A New Synthetic Route to the Preparation of a Series of Strong Photoreducing Agents: fac Tris-Ortho-Metalated Complexes of Iridium(III) with Substituted 2-Phenylpyridines

Table I. Emission and Cyclic Voltammetric Data for *fac* Tris-Ortho-Metalated Ir(III) Complexes

complex	τ, μs^a	λ_{em}, nm^b	$E_{1/2}(+1/0)^c$
$Ir(ppy)_3$	1.90	494	+0.77
$Ir(4\text{-Me-ppy})_3$	1.94	493	+0.70
$Ir(4\text{-Pr-ppy})_3$	1.93	496	+0.67
$Ir(4\text{-}t\text{-Bu-ppy})_3$	1.97	497	+0.66
$Ir(4\text{-F-ppy})_3$	2.04	468	+0.97
$Ir(4\text{-}F_3C\text{-ppy})_3$	2.16	494	+1.08
$Ir(4\text{-MeO-ppy})_3$	2.24	481	+0.75
$Ir(5\text{-MeO-ppy})_3$	2.86	539	+0.55

^{a}Emission lifetime in degassed acetonitrile at room temperature. ^{b}Shortest wavelength feature in emission spectrum in ethanol/methanol glass (1:1 by volume) at 77 K. ^{c}Half-wave potential for $[Ir(R\text{-}ppy)_3]^+/Ir(R\text{-}ppy)_3$ taken from cyclic voltammogram, V vs SCE (internal reference $E_{1/2}(Fc^{+/0})$ = 0.41 V vs SCE).

(III)[12-17,30-34] has motivated development of synthetic procedures to prepare these species in high yields. To this point it has been particularly difficult to isolate d^6 metal complexes that contain more than two metal–carbon bonds as is the case in tris-ortho-metalated complexes of ligands such as 2-phenylpyridine (Hppy). We report here a new procedure for high-yield synthesis of *fac* tris-ortho-metalated complexes of Ir(III) with (Hppy) and with substituted 2-phenylpyridine (R-Hppy) ligands. The prior procedure, in which Hppy reacted with iridium chlorides, was found to give high yields of the dichloro-bridged dimer[16,35] $[Ir(ppy)_2Cl]_2$ but only low yields (10%) of *fac*-$Ir(ppy)_3$.[22] Attempts to extend this procedure to methyl-substituted ppy ligands gave similarly high yields of the dichloro-bridged dimers[19] but only trace amounts of the *fac* tris-ortho-metalated complexes.[36] The procedure reported here utilizes the Ir(III) starting material $Ir(acac)_3$ (acac = 2,4-pentanedionate) and typically produces *fac* tris-ortho-metalated complexes in yields of 40%–75%.

In a typical reaction, $Ir(acac)_3$ (50 mg) and Hppy (0.09 mL) were dissolved in degassed glycerol (5 mL), and the solution was heated at reflux under nitrogen for 10 h. Addition of 1 M HCl (30 mL) after cooling resulted in precipitation of the product, which was collected on a glass filter frit. This product was dissolved in hot dichloromethane, the mixture was filtered, and the filtrate was flash-chromatographed on a silica gel column to remove darkly colored impurities. Addition of methanol to the chromatographed solution followed by heating to boiling to evaporate dichloromethane resulted in precipitation of the product as a flocculant yellow powder in 45% yield. The identity of the product as *fac*-$Ir(ppy)_3$ was confirmed by ^{1}H NMR, absorption, emission, and mass spectroscopies.

This procedure has been applied with similar success in the preparation of *fac*-$Ir(R\text{-}ppy)_3$ complexes for the series of substituted-phenyl complexes compiled in Table I. The substituted-phenyl R-Hppy ligands used in these preparations were prepared by cross-coupling of 2-bromopyridine with the appropriate substituted bromobenzene via treatment of the meta- or para-substituted bromobenzene with *n*-butyllithium and then with $ZnCl_2$ in tetrahydrofuran. The resulting ZnCl adduct was coupled with 2-bromopyridine by using $Pd[PPh_3]_4$ as a catalyst.[37] Each complex has been characterized by ^{1}H NMR, absorption, and emission spectroscopies, and crystals of *fac*-$Ir(4\text{-Me-ppy})_3$ have been grown by solvent vapor exchange between a solution of the compound in 2-methyltetrahydrofuran and neat methanol. Structural determination of this product by X-ray crystallography confirms the *fac* stereochemistry and reveals Ir–C bond lengths of 2.024 Å and Ir–N bond lengths of 2.132 Å.[38]

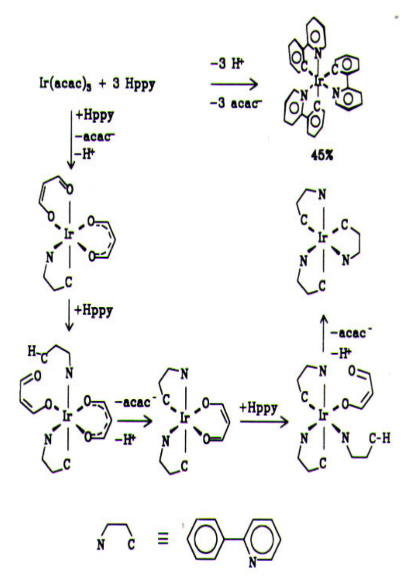

Figure 1. Schematic representation of the trans effect of Ir–C bonds in the synthesis of *fac* tris-ortho-metalated Ir(III) complexes from reaction of $Ir(acac)_3$ with 2-phenylpyridine.

Several factors might contribute to the success of this method for preparation of *fac* tris-ortho-metalated complexes of Ir(III). Elimination of chloride from the reaction mixture obviously prohibits formation of a dichloro-bridged dimer. Furthermore, the trans-directing effect of Ir–C bonds should lead to preferential labilization of Ir–O bonds located trans to the Ir–C bonds.[39] Since the initial binding of an incoming 2-phenylpyridine results from formation of an Ir–N′ bond at the labilized site, the anticipated result will be sterochemical positioning of Ir–C and Ir–N′ bonds trans to one another with mutually cis Ir–C, Ir–C′ and Ir–N, Ir–N′ bonds (Figure 1). A similar trans effect, which would lead to formation of the *fac* tris isomer, might be anticipated in reactions of Hppy with Ir(III) precursors of monodentate ligands, including chloride, where labilization of chloride trans to an Ir–C bond followed by formation of an Ir–N bond at the labilized position is again expected. However, the known stereochemistry of the dominant dichloro-bridged dimers[16,19,35] is characterized by mutually cis Ir–C bonds but mutually trans Ir–N bonds. This may result from formation of a 5-coordinate Ir(III) intermediate that could lead to a common, preferred stereochemistry for bischelated intermediates formed in reaction with starting materials containing monodentate ligands. Several theoretical studies of the relative stabilities of d^6 metal complexes with well-known square-pyramidal and trigonal-bipyramidal geometries have been presented.[40,41] Although relatively few 5-coordinate complexes of d^6 metals have been experimentally determined, the structures of the 5-coordinate chloro–bis(phosphinoethyl)silyl complexes of the d^6 metals Rh(III) and Ir(III) bear no close resemblance to either the square-py-

(30) Craig, C. A.; Garces, F. O.; Watts, R. J. *Proceedings of the Seventh International Symposium on the Photochemistry and Photophysics of Coordination Compounds*; Yersin, H.; Vogler, A., Eds.; Springer-Verlag: Berlin, 1987; p 135.
(31) Mader, U.; Jenny, T.; von Zelewsky, A. *Helv. Chim. Acta* **1986**, *69*, 1085.
(32) Zilian, A.; Maeder, U.; von Zelewsky, A.; Gudel, H. U. *J. Am. Chem. Soc.* **1989**, *111*, 3855.
(33) Maestri, M.; Sandrini, D.; Balzani, V.; Mader, U.; von Zelewsky, A. *Inorg. Chem.* **1987**, *26*, 1323.
(34) Sandrini, D.; Maestri, M.; Balzani, V.; Mader, U.; von Zelewsky, A. *Inorg. Chem.* **1988**, *27*, 2640.
(35) Nonoyama, M. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 767.
(36) Garces, F. O.; Escobar, J.; Watts, R. J. Unpublished results.
(37) Negishi, E.-I.; Luo, F.-T.; Frisbee, R.; Matsushita, H. *Heterocycles* **1982**, *18*, 117.
(38) Garces, F. O.; Keder, N.; Dedeian, K.; Watts, R. J. Unpublished results. Complete details of the X-ray structure determination will be published separately.
(39) Immirzi, A. *J. Organomet. Chem.* **1974**, *81*, 217.
(40) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.
(41) Vanquickenborne, L. G.; Ceulemans, A. *Inorg. Chem.* **1978**, *17*, 2730.

ramidal or the trigonal-bipyramidal geometry.[42] Thus, reaction of Hppy with any Ir(III) starting material containing simple monodentate ligands might lead to modification of the stereochemistry favored by trans-directing effects of Ir–C bonds via formation of a common 5-coordinate monomer and then a bridged dimer. The success of $Ir(acac)_3$ in promoting formation of *fac* tris complexes in reaction with Hppy and related ligands may arise from inhibition of formation of this common 5-coordinate intermediate as a result of the bidentate nature of $acac^-$.

The luminescence lifetime of each of the *fac*-$Ir(R\text{-}ppy)_3$ complexes (Table I) is approximately 2–3 μs in nitrogen-saturated acetonitrile at room temperature. The similarities in the lifetimes and emission energies of all of the *fac*-$Ir(R\text{-}ppy)_3$ complexes indicate that they, like $Ir(ppy)_3$,[22,23] each emit from an MLCT excited state. Each complex is characterized by a reversible oxidative wave in cyclic voltammetry in acetonitrile (+0.55 to +1.08 V vs SCE), which indicates the relative ease of oxidation of Ir(III) to Ir(IV) in these species. The position of the oxidative wave follows a pattern in which more positive values are found for complexes of ligands bearing electron-withdrawing substituents and less positive values result from ligands with electron-donating substituents (see Table I).

We are presently characterizing excited-state electron-transfer reactions of these *fac* tris-ortho-metalated complexes of Ir(III). These studies are intended to fully characterize the excited-state reducing power of *fac* tris-ortho-metalated Ir(III) complexes.

Acknowledgment. This work was supported by the Office of Basic Energy Sciences, U.S. Department of Energy (Contract DE-FG03-88ER13842). We wish to thank Dr. Nancy Keder for her assistance in determining the structure of $Ir(4\text{-}Me\text{-}ppy)_3$.

(42) Stobart, S. R.; Auburn, M. J. *Inorg. Chem.* **1985**, *24*, 318.

Department of Chemistry
University of California
Santa Barbara, California 93106

K. Dedeian
P. I. Djurovich
F. O. Garces
G. Carlson
R. J. Watts*

Received July 17, 1990