as noted. The last column in Table I lists reported k_s values for metalloporphyrins as determined by cyclic voltammetry with conventional platinum electrodes (Nicholson method). In several cases we also used the Nicholson method, after attempting to correct ΔE_p for iR distortion by extrapolation to zero concentration and/or by substracting the iR drop shown by ferrocene (assumed to be reversible) at equivalent currents. Nevertheless, for the metalloporphyrins, the k_s obtained from steady-state experiments is significantly larger in each case. This is true for electron transfer ranging from quite slow for the metal-centered reduction of Mn(p-ClTPP)(DMSO)$_2^+$ to very rapid (reversible) for the ring-centered reduction of Zn(TPP). Figure 2 shows a series of steady-state voltammograms for the former complex; the slow electron transfer in this case is responsible for the negative shift of $E_{1/2}$ as the electrode size is decreased.

Table I also contains some results for the reduction of ferricyanide in methanol and water. After small iR corrections based on ferrocene were applied, the k_s in methanol obtained with a 1.6-mm platinum electrode matched from that found with microelectrodes under steady-state conditions. Likewise, the two procedures gave similar results in water/KCl. (The NaCN was present to prevent electrode fouling.[25]) The conclusion is that steady-state and transient methods indeed give the same results when the medium is sufficiently polar so that resistance effects are insignificant. It may be noted that the oxidation of potassium ferrocyanide in water has been examined by others with microelectrodes. At a 12-μm-diameter carbon fiber disk electrode (0.5 M KNO$_3$) a k_s of 0.02 cm/s was found[21] under steady-state conditions. At a 15-μm-diameter platinum microdisk (1.0 M HCl) the steady-state voltammogram suggests[26] a k_s of 0.07 cm/s; however, these authors inexplicably found the voltammogram at a much smaller platinum disk to have the same shape and concluded that the redox couple is reversible. At a 10-μm carbon fiber microdisk (pH = 1, CF$_3$COOH/CF$_3$COO$^-$Na$^+$ buffer) conventional CV's obtained at 500 V/s gave $k_s = 0.06$ cm/s by the Nicholson method, while at the same electrode under steady-state conditions the ferrocyanide oxidation was reported[27] to be reversible; this is inconsistent because a k_s of 0.06 cm/s predicts a steady-state voltammogram that deviates significantly from a reversible shape; e.g., the value of $(E_{3/4} - E_{1/4})$ should be 68 mV.

In summary, we found that heterogeneous charge-transfer rate constants determined by cyclic voltammetry with conventional electrodes are subject to large errors if the solutions used are highly resistive. Furthermore, the discrepancy between the apparent and the real k_s becomes greater as the electron transfer becomes more reversible. Elimination or correction for iR and charging current distortions is not simple. The use of microelectrodes under steady-state conditions eliminates most of the distortions and thus provides a convenient alternative procedure for studying the kinetics of charge transfer. It should be noted that steady-state voltammetry with microelectrodes can also be applied to the study of various types of *homogeneous* reactions coupled to the redox process.[28-30] Thus, microelectrodes permit both heterogeneous and homogeneous reactions to be examined without the distortions that plague experiments with conventional electrodes.

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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

Current interest in the photophysics and photochemistry of ortho-metalated complexes of d^6 and d^8 metal ions such as Pt(II),[1-14] Ir(III),[13-23] Ru(II),[14,24,25] Pd(II)[10-14,26-30] and Rh-

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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 ^1H 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 ^1H 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]

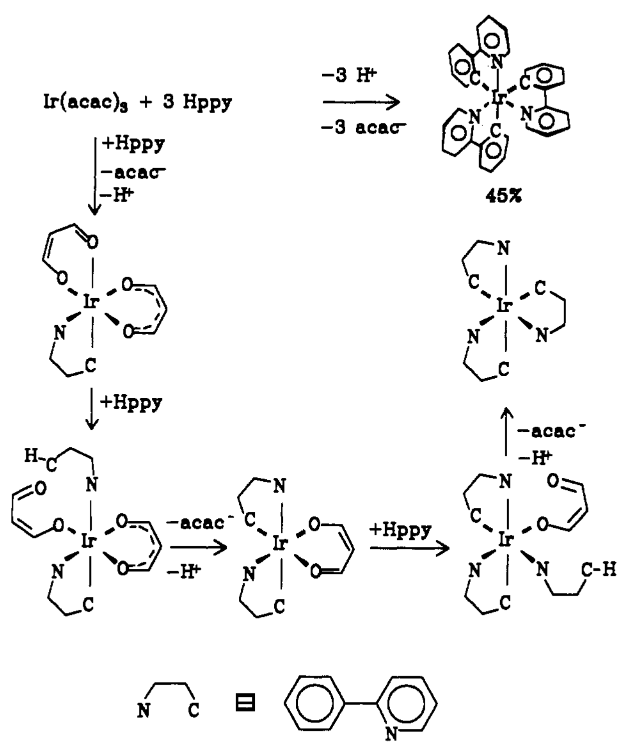

Figure 1. Schematic representation of the trans effect of Ir–C bonds in the synthesis of *fac* tris-ortho-metalated Ir(III) complexes from reaction of $Ir(acac)_3$ with 2-phenylpyridine.

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-

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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.

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Sulfur-Bridged Incomplete Cubane-Type Mixed-Metal Cluster Compounds of Molybdenum(IV) and Tungsten(IV). Syntheses, Characterization, and X-ray Structures of $[Mo_2WS_4(H_2O)_9](CH_3C_6H_4SO_3)_4\cdot 9H_2O$ and $[MoW_2S_4(H_2O)_9](CH_3C_6H_4SO_3)_4\cdot 9H_2O$

Molybdenum sulfur compounds have attracted much attention, and a large number of sulfur-bridged molybdenum compounds have appeared.[1] Among them, many molybdenum compounds with incomplete cubane-type Mo_3S_4 cores[2] have been reported and some tungsten analogues with W_3S_4 cores[3] also studied.

We now report the syntheses, characterization, and X-ray structures of incomplete cubane-type molybdenum(IV)–tungsten(IV) mixed-metal aqua cluster compounds $[Mo_2WS_4(H_2O)_9](CH_3C_6H_4SO_3)_4\cdot 9H_2O$ (Mo_2W') and $[MoW_2S_4(H_2O)_9](CH_3C_6H_4SO_3)_4\cdot 9H_2O$ (MoW_2'), which complete a series of clusters having the following cores:

$$Mo_3S_4 \qquad Mo_2WS_4 \qquad MoW_2S_4 \qquad W_3S_4$$

Only a few triangular molybdenum-tungsten mixed-metal compounds are known;[4-7] however, no reports on mixed-metal compounds with any sulfur bridge(s) have appeared so far.[8] Once aqua ions are prepared, the derivatives are prepared easily by substitution reactions.[9] The aqua ions $[Mo_3S_4(H_2O)_9]^{4+}$ (Mo_3)[2g,h] and $[W_3S_4(H_2O)_9]^{4+}$ (W_3)[3a,b,g] are well-known, and their X-ray structures have been determined.[2h,3b]

$(NH_4)_2WS_4$[10] (1.00 g, 2.87 mmol) and bis(μ-sulfido)(cysteinato)molybdenum(V) dimer $Na_2[Mo_2O_2S_2(cys)_2]\cdot 4H_2O$[11] (1.85 g, 2.87 mmol) were dissolved in water (50 mL), and small portions (ca. 2 mL each) of $NaBH_4$ (3.0 g in 20 mL H_2O) and 6 M HCl (20 mL) were added alternately to the solution. Then, an additional amount (80 mL) of 6 M HCl was added to the solution, which was heated at above 90 °C for 5 h with introduction of an air stream. During heating, 1 M HCl was added occasionally to keep the volume of the solution constant (ca. 150 mL). The solution was cooled to room temperature and filtered by suction. The filtrate was subjected to Sephadex G-15 column chromatography (4.0 cm × 85 cm, 1 M HCl). The sixth ($MoW_2(aq)^{4+}$ (MoW_2); gray) and seventh bands[12,13] ($Mo_2W(aq)^{4+}$ (Mo_2W); green) were concentrated by use of a cation exchanger, Dowex 50W-X2 (2 M HCl). Sephadex G-15 column chromatography (2.0 cm × 150 cm, 1 M HCl) was applied again for purification. This concentration–purification process is repeated again; yields of Mo_2W and MoW_2 (in solution) are 17% and 3%, respectively. The crystalline compounds[14] Mo_2W' (green plates) and MoW_2'

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(10) McDonald, J. M.; Frisen, G. D.; Rosenheim, L. D.; Newton, W. E. *Inorg. Chim. Acta* **1983**, *72*, 205–210.

(11) For example: (a) Ott, V. R.; Swieter, D. S.; Schultz, F. A. *Inorg. Chem.* **1977**, *16*, 2538–2545. (b) Shibahara, T. *Abstracts of Papers, Rational Synthesis of Metal Cluster Compounds and Cooperative Phenomena of Multinuclear Frameworks*, 35th Okazaki Conference, Okazaki, Japan, May 1989; Institute for Molecular Science: Okazaki, Japan, 1989.

(12) Other bands: 1st, $Mo_4S_4(aq)^{5+}$ (green); 2nd, $Mo_3O_2S_2(aq)^{4+}$ (gray); 3rd, unknown (greenish yellow); 4th, unknown (yellowish green); 5th, $Mo_3OS_3(aq)^{4+}$ (green); 8th, $Mo_3S_4(aq)^{4+}$ (green).

(13) The mixture of Mo_3 and W_3 clusters is clearly separated into two bands by Sephadex G-15 column chromatography, while the Mo_2W (or MoW_2) cluster is not separated by the method, which supports the existence of the mixed-metal clusters.

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