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Highly Efficient, Selective, and General Method for the Preparation of Meridional Homo- and Heteroleptic Tris-cyclometalated Iridium Complexes

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A highly efficient and general method based on transmetalation with an organozinc reagent is developed for selective preparation of homo- and heteroleptic meridional tris-cyclometalated iridium complexes. The molecular structure of *mer*-Ir(1-piq)$_2$(ppy) (**2**) has been determined by a single-crystal X-ray diffraction analysis. The emission properties of a series of meridional complexes are reported.

Cyclometalated iridium complexes including their tris-cyclometalated derivatives have recently attracted a great deal of attention because of their promise as efficient phosphorescent emitters[1] in organic light-emitting devices (OLEDs) and other applications such as oxygen sensors[2] and biological labeling reagents.[3] Tris-cyclometalated iridium complexes can have facial and meridional configurations. Although the preparation and characterization of the facial isomers have been very well documented in the literature, it was not until recently that meridional isomers were prepared and characterized.[4] The previous preparation of a meridional isomer involves the reaction of a bis-cyclometalated iridium complex with a cyclometalating ligand via C−H bond activation. However, the *mer*/*fac* selectivity of the reaction is very sensitive to the reaction conditions such as temperature and solvents and is also substrate-dependent.[4a,b] Furthermore, we have found, in the cases of the preparation of some heteroleptic complexes, that the contamination of ligand-scrambling byproducts represents yet another challenge when using previously reported methods. More recently, a modified procedure was reported,[2a] but it requires the preparation of triflate derivatives of bis-cyclometalated iridium complexes, and low yields have been reported in some cases.[5] One of the ultimate goals of chemical synthesis is to achieve 100% selectivity in a reaction. This has driven us to develop alternative methodologies for the preparation of these cyclometalated iridium complexes. Herein reported is an efficient and general method for the selective preparation of meridional tris-cyclometalated iridium complexes including both homo- and heteroleptic complexes via a transmetalation process as shown in Scheme 1.

The method features the transmetalation of a halide-bridged dinuclear bis-cyclometalated iridium complex with a transmetalating reagent to form a tris-cyclometalated iridium complex. Although a number of organometals such as Li, Mg, B, Sn, etc., could be potentially useful in transmetalation processes,[6] organozincs were chosen as the preferred reagents because of their several advantages over the others. First, the reactivity of organozincs toward the transmetalation reaction of organotransition metals such as palladium and nickel is proven to be much higher than those of organoborons and -tins, as indicated in Negishi coupling.[7] Second, organozincs are significantly more stable than

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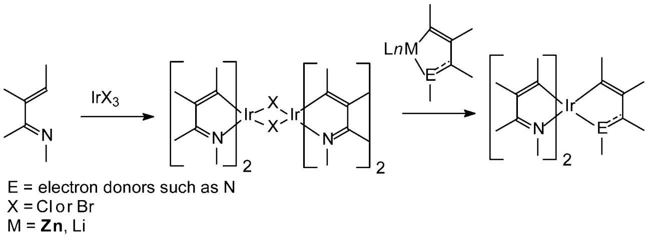
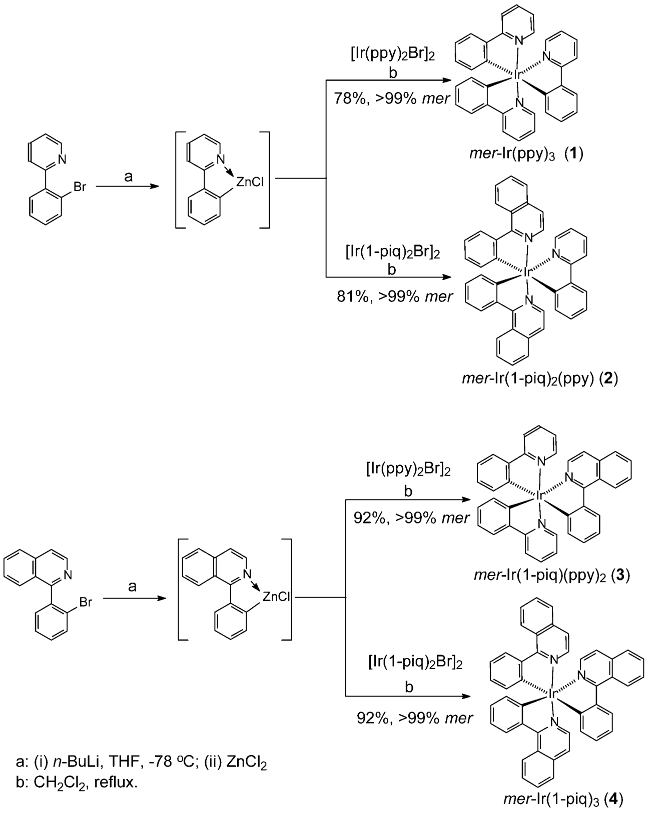
10.1021/ic060089v CCC: $33.50

Scheme 1



Scheme 2



organolithiums and -magnesiums and can tolerate a number of functional groups, which makes them unique reagents for transmetalation under various reaction conditions. Finally, organozincs can be readily accessible by transmetalation with organolithium or -magnesium reagents or by direct zinc insertion into organic halides.[8]

The effectiveness of the new approach is exemplified by the preparation of tris-cyclometalated iridium complexes with all four combinations of ligands ppy (2-phenylpyridine) and 1-piq (1-phenylisoquinoline) (Scheme 2). The precursor organic bromides were prepared by the coupling of (2-bromophenyl)boronic acid with the corresponding heteroaryl halides under the conditions reported by Lohse et al.[9] Treatment of the organic bromides with n-butyllithium in tetrahydrofuran (THF) at −78 °C followed by treatment with zinc chloride formed the organozinc reagents that were used directly for the next step of the reaction. Transmetalation of the bromide-bridged dimeric iridium complexes[10] with the organozincs proceeded smoothly to produce tris-cyclometalated iridium complexes in high yields and excellent selectivity.

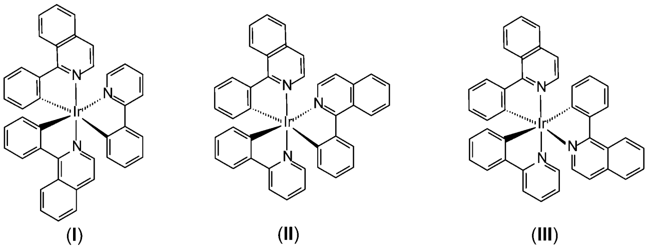


Figure 1. Meridional isomers of Ir(1-piq)$_2$(ppy).

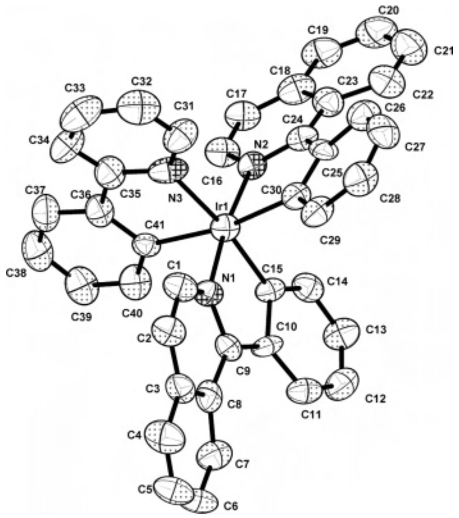


Figure 2. ORTEP diagram for **2** showing the atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. The solvent of crystallization 1,2-dichloroethane and hydrogen atoms were omitted for clarity.

When the ligand of the organozinc reagent is the same as those in the starting dinuclear bis-cyclometalated iridium complex, the homoleptic meridional tris-cyclometalated iridium complexes **1** and **4** are formed exclusively, as indicated by high-performance liquid chromatography (HPLC) analysis of the crude reaction products. In cases where the ligand of the organozinc reagent is different from the ligands in the halide-bridged dinuclear bis-cyclometalated starting material, the heteroleptic tris-cyclometalated iridium complexes **2** and **3** are formed. No formation of ligand-scrambling products was detected by HPLC analysis of the reaction mixture. A meridional heteroleptic tris-cyclometalated iridium complex can have more than one configuration. For example, *mer*-Ir(1-piq)$_2$(ppy) (**2**) can have three different meridional configurations, **I**−**III**, as shown in Figure 1. X-ray crystal structure analysis of the obtained **2** confirmed that it is a meridional isomer (**I**), where the two nitrogen atoms from the 1-piq ligands of the starting dinuclear bis-cyclometalated iridium complex [Ir(1-piq)$_2$Br]$_2$ are trans (Figure 2). The use of chloride-bridged dinuclear bis-cyclometalated iridium complexes gave comparable results. For example,

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(9) Lohse, O.; Thevenin, P.; Waldvogel, E. *Synlett* **1999**, 45. The Pd-catalyzed cross-coupling of (2-bromophenyl)boronic acid with 1-bromonaphthlene has been reported to produce 1-(2-bromophenyl)-naphthalene, but with a much higher Pd catalyst loading (20 mol %). Wegner, H. A.; Scott, L. T.; de Meijere, A. *J. Org. Chem.* **2003**, *68*, 883.
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reacting $[Ir(ppy)_2Cl]_2$ with the zinc reagent generated from 2-(2-bromophenyl)pyridine produced *mer*-$Ir(ppy)_3$ (**1**) selectively in 75% yield.

Although transmetalation proceeds in THF, the use of dichloromethane as a cosolvent significantly accelerates the reaction and facilitates the completion of the reaction. This is due to better solubility of the starting dinuclear bis-cyclometalated iridium complexes in dichloromethane than in THF. In some cases such as the preparation of *mer*-Ir(3-piq)$_2$(1-piq) (**5**; 77%, >99% *mer*) and *mer*-$Ir(btp)_2(ppy)$ (**6**; 93%, >99% *mer*) (where 3-piq = 3-phenylisoquinoline and btp = 2-benzothienylpyridine), dichloromethane must be used because of very poor solubility of the starting dinuclear iridium complexes, and an elevated temperature (refluxing) is required to achieve complete reaction within a reasonably short period of time. All of these complexes were formed selectively without any contamination of their facial isomers or ligand-scrambling byproducts.

When the reaction was performed with the use of the organolithium reagent[11] in situ generated from 2-(2-bromophenyl)pyridine and [Ir(1-piq)$_2$Br]$_2$, the desired product **2** was formed in very poor yield (15%). At −50 °C, no reaction was detected. When the temperature was raised to about −20 °C, formation of the desired product was observed; however, decomposition of organolithium apparently took place. Furthermore, because both the starting dinuclear bis-cyclometalated iridium complex and the product heteroleptic tris-cyclometalated complex were essentially insoluble in THF at low temperature, the entire reaction was a heterogeneous process and decomposition of the organolithium reagent may be faster than the desired reaction at an elevated temperature, therefore leading to the poor yield.

The selective preparation of meridional isomers, including heteroleptic compounds, now enables further probes of the electronic structure and photophysical properties of this important class of compounds. The emission spectra of **2**−**4**, as well as the previously reported[1b] *fac*-Ir(1-piq)$_3$, were compared in a poly(methyl methacrylate) (PMMA) host doped with the compounds (1%) (Figure 3). The spectra of **2** and **4** were almost the same as that of *fac*-Ir(1-piq)$_3$. The spectrum of **3** showed a large hypsochromic shift (30 nm) from the others as well as a marked change in the band shape. The great similarity in the band shape of **2** and **4** to *fac*-Ir(1-piq)$_3$ is in sharp distinction to the comparison reported for other *mer* and *fac* pairs, such as $Ir(ppy)_3$, for which the *mer* isomer has a significantly broadened spectrum indicative of greater excited-state distortion relative to the *fac* isomer. The emission spectrum of **3** may be assigned to the single 1-piq ligand present because it would be expected to provide the lowest-energy excited state. Hypsochromic shifts of emission spectra associated with a given ligand have been affected by introducing more strongly electron-withdrawing ancillary ligands,[5,12] but here the electron-withdrawing properties of the ppy and 1-piq ligands are expected to be similar. More likely, the hypsochromic shift may be attributed to the position of the 1-piq ligand in **3** where both coordination sites of the bidentate ligand are trans to strong σ-donor carbon atoms. While the crystal structure of **3** is not available, the structure of **2** shows that the Ir−N (2.118 Å) and Ir−C (2.105 Å) bonds of the ligand (ppy) with both coordination sites trans to Ir−C bonds are significantly longer than the other Ir−N (2.036 and 2.037 Å) and Ir−C (1.989 and 2.029 Å) bonds, respectively [similar observations were made concerning bond lengths in *mer*-Ir(tpy)$_3$[4a]]. Thus, the bonding of the 1-piq ligand in **3** is weakened, decreasing the admixture of the metal-to-ligand charge-transfer state with the ligand-based $\pi-\pi^*$ state and leading to the observed hypsochromic shift and change in the vibronic structure.

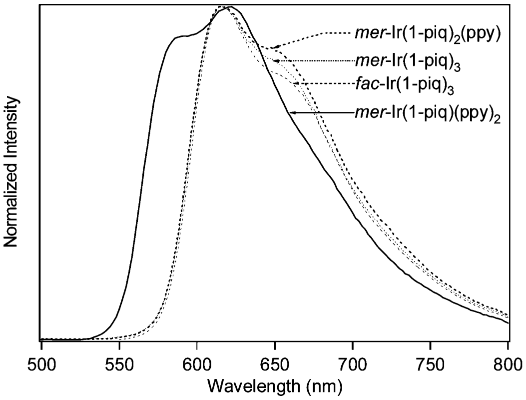

Figure 3. Photoluminescence spectra (in PMMA) of *mer*-Ir(1-piq)(ppy)$_2$, *mer*-Ir(1-piq)$_2$(ppy), *mer*-Ir(1piq)$_3$, and *fac*-Ir(1-piq)$_3$.

In summary, we have developed a new method that permits a highly selective preparation of homo- and heteroleptic *mer* tris-cyclometalated iridium complexes. These materials enable further elucidation of the electronic structure of cyclometalated iridium complexes through comparison of a wider range of emissive ligands in specific environments. Our subsequent reports will describe the isomerization to the *fac* isomers and include more detailed photophysical comparisons of the *mer* and *fac* compounds and their application in OLEDs.

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Supporting Information Available: Synthesis information; experimental details; ^1H NMR spectra of compounds **1**−**6**; ^1H and ^{13}C NMR chemical shifts; and a CIF file for complex **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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