminescence spectra for complexes 1b-6b are shown in Figure 4, as black solid lines for spectra recorded in CH₂Cl₂ solution and blue dashed lines for spectra recorded in PMMA film. All photophysical data is summarized in Table 2. Triazole compounds 1b-4b luminesce in both solution and polymer film, and the spectra for each compound do not differ much between solution and PMMA film. Comparing triazole complexes 1b-3b, there are only subtle differences in the photoluminescence spectra, which show in each case three vibronic maxima at room temperature. The E_{0-1} peak, the center peak of the vibronic progression, is the most intense, occurring at 438 nm for the F₂ptz complex (1b) and subtly shifted to the red, 446 nm (2b) and 444 nm (3b), for the CF_3 ptz complexes. Complex 4b, in which the $(CF_3)_2$ ptz ligand has a second CF₃ group, displays photoluminescence with poorly resolved vibronic structure, a characteristic we have previously observed in cationic bis-isocyanide complexes with the $(CF_3)_2$ ptz cyclometalating ligand.³⁵ The peak emission wavelength in compound 4b is at 462 nm in CH₂Cl₂ and 457 nm in PMMA thin film. Compared to the triazole-based complexes, the NHC-based complexes 5b and 6b phosphoresce deeper in the blue region when doped into PMMA. These NHC compounds exhibit a shoulder below 400 nm, with their maxima blue-shifted by at least 30 nm (1700 cm^{-1}) from those of the triazole-based complexes (1b-4b).

The red dotted lines shown in Figure 4 are spectra recorded at 77 K in frozen solvent glass. At low temperature, the vibronic structure becomes much more pronounced, and for pubs.acs.org/IC



Figure 4. Overlaid photoluminescence spectra of complexes 1b-6b. Photoluminescence spectra in solution (CH₂Cl₂) are drawn with black solid lines, spectra in 2 wt % PMMA film at room temperature are depicted as blue dashed lines, and low-temperature spectra in frozen CH₂Cl₂/toluene at 77 K are shown as red dotted lines. Excitation wavelengths for the samples are 287 nm for **5b** and 310– 320 nm for **1b–4b** and **6b**.

the compounds that show photoluminescence both at room temperature in CH₂Cl₂ solution and at 77 K in solvent glass, the peak maxima in these two conditions are nearly the same, with very minor rigidochromic blue shifts. The observation that the emission maxima vary little from fluid solution to rigid medium indicates that the emissive T₁ state has substantial C^N-centered ³($\pi \rightarrow \pi^*$) character, an observation we have made in many other isocyanide-ligated cyclometalated iridium complexes. Among all four triazole-based complexes, the vibronic structure in the room-temperature phosphorescence of (CF₃)₂ptz compound **4b** is least pronounced, sharpening considerably at 77 K.

Triazole-derived complexes 1b-4b are all moderately luminescent in CH₂Cl₂ solution at room temperature, with photoluminescence quantum yields (Φ_{PL}) spanning from 0.047 (1b) to 0.17 (4b). Excitation spectra for these four compounds were recorded, along with 2a which is the only chloride complex which luminesces in solution (see below). The excitation spectra overlay very well with the UV-vis absorption spectra (see Figures S27-S31 in the Supporting Information), ruling out luminescence from an impurity and indicating that Kasha's rule is followed. Photoluminescence lifetimes were determined for the solution samples that are luminescent at room temperature. These are summarized in Table 2 as well, and radiative and nonradiative rate constants (k_r and k_{nr}) for these samples are collected in Table S5 of the Supporting Information. For complexes 1b-3b, the lifetimes pubs.acs.org/IC

Table 2. Photophysical Data for Complexes 1b-6b

	UV-vis absorption	photoluminescence						
		CH ₂ Cl ₂ , RT			77 K	PMMA, RT		
	λ (nm) ($\varepsilon \times 10^{-3}$, M ⁻¹ cm ⁻¹)	λ (nm)	$\Phi_{ ext{PL}}$	τ (μs)	λ (nm)	λ (nm)	$\Phi_{ ext{PL}}$	(CIE <i>x,</i> CIEy)
1b	261 (34), 277 (22), 288 (13), 323 (4.8)	411, 437, 464, 495(sh)	0.047	6.4	406, 433, 465, 497, 537(sh)	413, 438, 465, 503(sh)	0.14	(0.16, 0.13)
2b	262 (20), 288 (7.7), 334 (2.6)	418, 445, 472, 508(sh)	0.090	7.6	414, 442, 464, 475, 497(sh)	419, 446, 473, 513(sh)	0.23	(0.16, 0.14)
3b	245 (40), 264 (30), 302 (11)	417, 444, 472, 507(sh)	0.064	4.0	413, 433(sh), 441, 446, 473, 500(sh), 510(sh), 539(sh)	417, 444, 472, 507(sh)	0.28	(0.16, 0.14)
4b	261 (39), 300 (15)	432(sh), 462, 484(sh)	0.17	31	422, 449, 479, 512(sh)	429(sh), 457, 473(sh)	0.38	(0.19, 0.24)
5b	259 (24), 288 (16)	а	а	а	388, 395, 411, 420, 433	379(sh), 402, 421	0.074	(0.16, 0.08)
6b	262 (21), 280 (16)	а	а	а	386, 396, 408, 420, 433	387, 408, 431(sh)	0.22	(0.16, 0.06)

^aNo room-temperature luminescence observed in solution.

span from 4.0 to 7.6 μ s, while the emission lifetime for complex 4b is 31 μ s, significantly longer than the rest. We likewise observed a substantially longer lifetime for the cationic bisisocyanide complex with the same C^N ligand,³⁵ and these observations suggest there is smaller SOC in the triplet states of these (CF₃)₂ptz compounds (see DFT Calculations section below).⁴⁹ The longer lifetimes may also be in part due to the additional steric bulk in the $(CF_3)_2$ ptz ligand rigidifying the excited state and inhibiting nonradiative decay. Consistent with this, the nonradiative rate constant (k_{nr}) is smallest for 4b, compared to all other compounds that luminesce in solution (Table S5). All six complexes are luminescent at room temperature when doped into PMMA (2 wt %). In this medium, the quantum yields are increased $2 \times$ or more compared to the solution values. Quantum yields for the ptz complexes span from 0.14 (1b) to 0.38 (4b), with little effect of the isocyanide given the very similar values for CF3ptz complexes 2b ($\Phi_{PL} = 0.23$, CNAr^{dmp}) and 3b ($\Phi_{PL} = 0.28$, CNAr^{4-CF₃}). In the NHC compounds, which phosphoresce deeper in the blue region, the quantum yields are 0.074 (5b) and 0.22 (6b), the latter being one of the highest observed for iridium complexes which phosphoresce the deep-blue extreme of the spectrum.^{32,33,38}

Among all six chloride precursors for these compounds, only the CF_3ptz complex (2a) is luminescent in solution with a quantum yield of 0.0024 and emission maximum at 455 nm. In polymer films, both the F₂ptz and CF₃ptz complexes with the CNAr^{dmp} ancillary ligand (1a and 2a) are weakly emissive (see Figures S32-S33 and Table S66 in the Supporting Information). The photoluminescence maxima of cyano complexes 1b and 2b in PMMA are only slightly blue-shifted from those of chloro complexes 1a and 2a, by about 300 cm⁻¹, indicating that the HOMO stabilization and larger HOMO-LUMO gap brought on by the π -accepting cyano ligand only have a small impact on the energy of the primarily ligandcentered triplet state. However, substitution of chloride for cyanide has a dramatic impact on the photoluminescence quantum yields. Most of the chloride complexes are completely nonluminescent, and Φ_{PL} for 1a and 2a in PMMA is modest, 0.013 and 0.043, respectively. The photoluminescence quantum yields of the cyano compounds are at least a factor of 5 larger, underscoring the importance of strong σ -donor ligand sets for efficient blue phosphorescence.

CIE 1931 coordinates, determined from the photoluminescence spectra in PMMA, are summarized in Figure 5. Complex



Figure 5. Chromaticity diagram showing the (CIE*x*, CIE*y*) coordinates of **1b**-**6b**.

4b, with the $(CF_3)_2$ ptz cyclometalating ligand, luminesces in the sky blue region with CIE coordinates = (0.19, 0.25). The remaining compounds have emission colors that fall in the deep blue region, previously defined as CIEy < 0.15 and (CIEx + CIEy) < 0.30.⁵⁰ The triazole compounds have (CIEx, CIEy) = (0.16, 0.13-0.14) for complexes **1b**-**3b**, whereas in the NHC-based compounds **5b** and **6b**, CIEy is <0.1, significantly deeper into the blue region. These CIE values show that the compounds described here, which pair up triazole- and NHC-based cyclometalating ligands with mixed cyano-isocyanide ancillary ligand sets, produce photoluminescence spectral profiles that are in the correct range for application in color displays.

DFT Calculations. DFT calculations were performed to provide insight into two key findings in this work: (i) the electronic consequences of substituting a Cl⁻ with CN⁻, and (ii) the large differences in photoluminescence between CF₃ptz complex **2b**, and its $(CF_3)_2$ ptz analogue **4b**, where a second CF₃ group is added to the cyclometalated aryl ring. Chemical structures of the truncated model complexes **2a**', **2b**', and **4b**', along with contour plots for their frontier orbitals, are shown in Figure 6. The truncated model compounds include phenylisocyanide instead of CNAr^{dmp} or CNAr^{4-CF₃} and replace the propyl group on the ptz ligand with a methyl group. The HOMO and LUMO compositions fall in

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Figure 6. Structures of the truncated model complexes used for DFT calculations and contour plots (0.02 au) and energies for the HOMO and LUMO orbitals. Geometries were optimized in the gas phase, using B3LYP-D3 functional and 6-311G(d,p) basis set for nonmetals and SDD with effective core potential for Ir.

line with what is normally observed for bis-cyclometalated iridium complexes. The HOMO is a mixture of Ir $5d\pi$ and ptz aryl π character, with significant contribution from the X⁻ ligand, Cl⁻ in 2a' and CN⁻ in 2b' and 4b'. In contrast, the LUMO is a π^* orbital almost exclusively localized on the ptz, with negligible contribution from Ir or the X⁻ ligand. Comparing chloride complex 2a' and cyanide complex 2b', we compute a 0.28 eV stabilization of the HOMO in the latter, with minimal difference in LUMO energy. The frontier orbital energy differences between 2b' and 4b' are in good agreement with the differences in their respective redox potentials (Figure 2 and Table 1). Addition of the second CF₃ group in 4b' stabilizes the HOMO by 0.28 eV and the LUMO by 0.21 eV.

One of the key findings from the experimental photophysics is that substitution of chloride for cyanide does not have a large effect on photoluminescence wavelength, but does result in a substantial increase in $\Phi_{\rm PI}$. Consistent with this, the computed T_1 energies of chloride complex 2a' (2.57 eV) and cyanide complex 2b' (2.58 eV) are nearly identical, and both are primarily HOMO \rightarrow LUMO in nature. Our hypothesis is that the higher quantum yields in the cyanide complexes are due to a destabilization of ligand-field d-d states brought on by the strong-field cyanide ligand, shutting off a nonradiative decay pathway that involves population of these nonemissive d-dstates. To investigate this possibility, we followed the approach outlined by Giussani et al. for computationally locating these dissociative d-d states,⁵¹ elongating the Ir-X bond and searching for a minimum on the triplet energy surface. A summary of these findings is given in Figure 7. In chloride complex 2a', the dissociative ${}^{3}(d-d)$ state is very close to the emissive T₁ state, higher by only 0.02 eV, nearly equal to $k_{\rm B}T$ at 298 K. In contrast, with the stronger-field cyanide ligand in **2b**', the energy separation between T_1 and ${}^3(d-d)$ increases to 0.97 eV, consistent with the idea that population of this



Figure 7. DFT-computed triplet states for model complexes **2a**' and **2b**'. Optimized triplet state energies were determined in the gas phase using the UB3LYP-D3 functional, with the same basis sets as the ground-state calculations (Figure 6). Excitation energies for T_1 were determined using the TD-M06-2X method, again with the same basis sets.

nonradiative state is no longer possible, leading to the large increase in $\Phi_{\text{PL}}.$

DFT also provides some insights into the origins of the disparate photoluminescence properties of CF_3ptz complexes **2b**/**3b** and complex **4b**, where a second CF_3 group has been added to the ptz ligand. We noted above that **4b** has a substantially red-shifted photoluminescence maximum, poorly resolved vibronic structure, and significantly longer lifetime than **2b**/**3b**. The computed HOMO–LUMO gap in complex **4b**' (4.60 eV) is slightly larger than that of **2b**' (4.53 eV). However, consistent with the photoluminescence data, the T_1 excitation energy for **4b**' is *lower* than that of **2b**' by 0.18 eV. These findings suggest that the singlet—triplet gap, S_1 — T_1 , is significantly larger in **4b**' than in **2b**'. The T_1 states in both

compounds are best described as ³MLCT states with predominant HOMO \rightarrow LUMO character. Thus, the triplet states in these molecules are very similar. However, SOC is a very important determinant of the radiative rate constant for phosphorescent compounds,⁴⁹ which involves mixing of T₁ with higher-lying ¹MLCT states. Strong SOC results in larger radiative rate constants and shorter lifetimes. Although a thorough evaluation of SOC pathways in these compounds is beyond the scope of this work, the DFT calculations we have performed suggest that the larger singlet-triplet gap in 4b results in weaker SOC, leading to the much longer phosphorescence lifetime. Consistent with this, the experimentally determined k_r value for **4b** is the smallest in the series (see Table S5). What is less clear from the available data is why the vibronic structure is less pronounced in 4b (see Figure 4) compared to the other ptz complexes. Normally a loss of vibronic structure indicates more charge-transfer character in the T₁ state, though as mentioned above the orbital compositions of the T_1 states are very similar in 2b' and 4b'. Nonetheless, DFT reproduces the trend in T_1 energies observed in the photoluminescence spectra and suggests a possible origin for the longer decay lifetime in 4b.

CONCLUSION

This work describes six charge-neutral blue-phosphorescent bis-cyclometalated iridium complexes with the general formula $Ir(C^Y)_2(CNAr)(CN)$, C^Y being a triazolyl or NHC-derived cyclometalating ligand and CNAr an aryl isocyanide. The combination of strong-field ligands in these complexes leads to relatively larger HOMO-LUMO gaps; the triazole or NHCs result in high-energy π^* LUMOs, and the π -acidic isocyanides and cyanide further stabilize the Ir $d\pi$ HOMOs. All compounds exhibit blue phosphorescence upon UV excitation, with moderate to good quantum yields for samples immobilized in PMMA. While emission color is mainly dictated by the identity of the cyclometalating ligand, introduction of the cyanide ligand, in addition to the isocyanide, pushes the spectral profile further to the highenergy region of the spectrum, generating neutral iridium(III) complexes that show pure deep-blue photoluminescence. The cyanide also contributes to the large ligand-field splitting in these compounds, which raises the energy of deleterious d-dstates and shuts off a common nonradiative decay pathway, increasing Φ_{PL} . In addition, this class of complexes presents some potential advantages for future development and applications. Unlike our previous cationic bis-isocyanide complexes, these complexes are charge-neutral, which may be advantageous for optoelectronic device fabrication by thermal evaporation.⁴² Furthermore, the cyanide and isocyanide can in principle be further derivatized with Lewis acids⁵² and nucleophiles,53 respectively, allowing further tuning and optimization of their photophysics. This work presents a promising new class of blue-phosphorescent emitters, addressing the long-standing challenge in the field of optoelectronics of designing materials that have efficient blue luminescence.

ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00103.

X-ray crystallography summary tables, additional X-ray crystal structures, NMR spectra, excitation spectra,

additional emission spectra, radiative and nonradiative rate constants for 2a and 1b-4b, summary of photophysical data for 1a-6a, and DFT-optimized Cartesian coordinates (PDF)

Accession Codes

CCDC 2052924–2052930 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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Notes

The authors declare no competing financial interest.

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