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"Click" Synthesis of Heteroleptic Tris-cyclometalated Iridium(III) Complexes: Cu(I) Triazolide Intermediates as Transmetalating Reagents

Shuang Liu, Peter Müller, Michael K. Takase, Timothy M. Swager*

Abstract

Efficient synthesis of heteroleptic tris-cyclometalated Ir(III) complexes *mer*-Ir(C^N)$_2$(trpy) (trpy = 2-(1*H*-[1,2,3]triazol-4-yl)pyridine) is achieved by using the Cu(I)-triazolide intermediates formed in "click" reactions as transmetalating reagents. Ligand preparation and cyclometalation of Ir(III) is accomplished in one pot. The robust nature of click chemistry provides opportunities to introduce different functional groups to the cyclometalated system, for example alkyl, perfluoroalkyl and aryl moieties. All the meridional isomers show short-lived phosphorescence at room temperature, both in solution and in the solid state. DFT calculations indicated that the phosphorescence of *mer*-Ir(C^N)$_2$(trpy) is attributed to the ^{3}MLCT and ^{3}LC mixed excited states, also supported by the broad spectral shape and hypsochromic shift upon media rigidification. The luminescence efficiency and excited state lifetimes of the cyclometalated complexes can be tuned by varying the substituents on the triazole ring, while the emission color is mainly determined by the phenylpyridine-based ligands. Moreover, the trpy ligand can acquire the N^N chelating mode under selective reaction conditions. *mer*-Ir(C^N)$_2$(trpy) complexes isomerize into cationic [Ir(C^N)$_2$(N^N_trpy)]$^+$ species instead of their *fac* isomers upon heating or UV radiation. This can be explained by the strong *trans* influence exerted by the phenyl groups. The weakened Ir-C(trpy) bonds are likely to be activated and protonated, leading to the switch of the trpy ligand to a thermodynamically more stable N^N chelating mode.

Introduction

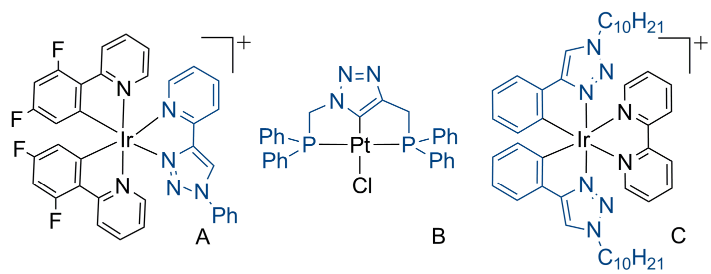
Phosphorescence-based organic light emitting diodes (OLEDs) have drawn significant attention due to their ability to harvest both singlet and triplet excitons for electroluminescence.[1] Cyclometalated iridium(III) complexes stand out as the most promising high performance emitters due to their strong Ir-C bonds, which ensure good photo and thermal stability and destabilize the thermally accessible, non-emissive metal centered (MC) states.[2] This family of complexes exhibits favorable photophysical properties, such as high quantum efficiency, short excited state lifetimes, and, most importantly, tunable emission colors. The triplet emission originates from a mixture of metal-to-ligand charge transfer (^{3}MLCT) and ligand centered (^{3}LC) excited states. This strong coupling between the d-orbitals of iridium and the π-orbitals of the ligands allows facile color tuning through the cyclometalating and ancillary ligands[3,4] Aside from their appealing applications as OLEDs, cyclometalated compounds can also be used in light-emitting electrochemical cells (LECs),[5,6] and as chemical sensors[7-11] and bioimaging labels.[12-16] Therefore, efficient and versatile synthetic methods that allow access to a library of cyclometalated compounds will greatly facilitate the screening process for various applications.

Bis- and tris-cyclometalated Ir(III) complexes are commonly synthesized from chloro-bridged Ir(III) dimers $[Ir(C^\wedge N)_2Cl]_2$, which can be readily prepared from $IrCl_3 \cdot nH_2O$ and cyclometalating ligands. Thompson *et al*. reported the first selective synthesis of *mer* and *fac* isomers by controlling the reaction temperatures,[17] which stimulated studies on differentiating the photophysical properties of the two isomers. More recently, μ-hydroxy-bridged Ir(III) dimers and solvated monomeric Ir(III) precursors have also been used to achieve *fac*/*mer* selectivity under mild reaction conditions.[18]

Transmetalation of metal-halide bonds with organometallic reagents has also been studied as an alternative approach. For example, Hg(ppy)Cl (ppy = 2-phenylpyridine) has been used to prepare mono-cyclometalated Ir(III) compounds.[19] However, this method has not been extensively applied due to reluctance to work with Hg compounds. Recently, organozinc reagents were used to selectively generate meridional tris-cyclometalated Ir(III) complexes.[20] The organozinc reagents were prepared *in-situ* via metal exchange reactions after the ligands were treated with *n*-BuLi. In all instances, the ligands were pre-functionalized to facilitate the lithiation. Unfortunately, the need for highly reactive *n*-BuLi and additional synthetic procedures limited the scope of this method. Organolithiums have proven to be inferior to organozincs due to the low stability,[20] despite their applications in the synthesis of bis-cyclometalated Pd(II)/Pt(II) complexes.[21-23] Therefore, it is highly desirable to explore new organometallic reagents that show high functional group tolerance and ease of preparation.

One of the most popular protocols of copper mediated reactions is the Huisgen 1,3-dipolar cycloaddition reaction of organic azides and alkynes. This well-known "click" reaction provides high yields and regioselectivities under mild reaction conditions, and has found numerous applications in organic synthesis, material science and biological chemistry.[24] The catalytic cycle has been widely accepted to proceed via a Cu(I)-acetylide intermediate and a weakly coordinating azide, followed by cyclization and then hydrolysis of the Cu-C bond.[24-26] Similar mechanistic steps have been convincingly characterized in a series of studies on Au(I) triazolides wherein the stable Au-C bond allows for the isolation of an intermediate similar to the postulated Cu(I) intermediate in "click" chemistry.[27,28] Moreover, Wu *et al.* reported that the Cu(I)-triazolide intermediate can be trapped with electrophiles, such as ICl, to give 1,4,5-trisubstituted triazoles.[29] These encouraging results indicate that organocopper intermediates can act as potential transmetalating reagents to "click" the *in-situ* generated triazole ligands onto metal centers, which is the critical step in the synthesis of cyclometalated iridium compounds.

Figure 1. Functionalized 1,2,3-triazoles as chelating ligands



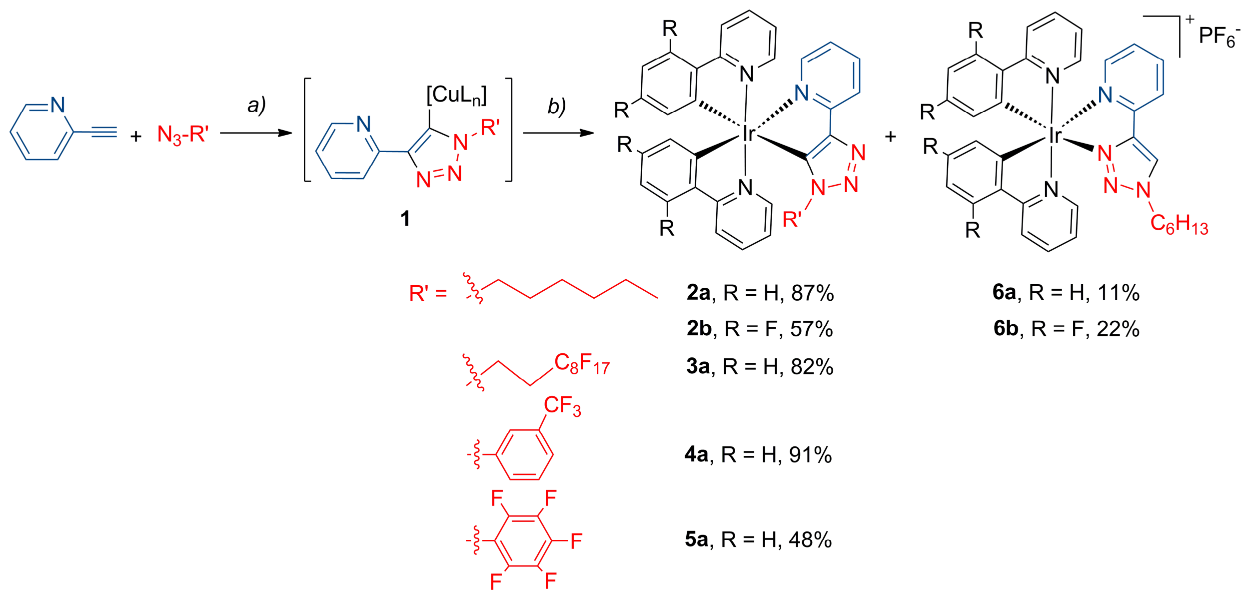
1,4-disubstituted 1,2,3-triazole derivatives prepared by "click" chemistry have been recently investigated as ligands for a variety of transition metals. This family of so called "click ligands" shows versatile coordination modes when combined with other functional groups. For example, they can act as N^N and N^N^N multi-dentate donors for Ru(III),[30-32] Pt(II),[33,34] Ir(III) (Figure 1A)[30,35,36] and other transition metals[37] as bipyridine and terpyridine equivalents. The resulting coordination complexes have potential applications as light-emitting materials[35] and in LECs.[38] Gandelman *et al.* developed a family of 1,2,3-triazole-based pincer ligands that react with Na_2PdCl_4 or (COD)$PtCl_2$ (COD = cyclooctadiene) to give cyclometalated Pd(II) and Pt(II) complexes, compound B in Figure 1.[39-41] Schubert *et al*. reported a series of bis-cyclometalated Ir(III) complexes using 4-phenyl-1*H*-[1,2,3]triazoles as cyclometalating ligands (Figure 1C).[36] It is important to note that all these 1,2,3-triazole type ligands were synthesized, isolated and purified separately before the cyclometalation was performed.

Herein, we present a highly efficient one-pot procedure to synthesize heteroleptic tris-cyclometalated Ir(III) complexes, ligated by derivatives of 2-phenylpyridine (ppy) and 2-(1*H*-[1,2,3]triazol-4-yl)pyridine (trpy) ligands. The Cu(I)-triazolide intermediates formed in the reaction of organoazides and commercially available 2-ethynylpyridine was used to transmetalate trpy as the third cyclometalating ligand on to the Ir(III) center.

Results and Discussion

Synthesis and structural characterization

Scheme 1. Synthesis of tri-cylometalated iridium(III) complexes.



a) $Cu(MeCN)_4PF_6$, NaH, Et_3N/THF, RT, 2 hours; *b)* $[Ir(ppy)_2Cl]_2$/$[Ir(FFppy)_2Cl]_2$, 65 °C, 2-4 hours.

Scheme 1 represents the general route to prepare tris-cyclometalated Ir(III) complexes using the *in-situ* generated Cu(I)-triazolides (**1**) as transmetalating reagents. 2-Ethynylpyridine was treated with stoichiometric $Cu(MeCN)_4PF_6$ in THF in the presence of NaH and Et_3N, before the addition of 1-azidohexane. ^{1}H-NMR spectra of the reaction mixture showed that the cyclization was very efficient and usually proceeded to completion within one hour at room temperature. To the organocopper compound containing mixture was added $[Ir(ppy)_2Cl]_2$ or $[Ir(FFppy)_2Cl]_2$ (FFppy = 2-(2,4-difluorophenyl)pyridine) at room temperature and then heated to 65 °C for 4 hours.

Crystalline Ir(ppy)$_2$(trpy) (**2a**) and Ir(FFppy)$_2$(trpy) (**2b**) were isolated in moderate to high yields, after purification by column chromatography. In order to maximize the yield of either **2a** or **2b**, it was essential to prevent intermediate **1** from being quenched by other electrophiles before the transmetalation reaction could occur. Therefore, a strong base, such as sodium hydride, was used as an efficient proton scavenger.

The tolerant and robust nature of the click reaction provides an ideal route to introduce different functional groups to the cyclometalated system. Alkyl, perfluoroalkyl and aryl azides, readily prepared from the respective halides in one step, were tested in this case. The 1,3-dipolar cycloaddition and subsequent transmetalation proceeded smoothly to give compounds **3a**-**5a** in high yields (> 80%). We attribute the slightly lower isolated yield of compound **5a** to repeated purification procedures. All the isolated compounds exhibit good solubility in common organic solvents, such as tetrahydrofuran, dichloromethane and toluene.

The tris-cyclometalated compounds obtained by this approach are expected to be meridional isomers. The pyridyl nitrogen atoms adopt a *trans* configuration in the dimeric Ir(III) precursors as confirmed by X-ray crystallography.[18] This coordination geometry has been proven to be stable and able to survive relatively harsh reaction conditions. Therefore, we hypothesized that the tris-cyclometalated Ir(III) complexes obtained would be meridional.[20] This hypothesis is supported by comparing the NMR spectra of **2a** and **2b** to literature compounds containing [Ir(ppy)$_2$]/[Ir(FFppy)$_2$] fragments.[17]

Table 1. Crystallographic data for compounds **2a**, **2b**, **6b** and **7b**

	2a	**2b**	**6b**	**7b**
Empirical formula	$C_{35}H_{33}IrN_6 \cdot 0.5\,C_6H_{14}$	$C_{35}H_{29}F_4IrN_6 \cdot CH_2Cl_2$	$C_{35}H_{30}F_{10}IrN_6P$	$C_{35}H_{30}ClF_4IrN_6 \cdot CH_2Cl_2 \cdot H_2O$
Formula weight	772.96	886.77	947.82	941.24

Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1$
a (Å)	20.3916(4)	22.2313(8)	12.9605(2)	12.9937(7)
b (Å)	15.2013(4)	16.1839(6)	14.0627(2)	10.5037(6
c (Å)	10.4538(2)	20.5272(8)	18.7948(3)	13.4237(7)
α	90°	90°	90°	90°
β	97.9110(10)°	116.927(2)°	92.2270(10)°	91.4950(10)°
γ	90°	90°	90°	90°
Volume (Å^3)	3209.62(12)	6584.4(4)	3422.95(9)	1831.47(17)
Z	4	8	4	2
Density (calcd) (g/cm^3)	1.600	1.789	1.83	1.707
Absorption coefficient (mm^{-1})	8.335	9.861	8.819	3.923
F(000)	1548	3488	1856	928
Θ range for data collection	2.19 to 66.21°	2.23 to 70.07°	3.41 to 67.73°	1.52 to 30.03°
Reflections collected	61406	133671	6186	41064
Independent reflections	5535 [R_{int} = 0.0869]	12423 [R_{int} = 0.0347]	6186 [R_{int} = 0.0486]	10300 [R_{int} = 0.0224]
Data / restraints / parameters	5535 / 57 / 434	12423 / 131 / 942	6186 / 149 / 479	10300 / 388 / 587
Goodness-of-fit on F^2	1.023	1.264	1.068	1.045
Final *R* indices [$I > 2\sigma(I)$]	$R1$ = 0.0264 $wR2$ = 0.0626	$R1$ = 0.0291 $wR2$ = 0.0705	$R1$ = 0.0251 $wR2$ = 0.0599	$R1$ = 0.0178 $wR2$ = 0.0441
R indices (all data)	$R1$ = 0.0330 $wR2$ = 0.0660	$R1$ = 0.0294 $wR2$ = 0.0706	$R1$ = 0.0268 $wR2$ = 0.0609	$R1$ = 0.0186 $wR2$ = 0.0445

Table 2. Selected bond lengths (Å) and bond angles (deg) for compounds **2a**, **2b**, **6b** and **7b**

	2a	**2b**[a]		**6b**	**7b**
Ir(1)-C(11)[b]	2.016(3)	2.003(4)	2.000(3)	2.007(3)	2.008(2)
Ir(1)-C(31)[c]	2.053(4)	2.048(3)	2.054(3)	2.004(3)	2.0044(19)
Ir(1)-C(47)[d]/N(4)[e]	2.088(4)	2.081(3)	2.091(3)	2.118(2)	2.1200(19)
Ir(1)-N(1)	2.046(3)	2.045(3)	2.039(3)	2.048(2)	2.051(2)
Ir(1)-N(2)	2.062(3)	2.059(3)	2.057(3)	2.047(3)	2.039(2)
Ir(1)-N(3)	2.188(3)	2.183(3)	2.184(3)	2.151(2)	2.172(2)
C(11)-Ir(1)-N(1)	79.93(13)	80.80(14)	80.69(14)	80.39(11)	80.62(9)
C(31)-Ir(1)-N(2)	79.73(13)	79.54(13)	79.93(14)	80.52(12)	80.56(10)
N(3)-Ir(1)-C(47)[d]/N(4)[e]	76.58(13)	77.27(13)	77.34(13)	76.18(9)	76.46(9)

[a] Data for the Δ (left column) and Λ (right column) isomers in the asymmetric unit cell.[b] *Trans* to Ir-N(trpy). [c] *Trans* to Ir-C(trpy). [d] For compound **2a** and **2b**.[e] For compound **6b** and **7b**.

Two representative compounds, **2a** and **2b**, were characterized by X-ray crystallography, using single crystals obtained from slow evaporation of respective dichloromethane/hexane solutions. Both compounds crystallize in the monoclinic space group $P2_1/c$, as racemates of the Δ and Λ enantiomers/helimers. Only the thermal ellipsoid plots of the Δ isomers are depicted in Figure 2 for simplicity. Details of the data quality and a summary of the residual values of the refinements are listed in Table 1, and selected bond lengths and angles are listed in Table 2. Full tables of bond lengths, bond angles and atomic coordinates are provided in the supporting information.

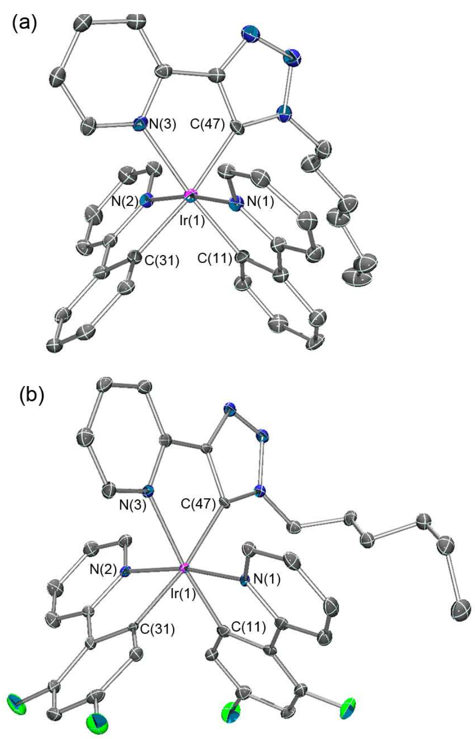


Figure 2. Ortep diagrams of **2a** (a) and **2b** (b). Thermal elliposoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Both tris-cyclometalated compounds adopt the meridional configuration, with the phenyl groups of the two ppy ligands mutually *cis* to each other. The *in-situ* generated trpy ligand completes the octahedral coordination sphere through the pyridyl nitrogen and triazolyl carbon at the 5-position. Compounds **2a** and **2b** are rare examples of crystallographically characterized complexes with the trpy ligands acting as C^N chelates, even though other binding modes have been reported before.[30,38]

The bond lengths and bond angles of **2a** are consistent with values reported for other meridional Ir(III) complexes in the literature. As the X-ray structure of *mer*-Ir(ppy)$_3$ is not available in the Cambridge Structural Database (CSD), the averaged bond lengths of the Δ and Λ isomers of *mer*-Ir(ppy)$_2$(tpy) (tpy = 2-(*p*-tolyl)pyridine)[42] are used as references. The length of the Ir-C(ppy) bond *trans* to Ir-N(trpy) in **2a** is 2.016(3) Å, which is comparable to its equivalent in *mer*-Ir(ppy)$_2$(tpy) (2.010 Å). However, the Ir-C(ppy) bond *trans* to Ir-C(trpy) (2.053(4) Å) is shorter than that of the Ir-C(ppy) *trans* to Ir-C(tpy) (2.074 Å). Meanwhile, the Ir-C(trpy) bond (2.088(4) Å) is longer than the Ir-C(tpy) bond (2.074 Å). Such variation in bond lengths suggests that the Ir-C(ppy) and Ir-C(tpy) bonds have a stronger *trans* influence relative to Ir-C(trpy). In other words, trpy appears to be a weaker cyclometalating ligand than the ppy derivatives based on the bond length analysis. This is probably due to the strongly σ electron-withdrawing nature of the triazolyl group.

The structure of **2b** resembles that of **2a**, except that the asymmetric unit of **2b** consists of two crystallographically independent molecules with little variation in individual bond lengths and bond angles (Table 2). The average bond lengths of the mutually *trans* Ir-C(FFppy) (2.051 Å) and Ir-C(trpy) (2.086 Å) bonds are the same as those observed in **2a**, indicating little perturbation upon fluorination of the ppy ligand. The two Ir-N(FFppy) bonds *trans* to each other have slightly longer bond lengths than those of *mer*-Ir(FFppy)$_3$.[43] The Ir-N(trpy) bond is elongated by roughly 0.13 Å in comparison with the *trans* Ir-N(FFppy) bonds.

It is worth noting that a minor Ir(III)-containing product **6a** was also isolated from the reaction mixture of **2a**. High resolution mass spectra (HRMS) of the minor product revealed a parent ion of m/z = 731.2446 m/e, which is the same as that of **2a** (m/z = 731.2498 m/e). The ^{1}H NMR spectrum of **6a** appeared to be similar to that of **2a**, with one additional peak as a sharp singlet at 8.75 ppm. Careful examination of the gCOSY NMR spectrum revealed that the ppy ligands and the pyridyl group of the trpy were intact and the extra proton giving rise to the new singlet was completely isolated. Addition of base to a solution of **6a** had no effect on its ^{1}H NMR spectrum, excluding the possibility of **6a** being a protonated version of **2a**. The ^{19}F NMR spectrum had a doublet signal at -72.99 ppm (J = 711.0 Hz), suggesting the presence of fluorophosphate anions (PF_6^-). Based on these characterizations, this minor product was tentatively assigned as a cationic $[Ir(ppy)_2(N^\wedge N\_trpy)]^+$ complex similar to those reported in the literature.[30,38] The counterion PF_6^- was obtained from the reagent $Cu(MeCN)_4PF_6$. The formation of a similar minor product **6b** (22%) was also observed during the synthesis of **2b**. The ^{1}H NMR spectrum of **6b** also showed a sharp singlet at 8.78 ppm, in addition to the characteristic ^{19}F NMR signal for PF_6^-. Extensive heating or prolonged reaction time were found to increase the yields of **6a** and **6b**. However, no isolable amount of side products was obtained in other cases.

Single crystal structure of **6b** confirmed the formation of positively charged $[Ir(FFppy)_2(N^\wedge N\_trpy)]^+$. As shown in Figure 3a, the two Ir-N(FFppy) bonds remain *trans* to each other. The pseudo-octahedral geometry of the $[Ir(FFppy)_2]$ fragment is completed by the pyridyl group and N at the 3-position of the triazole. The Ir-C(trpy) bond in **2b** is cleaved and the triazolyl group flips to offer a N^N binding mode. The hydrogen atom of the newly formed triazolyl C-H bond is located on the residual electron density map and gives rise to the sharp singlet ^{1}H NMR signal. One hexafluorophosphate anion is also found in the asymmetric unit, in agreement with the [19]F NMR spectrum. The two Ir-N(FFppy) bonds *trans* to each other (2.048(2) and 2.047(3) Å) are the same as those previously reported for [Ir(FFppy)$_2$(N^N_trpy)]BF_4 (2.056 and 2.048 Å), where N^N_trpy refers to pyridine-N-biphenyl-1,2,3-triazole.[38] The two trpy-based Ir-N bonds are elongated due to the strong *trans* influence of the Ir-C(FFppy) bonds. It is interesting to note that the Ir-N(triazolyl_trpy) bond (2.118(2) Å) is shorter than the N(pyridyl_trpy) bond (2.151(2) Å).

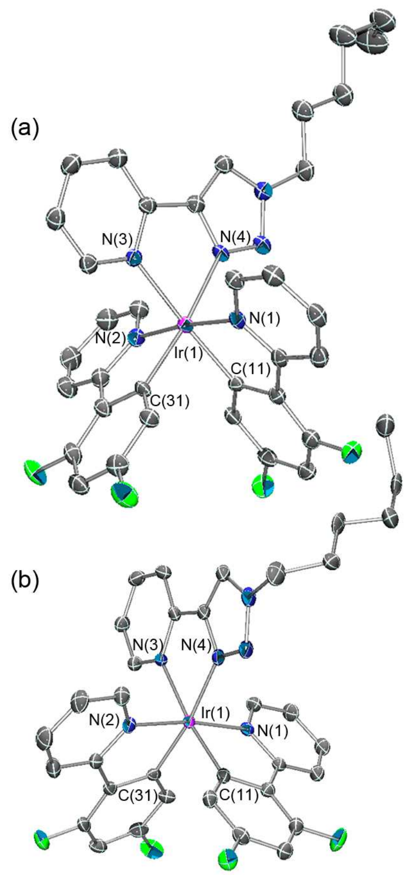
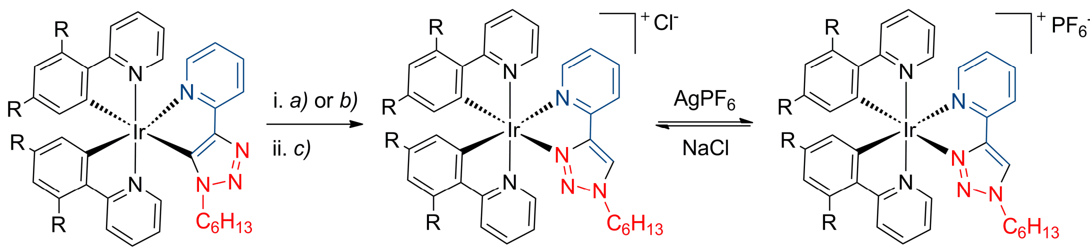


Figure 3. Ortep diagram of **6b** (a) and **7b** (b). Thermal elliposoids are drawn at the 50% probability level. Hydrogen atoms and counter ions are omitted for clarity.

Isomerization

In an attempt to obtain *fac*-Ir(C^N)$_2$(trpy), **2a** and **2b** were heated in glycerol at 200 °C for twenty hours before treated with saturated NaCl solution (Scheme 2). Unlike previous cases reported in the literature, ligand scrambling products were not observed, based on ^{1}H NMR and HRMS characterization of the crude reaction mixture. Nevertheless, ^{1}H NMR spectra indicated that compounds **7a** and **7b** had similar structure to **6a** and **6b**. The characteristic singlet peak from the triazolyl C-H bond was shifted downfiled to 9.07 ppm and 10.95 ppm for **7a** and **7b**, respectively. Additionally, a PF_6^- signal was not observed in the ^{19}F NMR spectrum.

Scheme 2. Thermal and photochemical isomerization of compounds **2a** and **2b**.



2a, R = H
2b, R = F

7a, R = H
7b, R = F

6a, R = H
6b, R = F

a) glycerol, 200 °C, 20 hours; *b)* DMSO-*d*$_6$, UV, 88 hours; *c)* aqueous NaCl.

Single crystals of compound **7b** were obtained by slow diffusion of hexane into a dichloromethane solution. It is worth noting that **7b** crystallizes in the $P2_1$ space group (Z = 2) with only the Δ helimer (Figure 3b). Such enrichment of one optical isomer from a racemic mixture is very rare for transition metal complexes with bidentate ligands. Limited literature reports on the separation of Δ and Λ isomers of cyclometalated compounds indicate the need for either rigid chiral ligands[44] or chiral chromatography techniques[45]. The coordination around the Ir(III) center in **7b** greatly resembles that of **6b**, with the trpy ligand acting as a neutral N^N chelate. However, the counter anion is a chloride ion in this case, which likely arise from the saturated brine solution used during the work-up procedure. Indeed, **6b** and **7b** are interchangeable through simple ion exchange reactions. Treatment with one equivalent of $AgPF_6$ in dichloromethane, affords **6b** from **7b** quantitatively. Conversely, **6b** can be converted back to **7b** using excess NaCl.

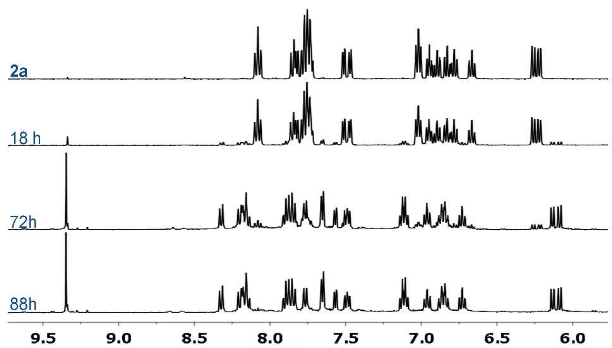


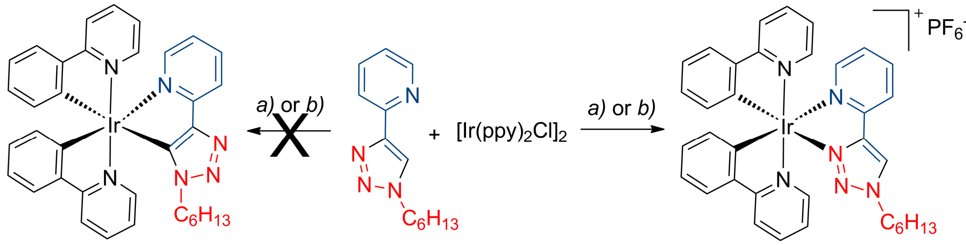
Figure 4. Photoisomerization of **2a** in DMSO-d_6, monitored by ^{1}H NMR.

Such switching of the binding mode of trpy ligands, from C^N to N^N, could also be achieved photochemically. Broadband UV radiation of DMSO-d_6 solutions of **2a** and **2b** afforded the respective cationic Ir(III) species. The conversion was monitored by ^{1}H NMR spectroscopy, and only a single product was observed (Figure 4). After the isomerization was completed, the reaction mixtures were treated with excess saturated NaCl solution. The isolated products showed identical NMR and HRMS spectra to those of **7a** and **7b**, respectively. Evidence of the formation of *fac*-Ir(C^N)$_2$(trpy) under either the thermal or the photochemical conditions was not obtained. Moreover, treatment of **2a** with acetic acid and silica gel in dichloromethane also failed to produce the *fac* isomer.[46]

The mechanism of the *mer*-to-*fac* isomerization of tris-cyclometalated Ir(III) compounds is believed to involve the dissociation of one of the mutually transoid nitrogen atoms and protonation of at least one of the Ir-C bonds as indicated by the unavoidable ligand scrambling.[17,42] The proton source is either the alcoholic solvent or the activated C-H bond of an incoming ligand. The energy needed for the C-H activation is compensated by the rearrangement of the coordination geometry and the chelation effect. However, the trpy ligand used in this study can offer both C^N and N^N coordination modes, the latter being an analogue of the commonly-used bipyridine ligand. As discussed in the previous section, the Ir-C(trpy) bond is considerably longer than the Ir-C(ppy) bonds in **2a** and **2b**. Therefore, it is most likely to be activated prior to either the Ir-C(ppy) or Ir-C(FFppy) fragments upon heating or UV radiation. Once the triazole C-5 is protonated, the N^N chelating mode of the trpy offers a thermodynamically stable product, which prevents isomerization of the ppy ligands. It should be pointed out that the proton source is the glycerol solvent during the thermal isomerization, as previously reported for the *mer*-to-*fac* isomerization.[17,42] The counterion during the thermal isomerization is likely to be glycerolate ions before the addition of NaCl. In the case of photochemical isomerization, the integration of the singlet corresponding to the triazolyl C-H increased proportionally with other aromatic protons from the ppy and trpy ligands, which precluded the formation of C-D bond (Figure S5). A slight increase of the pH values of the reaction mixture was also observed, in agreement with the formation of hydroxide counterions. Therefore, it is likely that the residual water acted as the proton source instead of DMSO_d_6.

This speculation is further supported by control reactions attempted to prepare heteroleptic cyclometalated Ir(III) compounds following the established procedures (Scheme 3).[18,47] However, only the N^N chelating complexes could be isolated even in refluxing ethoxyethanol. Therefore, the transmetalation approach described in this work is most likely the only way to use the trpy ligand as a C^N chelator.

Scheme 3. Failed attempts to synthesize tris-cylometalated iridium(III) complexes by literature methods.



a) (1) $AgPF_6$, MeCN; (2) *o*-dichlorobenzene, 100 °C, 48 hours; *b)* $AgPF_6$, 2-ethoxyethanol, 140 °C, 24 hours.

Electronic Spectroscopy

The absorption spectra of all the meridional tris-cyclometalated Ir(III) complexes are given in Figure 5a. Compounds **2a-5a** show intense absorption between 235 and 350 nm, which can be assigned to ligand-centered transitions.[3] These spin-allowed π-π* bands are accompanied by weaker spin-allowed and spin-forbidden charge transfer transitions in the visible region up to 480 nm. The band shapes and extinction coefficients are comparable to other ppy-based cyclometalated complexes, such as *mer*-$Ir(ppy)_3$.[17]

All the ppy-based meridional isomers show green phosphorescence at room temperature. Normalized photoluminescence (PL) spectra recorded in deoxygenated THF solutions and poly(methyl methacrylate) (PMMA) thin films are provided in Figure 5. Broad and structureless PL emission bands are observed across the series of *mer*-$Ir(ppy)_2$(trpy) in solution. In contrast, blue-shifted and relatively structured emission spectra and higher quantum yields are observed in the solid state. These observations suggest that the phosphorescence is based on excited states with strong ^{3}MLCT character. The low quantum efficiency and short triplet state lifetime in solutions likely arise from the distortion or even cleavage of Ir-N and Ir-C bonds upon excitation, which may be responsible for the photoisomerization processes described in the previous section.

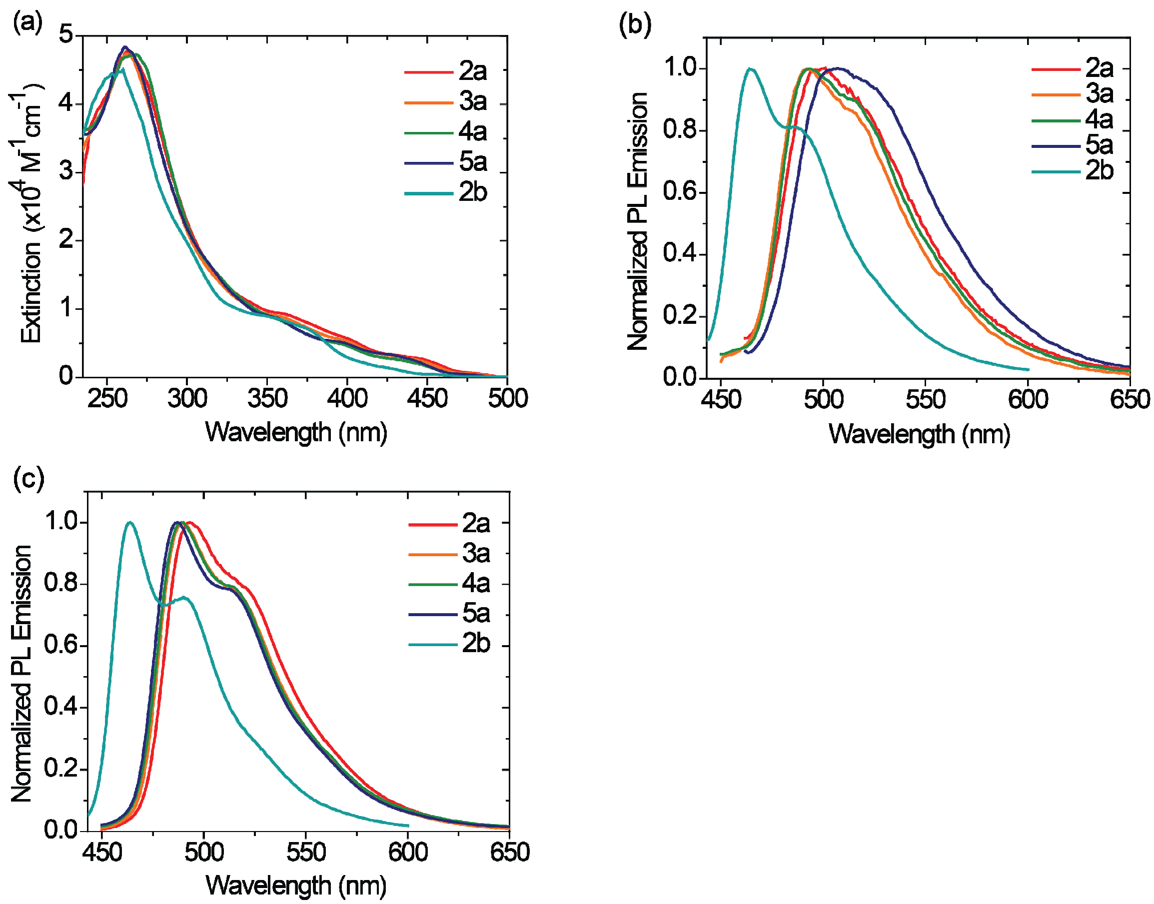


Figure 5. UV-vis absorption (a) and emission (b) spectra of all the *mer*-Ir(C^N)$_2$(trpy) compounds in THF (10^{-6} M, under Ar), as well as the photoluminescence spectra in PMMA thin films (c).

The absorption spectrum of FFppy-based **2b** exhibits similar spectral features to **2a**, except for a hypsochromic shift, consistent with the absorption spectra of the free ppy and FFppy ligands. Unlike its ppy-based analogues, **2b** exhibits a more structured and narrower PL spectrum in solution, with an emission maximum at 464 nm. Similar trends have also been observed with other Ir and Pt compounds bearing FFppy ligands.[17,48] It has been recognized that the difluoro substitution stabilizes the HOMO more than the LUMO level, resulting in an increase in the band gap.[4,49]

Table 3. Selected photophysical data of complexes **2**-**7**

	Solution[a]				Thin film[c]	
	λ_{max} [nm] ($\varepsilon\times10^{-3}$ M^{-1} cm^{-1})	λ_{em} [nm]	Φ_{em} [b]	τ [μs]	λ_{em} [nm]	Φ_{em} [d]
2a	263(47.7), 355(9.5), 397(6.0), 440(3.0)	500	0.002	0.90	493	0.10
2b	254(44.1), 346(9.1), 372(7.4), 427(1.3)	464, 485	0.003	0.40	464, 490	0.09
3a	262(47.3), 356(9.0), 396(5.6), 436(2.9)	492	0.007	1.6	490	0.17
4a	266(47.1), 359(8.3), 393(5.1), 432(2.6)	493	0.003	0.23	489	0.09
5a	263(48.0), 355(8.8), 396(5.2), 429(3.2)	505	0.015	1.9	488	0.07
6a	256(37.9), 384(4.8), 411(3.7)	477, 507	0.20	1.7	478, 508	0.35
6b	249(37.5), 362(5.1), 387(3.7)	453, 482	0.24	2.0	454, 483	0.57
7a[e]	255(44.0), 386(4.6), 415(3.0)	479, 508	0.35	3.5	479, 508	0.28
7b	248(47.1), 364(4.2), 390(1.7)	454, 483	0.45	3.5	455, 483	0.51

[a] Measured in deoxygenated THF solution (~10^{-5} M) at room temperature. [b] Determined by comparison with Coumarin-343 (ethanol, Φ = 0.63).[53] [c] Measured in PMMA films doped with 2-5 wt % of the Ir(III) compounds. [d] Determined by comparison with perylene (PMMA film, QY = 0.98)[54] and 9,10-diphenylanthracene (PMMA film, QY = 0.83).[55] [e] Measured in THF with 5% v/v of CH_2Cl_2 due to the low solubility of **7a** in THF.

Although there is little change in terms of the band shape or emission color of compounds with different substituents on the trpy ligands (**2a**-**5a**), greater differences are observed in the luminescence efficiency. The perfluorooctyl pedant chain rigidifies the molecule and provides efficient insulation between individual molecules.[50] As a result, aggregation induced quenching processes are minimized. Consistent with these arguments, **3a** exhibits the highest quantum yield (17%) in the solid state across the series. On the other hand, the pentafluorophenyl group introduces strong intermolecular interactions. Accordingly, aggregation induced bathochromic shift in the PL spectrum of **5a** is observed even when the concentration is as low as 4×10^{-6} M. Moreover, crystals of **5a** exhibit yellow phosphorescence under UV radiation instead of the green emission observed for all the other *mer*-Ir(ppy)$_2$(trpy) complexes. Differences are also evident in terms of lifetimes. Compounds **2a** and **4a** show comparable lifetimes to those of previously reported meridional tris-cyclometalated Ir(III) complexes, such as *mer*-Ir(ppy)$_3$ (0.15 μs),[17] while highly fluorinated **3a** and **5a** both show longer lifetimes. Hence, it can be established that certain photophysical properties can be tuned by varying the substituents on the triazole ring.

Many potential applications can be envisioned considering the huge library of organo azides established in the literature.

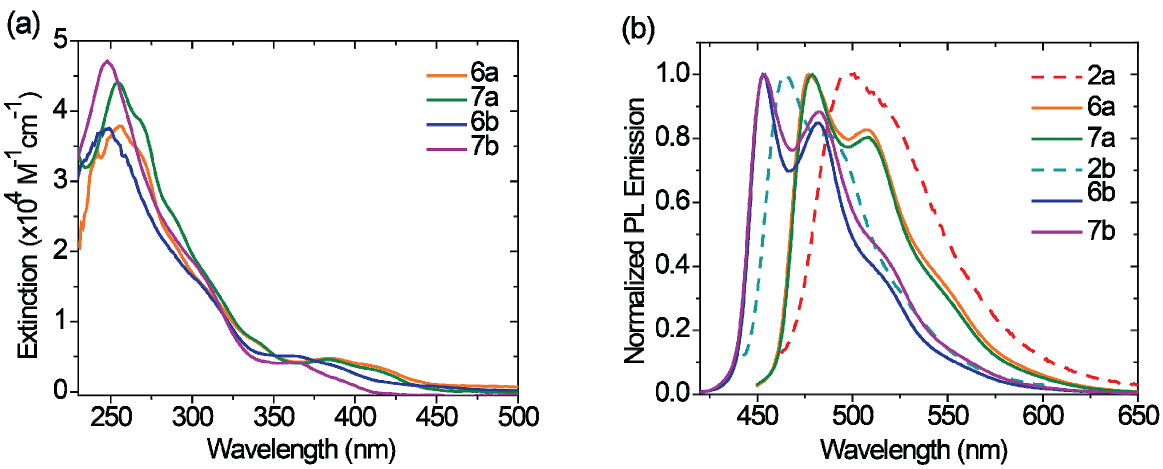


Figure 6. UV-vis absorption (a) and emission (b) spectra of the $[Ir(C$^$N)_2(N$^$N\_trpy)]^+$ compounds in THF (10^{-6} M, under Ar).

The positively charged $[Ir(C$^$N)_2(N$^$N\_trpy)]^+$ complexes exhibit photophysical properties distinct from those of their tris-cyclometalated counterparts (Figure 6). The absorption spectra show well defined absorption bands at around 385 nm for **6a/7a** and 363 nm for **6b/7b**. The room temperature solution PL spectra show well resolved vibronic structures typical of this type of complexes.[30,38] These highly structured emission spectra indicate that the excited state is primarily ligand based. The emission maximum is also slightly blue shifted relative to the corresponding meridional compounds. For complexes with PF_6^- and Cl^- anions, the excited state lifetimes and PL quantum efficiencies show counter ions dependency, despite their nearly identical absorption and PL spectra. The excited states of the chlorides **7a** and **7b** display longer lifetimes and higher quantum yields than **6a** and **6b,** respectively. This difference has been observed previously between $[Ir(FFppy)_2(N$^$N\_trpy)]PF_6$ and $[Ir(FFppy)_2(N$^$N\_trpy)]BF_4$, and it is attributed to varying packing interactions when the cations are not fully solvated.[38] Indeed, an examination of the packing diagrams of **6b** and **7b** reveals that PF_6^- and Cl^- ions show different H-bonding interactions with the FFppy and trpy ligands in the solid state (Figure S1-2).

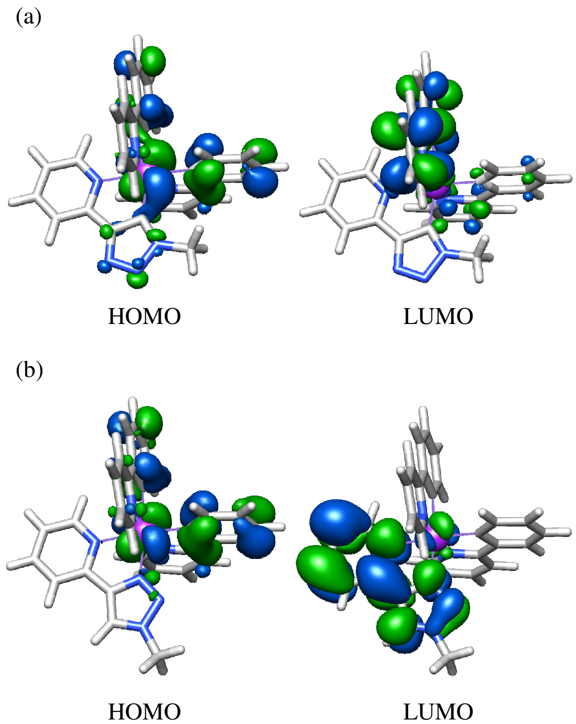


Figure 7. Contour plots of frontier orbitals of *mer*-Ir(ppy)$_2$(trpy) (a) and [Ir(ppy)$_2$(N^N_trpy)]$^+$ (b).

In order to gain insights into the different electronic structures and photophysical properties of the neutral and cationic Ir(III) complexes, density functional theory (DFT) calculations were performed on two simplified structures *mer*-Ir(ppy)$_2$(trpy) and [Ir(ppy)$_2$(N^N_trpy)]$^+$. The optimized ground-state geometries closely resemble the solid state structures determined by X-ray diffraction. The most important frontier orbitals of the two model compounds are shown in Figure 7. The highest occupied molecular orbitals (HOMOs) of the two model compounds are both composed of a mixture of the d-orbitals of iridium and the π-orbitals of the two ppy-based phenyl groups, typical for bis- or tris-cyclometalated Ir(III).[3,4] However, the lowest unoccupied molecular orbitals (LUMOs) appear to be remarkably different. As for *mer*-Ir(ppy)$_2$(trpy), the

LUMO is localized primarily on the ppy ligand that has transoid Ir-C bond with the trpy. Such atomic orbital composition of the frontier molecular orbitals is very typical for meridional bis-cyclometalated Ir(III) complexes.[17] The absence of a significant contribution from the substituted triazolyl group to the frontier orbitals explains the almost identical absorption and emission spectra observed for **2a**-**5a**. The LUMO for $[Ir(ppy)_2(N^\wedge N\_trpy)]^+$, on the other hand, is dominated by the π*-orbital of the N^N_trpy ligand with little overlap with the HOMO. The orbital diagram of the Ir(III) cation greatly resembles that of bis-cyclometalated complexes with neutral diimine ligands, such as 2,2'-bipyridine (bpy) and 1,10-phenanthroline. The HOMO of $[Ir(ppy)_2(bpy)]^+$ is also a mixture of iridium d and phenyl π-orbitals, while the LUMO is primarily on the bpy ligand.[51,52] Studies on the excited states have confirmed the mixed ^{3}MLCT and ligand-to-ligand charge transfer (^{3}LLCT) character of the low-lying triplet states. Therefore, the low energy absorption of *mer*-$Ir(ppy)_2(trpy)$ can be attributed to excitation to mixed ^{3}MLCT and ^{3}LC excited states of ppy, while the low-lying excited states of $[Ir(ppy)_2(N^\wedge N\_trpy)]^+$ have an important ^{3}LLCT character between the ppy and trpy ligands. This is in good agreement with the highly structured emission spectra and longer phosphorescence lifetimes observed for **6**-**7** relative to their C^N_trpy counterparts. Since the neutral N^N_trpy ligands are better π acceptors than the anionic C^N_trpy, stronger back bonding from the metal center to N^N_trpy would further stabilize the Ir d-orbitals while destabilized the ligand π*-orbitals. This stabilization of the HOMO and destabilization LUMO led to the hypsochromic shift observed upon switching from the C^N chelating mode to N^N.

Conclusion

In summary, we demonstrated that Cu(I)-triazolides generated by click chemistry can be used to facilitate the synthesis of tris-cyclometalated Ir(III) complexes. This route represents an efficient one-pot procedure for both ligand preparation and cyclometalation. *mer*-Ir(C^N)$_2$(trpy) with various substituents of the triazole groups are isolated in moderate to high yields and fully characterized. These meridional Ir(III) compounds show short-lived phosphorescence at room temperature, and their quantum efficiencies can be perturbed by varying the cyclometalating ligands. The robust nature of the click chemistry affords the possibility of introducing different lateral functional groups to the ligand that can act as sensing receptors or anchor groups. Many potential applications can be envisioned considering the diversity of organo azides established in the literature. The isomerization of neutral *mer*-Ir(C^N)$_2$(trpy) to positively charged [Ir(C^N)$_2$(N^N_trpy)]$^+$ is also discussed in detail. The neutral N^N chelating mode is thermodynamically favored comparing to the anionic C^N mode. Therefore, the transmetalation approach described in this work is required to utilize trpy as a cyclometalating ligand.

Experimental Section

General Methods and Instrumentation. All reactions were performed under an argon atmosphere, using oven-dried glassware and standard Schlenk techniques. ^{1}H and ^{13}C{^{1}H}NMR spectra were recorded on either a Bruker 400 MHz or Varian 500 MHz spectrometer and referenced to the residual proton or carbon resonance of the deuterated solvent. ^{19}F NMR spectra were recorded on a Varian 300 MHz spectrometer and referenced to an external standard $CFCl_3$ (0 ppm). Electrospray ionization (ESI) high resolution mass spectrometry (HRMS) was measured on a Bruker Daltonics APEXIV 4.7 Tesla Fourier Transform Ion Cyclotron Resonance Mass Spectrometer and the most abundant masses are reported.

UV/Vis spectra were recorded on an Agilent 8453 diode-array spectrophotometer. Emission spectra were acquired on a SPEX Fluorolog fluorometer (model FL-321, 450 W xenon lamp) using either right-angle detection (solution measurements) or front-face detection (thin film measurements). All room temperature solution samples for emission spectra were degassed by at least three freeze-pump-thaw cycles in an anaerobic cuvette. Solution photoluminescence quantum yields were determined against Coumarin-343 (ethanol, QY = 0.63)[51] and corrected for solvent refractive index and absorption differences at the excitation wavelength. Thin films were prepared by spin-coating a chloroform solution of poly(methyl methacrylate) (PMMA) and the target compound (5-10 % w/w relative to PMMA). Perylene (PMMA film, QY = 0.98)[52] or 9,10-diphenylanthracene (PMMA film, QY = 0.83)[53] were used as the reference materials. Phosphorescence lifetimes were determined by time-resolved phosphorescence spectroscopy. The radiation source was an Oriel nitrogen laser (Model 79111) with a 5 ns pulse width operating at approximately 25 Hz. The emitted light was dispersed in an Oriel MS-260i spectrograph with a 600 lines/mm grating. The detector was an Andor Technologies Intensified CCD camera (1024 x 128 pixels) with an onboard delay generator and a minimum gate width of 5 ns operating in full vertical binning mode and triggered by a TTL prepulse from the nitrogen laser. The detector was calibrated with a Hg(Ar) pencil-style calibration lamp. Solution data was acquired with a horizontal binning of 2 or 3. 15 spectra at different delay times after the laser pulse were taken per lifetime measurement, the integrated intensities of which were fit to a single-exponential function.

Materials and Synthesis. Iridium(III) chloride hydrate ($IrCl_3{\cdot}nH_2O$) and *tetrakis*(acetonitrile)copper(I) hexafluorophosphate ($Cu(MeCN)_4PF_6$) were purchased from Strem Chemicals. 2-Ethynylpyridine, 2-(2,4-difluorophenyl)pyridine and all other reagents were obtained from Aldrich Chemicals and used as received. Anhydrous tetrahydrofuran was obtained from a solvent purification system (Innovative Technologies). Triethylamine (Et_3N) was distilled over sodium hydroxide pellets and stored under argon. μ-chloro-bridged Ir(III) dimers[17], 1-azidohexane,[54] 1-azidoperfluorodecane,[55] 1-azido-3-(trifluoromethyl)benzene[56] and 1-azidopentafluorobenzene[56] were prepared according to the literature methods.

CAUTION: There have been safety concerns about handling organoazides, especially the ones with short alkyl groups. Therefore, all the organoazides used in this report were synthesized on small scales and handled with great care.

Preparation of *mer*-Ir(ppy)$_2$(trpy-C$_6$H$_{13}$) (2a). 2-Ethynylpyridine (41 mg, 0.4 mmol) in THF (8 ml)/ Et_3N (0.1 ml) was added to a mixture of $Cu(MeCN)_4PF_6$ (149 mg, 0.4 mmol) and NaH (19 mg, 0.8 mmol), and the resulting suspension was stirred for 0.5 h at room temperature before 1-azidohexane (51 mg, 0.4 mmol) in THF (2 ml) was added. After stirring at room temperature for another 1-1.5 h, $[Ir(ppy)_2Cl]_2$ (107 mg, 0.1 mmol) was added to the mixture as a solid and heated to 65 °C for 4 h. After cooling, the solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel, using CH_2Cl_2/ethyl acetate (15:1) as the eluent to remove small amount of side product **6a**, then CH_2Cl_2/ethyl acetate (6:1) to collect the desired product **2a**. After recrystallization from CH_2Cl_2/hexane, **2a** was isolated as bright yellow crystals (127 mg, 87%). HRMS (ESI): 731.2498 [calcd for $(M+H)^+$: 731.2415]. ^1H NMR (400 MHz, DMSO-d_6, ppm): 0.76 (t, J=7.2 Hz, 3 H), 0.87-1.00 (m, 4 H), 1.06 (m, 2 H), 1.21 (m, 2 H), 3.4 (m, 2H), 6.27 (d, J=7.2 Hz, 1 H), 6.31 (d, J=7.6 Hz, 1 H), 6.72 (t, J=7.4 Hz, 1 H), 6.83 (t, J=7.4

Hz, 1 H), 6.88 (t, *J*=7.4 Hz, 1 H), 6.95 (t, *J*=7.6 Hz, 1 H), 6.99 (t, *J*=6.3 Hz, 1 H), 7.07 (m, 2 H), 7.52 (d, *J*=5.4 Hz, 1 H), 7.56 (d, *J*=5.7 Hz, 1 H), 7.75-7.84 (m, 5 H), 7.87 (d, *J*=5.7 Hz, 1 H), 7.91 (d, *J*=7.9 Hz, 1 H), 8.12 (d, *J*=7.9 Hz, 1 H), 8.13 (d, *J*=7.9 Hz, 1 H). ^{13}C NMR (126 MHz, CD_2Cl_2, ppm): 14.4, 23.1, 26.7, 32.7, 51.1, 118.1, 119.0, 119.5, 120.4, 121.5, 122.1, 122.5, 123.2, 124.6, 124.9, 130.0, 130.6, 131.6, 132.3, 136.0, 137.0, 138.2, 143.5, 145.5, 149.4, 151.1, 152.5, 154.1, 158.8, 162.8, 168.1, 169.4, 170.1.

Compound **6a** was isolated as a bright yellow solid (20 mg, 11%). HRMS (ESI): 731.2446 [calcd for $(M\text{-}PF_6)^+$: 731.2415]. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): 0.84 (t, *J*=6.82 Hz, 3 H), 1.12-1.38 (m, 6 H), 1.83-1.98 (m, 2 H), 4.45 (t, *J*=7.4 Hz, 2 H), 6.30 (d, *J*=5.3 Hz, 1 H), 6.32 (d, *J*=5.3 Hz, 1 H), 6.87 (t, *J*=7.5 Hz, 1 H), 6.93 (t, *J*=7.5 Hz, 1 H), 6.97-7.11 (m, 4 H), 7.30 (t, *J*=6.3 Hz, 1 H), 7.51 (d, *J*=5.8 Hz, 1 H), 7.66-7.71 (m, 2 H), 7.73 (d, *J*=7.3 Hz, 1 H), 7.75-7.82 (m, 2 H), 7.84 (d, *J*=5.3 Hz, 1 H), 7.95 (d, 2 H), 8.02 (t, *J*=7.6 Hz, 1 H), 8.22 (d, *J*=7.8 Hz, 1 H), 8.75 (s, 1 H). ^{13}C NMR (126 MHz, CD_2Cl_2, ppm): 14.2, 22.9, 26.3, 30.2, 31.4, 53.1, 120.1, 120.2, 122.7, 123.3, 123.5, 123.6, 123.9, 124.9, 125.3, 126.2, 127.0, 130.4, 131.1, 132.1, 132.4, 138.6, 138.7, 140.2, 144.5, 146.8, 149.0, 149.8, 149.9, 150.0, 150.8, 167.9, 168.5. ^{19}F NMR (282 MHz, CD_2Cl_2, δ ppm): -72.99 (d, *J* = 711.0 Hz).

Preparation of *mer*-Ir(FFppy)$_2$(trpy-C$_6$H$_{13}$) (2b). 2-Ethynylpyridine (21 mg, 0.2 mmol), $Cu(MeCN)_4PF_6$ (75 mg, 0.2 mmol), NaH (10 mg, 0.4 mmol), and 1-azidohexane (25 mg, 0.2 mmol) were reacted with $[Ir(FFppy)_2Cl]_2$ (61 mg, 0.05 mmol) following the procedure detailed for the synthesis of **2a**. The reaction mixture was purified by chromatography on silica gel, using CH_2Cl_2/ethyl acetate (10:1 to 8:1) as the eluent to remove small amount of side product **6b**, then CH_2Cl_2/ethyl acetate (4:1) to collect the desired product **2b**. Compound **2b** was isolated as light yellow crystals (91 mg, 57%). HRMS (ESI): 803.2108 [calcd for $(M+H)^+$: 803.2101]. ^{1}H NMR

(400 MHz, CD_2Cl_2, δ ppm): 0.82 (t, *J*=7.3 Hz, 3 H), 1.04 (quin, *J*=7.4 Hz, 2 H), 1.09-1.22 (m, 4 H), 1.33-1.45 (m, 2 H), 3.57-3.74 (m, 2 H), 5.87 (m, 2 H), 6.48 (m, 2 H), 6.83-6.93 (m, 3 H), 7.59-7.65 (m, 2 H), 7.66-7.75 (m, 3 H), 7.97 (d, *J*=5.3 Hz, 1 H), 8.02 (br. d, *J*=5.3 Hz, 1 H), 8.25 (d, *J*=8.3 Hz, 2 H). ^{13}C NMR (126 MHz, CD_2Cl_2, δ ppm): 14.3, 23.1, 26.9, 32.0, 32.8, 51.2, 96.7 (t, *J*=27.6 Hz), 98.5 (t, *J*=27.6 Hz), 113.4 (dd, *J*=16.7, 2.9 Hz), 113.8 (dd, *J*=15.3, 2.6 Hz), 118.5, 121.9, 122.9, 123.1 (d, *J*=19.6 Hz), 123.5, 123.7 (d, *J*=19.0 Hz), 127.8, 128.8, 137.1, 138.1, 138.9, 149.5, 150.9, 154.0, 156.7 (d, *J*=6.9 Hz), 158.4, 160.91 (d, *J*=13.2 Hz), 161.5 (d, *J*=11.5 Hz), 162.8 (d, *J*=12.1 Hz), 163.0 (d, *J*=13.2 Hz), 163.6 (d, *J*=11.5 Hz), 163.8 (d, *J*=10.9 Hz), 164.7, 164.8, 165.9 (d, *J*=10.9 Hz), 166.5 (d, *J*=8.1 Hz), 174.3. ^{19}F NMR (282 MHz, CD_2Cl_2, δ ppm): -111.24 (t, *J*=9.2 Hz), -110.16 (t, *J*=12.2 Hz), -109.46 (d, *J*=9.2 Hz), -108.83 (d, *J*=9.2 Hz).

Compound **6b** was isolated as light yellow solids (43 mg, 22%). HRMS (ESI): 803.2056 [calcd for $(M\text{-}PF_6)^+$: 803.2101]. ^{1}H NMR (400 MHz, CD_2Cl_2, δ ppm): 0.84 (t, *J*=6.8, 3 H), 1.15-1.30 (m, 6 H), 1.86-1.97 (m, 2 H), 4.46 (t, *J*=7.3 Hz, 2 H), 5.73 (dd, *J*=8.6, 2.1 Hz, 1 H), 5.79 (dd, *J*=8.4, 2.1 Hz, 1 H), 6.55 (ddd, *J*=12.2, 9.5, 2.1 Hz, 1 H), 6.61 (ddd, *J*=12.1, 9.5, 2.2 Hz, 1 H), 7.04 (t, *J*=6.4 Hz, 1 H), 7.10 (t, *J*=6.3 Hz, 1 H), 7.37 (t, *J*=6.4 Hz, 1 H), 7.50 (d, *J*=5.7 Hz, 1 H), 7.64 (d, *J*=5.7 Hz, 1 H), 7.80-7.89 (m, 3 H), 8.08 (td, *J*=7.8, 1.0 Hz, 13 H), 8.26 (d, *J*=8.1 Hz, 1 H), 8.31 (d, 2 H), 8.78 (s, 1 H). ^{13}C NMR (126 MHz, CD_2Cl_2, δ ppm): 14.2, 22.9, 29.3, 30.1, 31.3, 53.3, 99.2 (t, *J*=27.1 Hz), 99.7 (t, *J*=27.1 Hz), 114.5, 1114.6 (d, *J*=12.1 Hz), 114.7 (d, *J*=12.1 Hz), 114.8, 123.9, 124.0, 124.2-124.3 (m), 126.7, 127.3, 128.5, 139.6, 139.7, 140.9, 148.8, 149.1, 149.9, 150.0, 150.4 (d, *J*=6.9 Hz), 150.7, 153.8 (d, *J*=6.3 Hz), 160.5 (d, *J*=12.7 Hz), 160.9 (d, *J*=12.7 Hz), 162.5 (d, *J*=8.6 Hz), 162.6 (d, *J*=9.2 Hz), 163.0 (d, *J*=12.7 Hz), 163.1 (d, *J*=12.7 Hz), 164.5-164.6 (m), 165.1-165.2 (m). ^{19}F NMR (282 MHz, CD_2Cl_2, δ ppm): -111.09 (1 F), -109.23 (1 F), -107.75 (1 F), -106.85 (1 F), -72.86 (d, *J* = 717.2 Hz, 6 F).

Preparation of *mer*-Ir(ppy)$_2$(trpy-$C_2H_4C_8H_{17}$) (3a). 2-Ethynylpyridine (41 mg, 0.4 mmol), Cu(MeCN)$_4$PF$_6$ (149 mg, 0.4 mmol), NaH (19 mg, 0.8 mmol), and 1-azidoperfluorodecane (196 mg, 0.4 mmol) were reacted with [Ir(ppy)$_2$Cl]$_2$ (107 mg, 0.1 mmol) following the procedure detailed for the synthesis of **2a**. The reaction mixture was purified by chromatography on silica gel, using CH_2Cl_2/ethyl acetate (8:1) as the eluent. Compound **3a** was isolated as bright yellow crystals (133 mg, 61%). HRMS (ESI): 1093.1473 [calcd for $(M+H)^+$: 1091.1503]. ^{1}H NMR (500 MHz, CD_2Cl_2, ppm): 1.85-2.05 (m, 1 H), 2.10-2.27 (m, 1 H), 3.99-4.12 (m, 2 H), 6.44 (d, *J*=7.2 Hz, 1 H), 6.46 (d, *J*=7.7 Hz, 1 H), 6.78-6.89 (m, 4 H), 6.92 (t, *J*=7.6 Hz, 1 H), 6.96 (t, *J*=7.4 Hz, 1 H), 7.03 (t, *J*=7.2 Hz, 1 H), 7.59-7.76 (m, 7 H), 7.87 (d, 2 H), 7.98 (d, *J*=5.4 Hz, 1 H), 8.06 (d, *J*=7.7 Hz, 1 H). ^{13}C NMR (126 MHz, CD_2Cl_2, ppm): 32.9 (t, *J*=21.3 Hz), 42.8 (t, *J*=4.0 Hz), 108.9-120.12 (m, CF_2 and CF_3), 118.4, 119.1, 119.7, 120.9, 121.9, 122.4, 122.7, 123.3, 124.9, 125.0, 130.3, 130.8, 131.4, 132.2, 136.2, 137.2, 138.4, 143.3, 145.4, 149.6, 151.2, 151.6, 153.9, 158.5, 163.6, 168.0, 168.7, 170.1. ^{19}F NMR (282 MHz, CD_2Cl_2, ppm): -126.63, -124.31, -123.21, -122.41, -122.23, -115.20, -81.40.

Preparation of *mer*-Ir(ppy)$_2$(trpy-$C_6H_4CF_3$) (4a). 2-Ethynylpyridine (21 mg, 0.2 mmol), Cu(MeCN)$_4$PF$_6$ (75 mg, 0.2 mmol), NaH (10 mg, 0.4 mmol), and 1-azido-3-(trifluoromethyl)benzene (37 mg, 0.2 mmol) were reacted with [Ir(ppy)$_2$Cl]$_2$ (54 mg, 0.05 mmol) following the procedure detailed for the synthesis of **2a**. The reaction mixture was purified by chromatography on silica gel, using CH_2Cl_2/ethyl acetate (15:1) as the eluent. Compound **4a** was isolated as bright yellow crystals (72 mg, 91%). HRMS (ESI): 791.1709 [calcd for $(M+H)^+$: 791.1726]. ^{1}H NMR (400 MHz, CD_2Cl_2, ppm): 6.08 (d, *J*=7.6 Hz, 1 H), 6.33 (d, *J*=7.3 Hz, 1 H), 6.53 (t, *J*=8.1 Hz, 1 H), 6.75 (t, *J*=7.3 Hz, 1 H), 6.81-6.89 (m, 4 H), 6.92 (t, *J*=7.3 Hz, 1 H), 7.00 (t, *J*=7.6 Hz, 1 H), 7.04 (d, *J*=8.1 Hz, 1 H), 7.28 (d, *J*=7.8 Hz, 1 H), 7.48 (d, *J*=7.6 Hz, 1 H), 7.59-7.69 (m, 6 H), 7.72 (t, *J*=7.8 Hz, 1 H), 7.81 (d, *J*=8.1 Hz, 1 H), 7.84 (d, *J*=8.1 Hz, 1 H), 8.06 (d, *J*=5.6 Hz, 1 H), 8.13 (d, *J*=7.8 Hz, 1 H). ^{13}C NMR (126 MHz, CD_2Cl_2, ppm): 118.7, 119.1, 119.7, 120.5, 120.9, 122.1, 122.4, 122.5, 123.5, 123.8, 124.6, 124.9, 125.9, 127.6, 129.1, 129.8, 130.8, 131.6, 132.0, 136.2, 137.2, 138.4, 141.1, 143.2, 145.3, 149.5, 150.9, 153.0, 154.1, 158.3, 159.1, 163.8, 167.1, 168.0, 169.8. ^{19}F NMR (282 MHz, CD_2Cl_2, ppm): -62.82.

Preparation of mer-Ir(ppy)2(trpy-C_6F_5) (5a). 2-Ethynylpyridine (41 mg, 0.4 mmol), $Cu(MeCN)_4PF_6$ (149 mg, 0.4 mmol), NaH (19 mg, 0.8 mmol), and 1-azidopentafluorobezene (84 mg, 0.4 mmol) were reacted with $[[Ir(ppy)_2Cl]_2$ (107 mg, 0.1 mmol) following the procedure detailed for the synthesis of **2a**. The reaction mixture was purified by chromatography on silica gel, using CH_2Cl_2/ethyl acetate (15:1) as the eluent. Compound **5a** was isolated as bright yellow crystals (77 mg, 48%). Samples for photophysical study were purified by preparative thin layer chromatography (PTLC) to remove trace amount contaminants using CH_2Cl_2/ethyl acetate (30:1) as the eluent. HRMS (ESI): 813.1367 [calcd for $(M+H)^+$: 813.1381]. ^{1}H NMR (400 MHz, CD_2Cl_2, ppm): 6.15 (d, *J*=7.6 Hz, 1 H), 6.40 (d, *J*=7.1 Hz, 1 H), 6.54 (t, *J*=7.4 Hz, 1 H), 6.72 (t, *J*=7.4 Hz, 1 H), 6.85-6.95 (m, 4 H), 7.00 (t, *J*=7.6 Hz, 1 H), 7.45 (d, *J*=7.6 Hz, 1 H), 7.62-7.78 (m, 6 H), 7.81 (d, *J*=8.3 Hz, 1 H), 7.85 (d, *J*=8.1 Hz, 1 H), 8.10 (d, 2 H). ^{13}C NMR (126 MHz, CD_2Cl_2, ppm): 118.8, 118.9, 119.6, 120.2, 122.4, 122.7, 123.4, 123.9, 124.9, 129.3, 130.7, 131.3, 132.3, 136.5, 137.3, 138.6, 143.4, 145.4, 149.5, 151.1, 151.3, 154.1, 157.8, 158.0, 168.0, 168.2, 168.4, 169.8. ^{19}F NMR (282 MHz, CD_2Cl_2, ppm): -163.24 (d, *J*=24.4 Hz), -163.27 (d, *J*=24.4 Hz), -154.92 (t, *J*=21.4 Hz), -146.87 ~ -146.80 (m).

Thermal Isomerization from 2a to 7a. 20 mg of **2a** was suspended in 5 ml glycerol under Ar. The mixture was heated to 200 °C for 12 h. After cooling to room temperature, the slurry was added with saturated NaCl aqueous solution and extracted with CH_2Cl_2. The crude mixture was subjected to HRMS (ESI), which showed that there is only trace amount of Ir(ppy)(tzpy)$_2$ (<1%). Compound **7a** was purified by flash chromatography on partially deactivated neutral aluminum oxide (5% H_2O), using CH_2Cl_2/CH_3OH (97:3) as eluent. After recrystallization from CH_2Cl_2/hexane, **7a** was isolated as light yellow crystals (14mg, 63%). HRMS (ESI): 731.25 [calcd for $(M\text{-}Cl)^+$: 731.25]. ^{1}H NMR (400 MHz, MeOH-d_4, δ ppm): 0.85 (t, *J*=6.8 Hz, 3 H), 1.10-1.30 (m, 6 H), 1.81-1.95 (m, 2 H), 4.47 (t, *J*=7.1 Hz, 2 H), 6.24 (d, *J*=7.3 Hz, 1 H), 6.31 (d, *J*=7.3 Hz, 1 H), 6.78 (t, *J*=7.0 Hz, 1 H), 6.88 (t, *J*=7.0 Hz, 1 H), 6.93 (t, *J*=7.2 Hz, 1 H), 7.02 (d, *J*=7.1 Hz, 1 H), 7.04 (d, *J*=7.8 Hz, 1 H), 7.09 (t, *J*=6.7 Hz, 1 H), 7.40 (t, *J*=6.2 Hz, 1 H), 7.63 (d, *J*=5.8 Hz, 1 H), 7.73 (d, *J*=7.8 Hz, 1 H), 7.76 (d, *J*=5.6 Hz, 1 H), 7.81 (d, *J*=7.8 Hz, 1 H), 7.84-7.91 (m, 3 H), 8.04-8.14 (m, 3 H), 8.26 (d, *J*=7.8 Hz, 1 H), 9.07 (s, 1 H). ^{13}C NMR (126 MHz, CD_2Cl_2, δ ppm): 14.2, 22.9, 26.4, 30.4, 31.4, 52.8, 120.0, 120.1, 122.6, 123.1, 123.5, 123.8, 124.8, 125.0, 125.2, 126.5, 129.4, 129.5, 130.3, 131.0, 132.1, 132.4, 138.4, 138.5, 140.2, 144.5, 147.3, 149.1, 149.3, 149.9, 150.2, 150.4, 150.8, 168.0, 168.5.

Thermal Isomerization from 2b to 7b. 7b was prepared following the procedure outlined for **7a**, and purified by flash column chromatography on partially deactivated neutral aluminium oxide (5% H_2O), using CH_2Cl_2/CH_3OH (97:3) as the eluent. After recrystallization from CH_2Cl_2/hexane, **7b** was isolated as light yellow crystals (12 mg, 58%). HRMS (ESI): 803.2095 [calcd for $(M\text{-}Cl)^+$: 803.2101] ^{1}H NMR (400 MHz, CD_2Cl_2, ppm): 0.83 (t, *J*=6.6 Hz, 3 H), 1.24 (m, 6 H), 1.83-2.03 (m, 2 H), 4.51 (t, *J*=7.3 Hz, 2 H), 5.73 (dd, *J*=8.6, 2.3 Hz, 1 H), 5.80 (dd, *J*=8.6 Hz, 2.3 Hz, 1 H), 6.54 (ddd, *J*=13.1, 9.4, 2.3 Hz, 1 H), 6.60 (ddd, *J*=12.9, 9.3, 2.3 Hz, 1 H), 7.01 (t, *J*=6.7 Hz, 1 H), 7.06 (t, *J*=6.8 Hz, 1 H), 7.31 (t, *J*=6.6 Hz, 1 H), 7.49 (d, *J*=5.8 Hz, 1 H), 7.65 (d, *J*=5.6 Hz, 1 H), 7.74-7.90 (m, 3 H), 8.10 (t, *J*=7.8 Hz, 1 H), 8.30 (d, 2 H), 9.26 (d, *J*=7.8 Hz, 1 H), 10.95 (s, 1 H). ^{13}C NMR (126 MHz, CD_2Cl_2, ppm): 14.2, 23.0, 26.4, 30.2, 31.4, 53.0, 99.0 (t, *J*=26.5 Hz), 99.5 (t, *J*=27.1 Hz), 114.6 (dd, *J*=6.9, 2.9 Hz), 114.7 (dd, *J*=6.9, 2.9 Hz), 123.8, 124.0, 124.1, 124.3, 125.7, 126.8, 128.5, 130.1 (d, *J*=23.6 Hz), 139.5, 139.6, 140.9, 149.2, 150.0, 150.1, 150.6, 150.9 (d, *J*=6.9 Hz), 154.4 (d, *J*=6.3 Hz), 160.5 (d, *J*=12.7 Hz), 160.9 (d, *J*=12.7 Hz), 162.5 (d, *J*=11.5 Hz), 162.6 (d, *J*=11.5 Hz), 163.0 (d, *J*=12.7 Hz), 163.1 (d, *J*=12.7 Hz), 164.5-164.6 (m), 165.1-165.2 (m). ^{19}F NMR (282 MHz, CD_2Cl_2, ppm): -111.16, -109.37, -107.92, -106.01.

Photochemical Isomerization. 15 mg of **2a** or **2b** was dissolved in DMSO-d_6 in a NMR tube capped with a rubber septum, and purged with Ar for 15 min. The sealed tube was irradiated with a portable pen light with broadband UV radiation, and the reaction completed after 3 days based on ^{1}H NMR. Saturated NaCl aqueous solution was added and the mixture was extracted with CH_2Cl_2. **7a** and **7b** were isolated as light yellow crystals (12 mg, 58%).

Crystal Structure Determinations. Low-temperature diffraction data (*φ*-and *ω*-scans) were collected on a Bruker D8 three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Cu *Kα* radiation (*λ* = 1.54178 Å) for the structures of compounds **2a**, **2b** and **6b**, and on a Bruker-AXS X8 Kappa Duo diffractometer coupled to a Smart Apex2 CCD detector with Mo *Kα* radiation (**λ** = 0.71073 Å) from an IμS micro-source for the structure of compound **7b**. The structures were solved by direct methods using SHELXS[57] and refined against F^2 on all data by full-matrix least squares with SHELXL-97[58] following established refinement strategies.[59] All non-hydrogen atoms were refined anisotropically. Except for the two hydrogen atoms on the water molecule in the structure of **7b**, all hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. Coordinates for the two water-hydrogen atoms were taken from the difference Fourier analysis and the hydrogens were subsequently refined semi-freely with the help of distance restraints. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups).

Compounds **2a**, **2b**, and **6b** crystallizes in the monoclinic space group $P2_1/c$, **2a** and **6b** contain one molecule and **2b** contains two molecules in the asymmetric unit. Compound **2a** contains half a molecule of hexane which is located near a crystallographic inversion center and disordered accordingly. Compound **2b** contains two molecules of CH_2Cl_2, one of which is disordered over three positions. Compound **7b** crystallizes in the monoclinic space group $P2_1$ with one molecule of **7b**, its chloride counter ion, one water molecule and one disordered molecule of dichloromethane. The N-bound *n*-hexyl group is heavily disordered and was modeled to be distributed over three independent, mutually exclusive positions. All disorders in all structures were refined with the help of similarity restraints on 1,2- and 1,3-distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters.

CCDC 817543 - 817546 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details. Ground-state geometries of [Ir(ppy)2(CN-tzpy)] and [Ir(ppy)2(N^N_tzpy)]+ were optimized by DFT calculations, which were performed using the Gaussian03 software (Gaussian Inc.)[60] with a B3LYP exchange-correlation functional and the LANL2DZ basis set under an effective core potential. The initial geometries were based on simplified X-ray structures of **2a** and **6b** respectively, with the hexyl groups replaced with methyl groups and F atoms with H atoms, and optimized without any constraints.

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Supporting Information Available: Crystallographic data in CIF format for compounds **2a**, **2b**, **6b** and **7b**, photo isomerization of *mer*-Ir(ppy)$_2$(trpy), packing diagrams of compounds **6b** and **7b**, NMR spectra of all the compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Table of Contents Synopsis and Graphic

Efficient synthesis of heteroleptic tris-cyclometalated Ir(III) complexes is achieved by using the Cu(I)-triazolide intermediates formed in "click" reactions as transmetalating reagents. Ligand preparation and cyclometalation of Ir(III) is accomplished in one pot. This method is general and provides opportunities to introduce different functional groups to the cyclometalated system for various applications. Moreover, this transmetalation approach is required to utilize trpy as a cyclometalating ligand, since the neutral N^N chelating mode is thermodynamically more favored than the anionic C^N mode.