

Excited-State Properties of a Triply Ortho-Metalated Iridium(III) Complex

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Recent studies¹⁻³ of photophysical properties of ortho-metalated complexes of 2-phenylpyridine (ppy) with Ir(III) and Rh(III) suggest significant utility of this ligand in preparing useful photocatalysts. We report here characterization of the ground and luminescent excited states of a triply ortho-metalated complex of ppy, *fac*-Ir(ppy)₃. This complex, which is the first triply ortho-metalated ppy species to be characterized, is one of the strongest transition-metal photoreductants thus far reported.

Reactions of ppy with chloride salts of Rh(III) and Ir(III) give high yields of dichloro-bridged dimers of the type [Rh(ppy)₂Cl]₂ and [Ir(ppy)₂Cl]₂.³⁻⁵ Although these dimers undergo facile reactions⁴⁻⁷ with a variety of monodentate (L) and bidentate (LL') chelating ligands to yield monomeric species of the type M(ppy)₂ClL or M(ppy)₂LL'+, attempts to react the dimers with excess ppy have failed to yield a tris-ortho-metalated species of the type *mer*-Ir(ppy)₃.⁸ However, the facial isomer of ppy with Ir(III) *fac*-Ir(ppy)₃ is formed as a side product to [Ir(ppy)₂Cl]₂ in the reaction of ppy with hydrated IrCl₃. A few examples of triply ortho-metalated mononuclear complexes of other ligands have been reported,⁹⁻¹¹ but these are rare, and no prior reports of a triply ortho-metalated ppy complex or of the photophysical properties of any triply ortho-metalated species have appeared.

In the previously described³ preparation of [Ir(ppy)₂Cl]₂, the initially formed yellow precipitate was washed with ethanol and acetone prior to final purification procedures, which gave the dichloro-bridged dimer in 72% yield. In the present study, the ethanol and acetone washes were evaporated to dryness and combined by dissolution in CH₂Cl₂. This solution was washed with 1 M HCl and dried over MgSO₄. Evaporation of the solvent gave a yellow solid, which was dissolved in methanol and chromatographed on a column of Sephadex LH-20 using methanol for elution. Evaporation of methanol from the solution of the product gave an air-stable yellow solid in 10% yield. Elemental analysis confirmed the formulation of this product as a tris complex of ppy with Ir(III), Ir(C₁₁H₈N)₃; mass spectral analysis showed a parent peak at *m/e* 655 (Ir(ppy)₃⁺) with fragments at *m/e* 500 and 155 (Ir(ppy)₂⁺ and ppy⁺), further confirming this formulation. The facial geometry of the product was established with ¹H NMR spectroscopy in CD₂Cl₂ (eight chemical shifts in the range δ 6.7-8.0) and with proton-decoupled and SFORD ¹³C NMR spectroscopy (11 resonances, three of which remained unsplit in SFORD measurements).

The absorption spectrum and emission spectrum of *fac*-Ir(ppy)₃ are illustrated in Figure 1. A luminescence lifetime of 5.0 μs

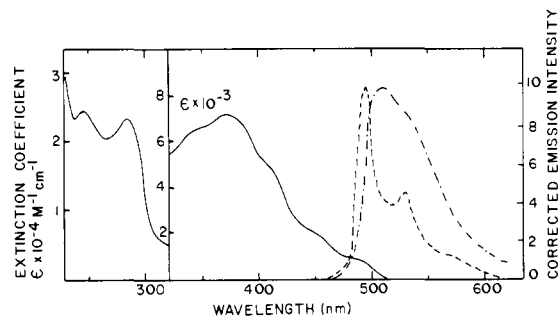


Figure 1. Absorption and emission spectra of tris(2-phenylpyridine-C₂,N')iridium(III). Absorption in toluene at 295 K (—); emission in ethanol/methanol glass (4/1 by volume) at 77 K (---); emission in toluene at 295 K (-.-.-).

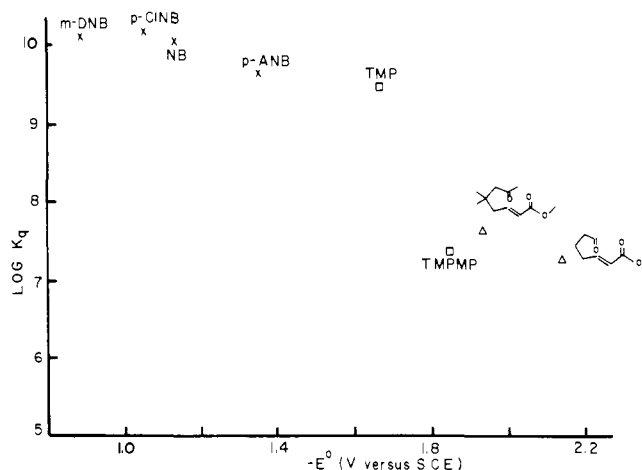


Figure 2. Quenching constants (k_q , M⁻¹ s⁻¹) for luminescence lifetime quenching of Ir(ppy)₃ by oxidative quenchers. (X) Nitrobenzene series: *m*-DNB = *m*-dinitrobenzene, *p*-CINB = *p*-chloronitrobenzene, NB = nitrobenzene, *p*-ANB = *p*-aminonitrobenzene. (□) Methylpyridinium series: TMP = 1,2,4,6-tetramethylpyridinium hexafluorophosphate, TMPMP = 1,2,6-trimethyl-4-methoxypyridinium hexafluorophosphate. (Δ) α,β-Unsaturated keto and aldehyde esters (structures indicated).

was observed in ethanol/methanol glass (4:1 v/v) at 77 K. Under ambient temperature conditions a luminescence lifetime as long as 2.0 μs could be obtained after repeated freeze-pump-thaw cycles in toluene or in acetonitrile, but a lifetime of only 100 ns was observed in ambient CH₂Cl₂. The complex was found to be photoactive in deoxygenated CH₂Cl₂, as well as in deoxygenated CHCl₃ and CCl₄, confirming that photochemical quenching of the excited state is at least partially responsible for the short lifetime observed in CH₂Cl₂. No photoactivity was noted in ambient toluene solutions, where a luminescence quantum yield of 0.4 ± 0.1 was observed under carefully deoxygenated conditions. This indicates a radiative lifetime of about 5 μs in ambient toluene solutions; the observed 5-μs lifetime in a 77 K ethanol/methanol glass would then suggest a near-unity luminescence yield at 77 K if temperature and solvent effects on the radiative decay rate are negligible. This radiative decay rate indicates a MLCT assignment of the luminescent excited state.¹²⁻¹⁵

The observed photoactivity in halocarbon solvents suggested that Ir(ppy)₃ may be a strong reducing agent in its excited state; this led us to study quenching of its luminescence lifetime by several series of oxidative quenchers. Results of this study are summarized in Figure 2 with a plot of the log of the quenching constant, k_q , as a function of the reduction potential of the quenching species. Quenching by the entire series of nitrobenzene-type quenchers¹⁶ occurs at near-diffusion-controlled rates

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in toluene; however, quenching by two alkylated pyridinium acceptors¹⁷ in acetonitrile reveals a sharp decrease in the quenching rate in the region around -1.8 V. Quenching by α,β -unsaturated keto and aldehyde esters in acetonitrile confirms the diminished quenching rate in the region where the reduction potential of the acceptor is below -1.8 V. The functional dependence of the quenching rates upon the reduction potential of the quencher indicates that quenching is due to outer-sphere electron transfer from the excited complex to the quenching agent.¹⁸ These quencher/solvent combinations do not constitute a homologous series;¹⁸ however, the rather sharp break in quenching rates of the alkylated pyridinium acceptors suggests a rough estimate of -1.8 V vs. SCE for the reduction potential of the oxidized ground-state/excited-state couple, $\text{Ir}(\text{ppy})_3^+/\text{*Ir}(\text{ppy})_3$. This value agrees well with an estimate based upon the excited-state energy taken from emission measurements (2.5 V) and the $E_{1/2}$ value of $+0.7$ V vs. SCE for $\text{Ir}(\text{ppy})_3^+/\text{Ir}(\text{ppy})_3$ in cyclic voltammetric measurements in acetonitrile.¹⁹ The contrast of the strong reducing power of $\text{*Ir}(\text{ppy})_3$ compared to the strong oxidizing power of $\text{*Ir}(\text{bpy})_3^{3+}$ ($E^\circ(\text{*Ir}(\text{bpy})_3^{3+}/\text{Ir}(\text{bpy})_3^{2+}) > 2$ V)²⁰ illustrates the large effects of Ir-C bonding in altering the electron-transfer properties in ortho-metalated species relative to those in N-chelated complexes.

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Gas-Phase Photofragmentation of $\text{Cr}(\text{CO})_6$: Time-Resolved Infrared Spectrum and Decay Kinetics of "Naked" $\text{Cr}(\text{CO})_5$

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The photochemistry of transition-metal carbonyl complexes continues to be an area of active research with $\text{Cr}(\text{CO})_6$ receiving particularly heavy investigation.¹ In condensed media, photolysis of $\text{Cr}(\text{CO})_6$ leads to formation of $\text{Cr}(\text{CO})_5$ which weakly interacts with a matrix atom (20 K)² or solvent molecule (293 K).³⁻⁵ However, surprisingly few details are known regarding the gas-phase photofragmentation of $\text{Cr}(\text{CO})_6$. The nature of the photoproducts may in fact be sensitive to photolysis wavelengths.⁶⁻⁸

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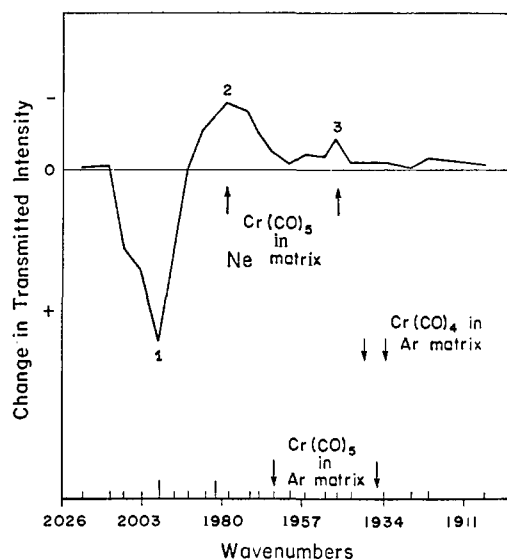


Figure 1. Time-resolved IR spectrum obtained 500 ns after XeF laser excitation ($\lambda = 351$ nm) of a mixture of ~ 30 mtorr of $\text{Cr}(\text{CO})_6$ with 0.3 torr of CO and 5 torr of Ar buffer at 20 °C. The + and - on the ordinate correspond to increased and decreased transmitted light, respectively. Feature 1 corresponds to photolyzed $\text{Cr}(\text{CO})_6$ (increase in transmitted light intensity). Features 2 and 3 are assigned to photogenerated $\text{Cr}(\text{CO})_5$ (decrease in transmitted light intensity). Absorptions of matrix-isolated $\text{Cr}(\text{CO})_5$ and $\text{Cr}(\text{CO})_4$ are displayed for comparison (see text). The tick marks on the abscissa show the CO laser lines used to construct the spectrum. The two large tick marks are the frequencies at which the kinetic measurements, displayed in Figure 2, were performed.

Recent advances in fast monitoring of photochemical reactions via infrared (IR) probes have yielded valuable information concerning the structure and kinetics of transient metal carbonyl species.^{3,8-11} Indeed, the square pyramidal structure of $\text{Cr}(\text{CO})_5$ in solution has recently been verified by fast IR spectroscopy.⁵ We wish to report here that XeF laser (351 nm) photolysis of $\text{Cr}(\text{CO})_6$ in the gas phase leads to predominant formation of "naked" $\text{Cr}(\text{CO})_5$. We also report on the structure of $\text{Cr}(\text{CO})_5$ and the rate of its reaction with CO.

The time-resolved IR apparatus used for monitoring photochemically generated metal carbonyl transients in the gas phase has been previously described.¹⁰ In this study a Questek excimer laser was used as the photolysis source and a line-tunable liquid nitrogen cooled CO laser as the IR probe. Changes in intensity of transmitted IR light were detected via a high-speed InSb detector. The output of the detector was fed to appropriate amplifiers and was subsequently signal averaged. Spectral data were obtained from the transient absorption signals for each CO laser line of interest by having a computer join points corresponding to the amplitude of the transient signal at these frequencies for a given time delay following the photolysis pulse. Kinetic data for CO recombination were obtained from transients at a given probe laser wavelength.

Figure 1 shows the IR spectrum obtained 500 ns after photolysis of a mixture of ~ 30 mtorr of $\text{Cr}(\text{CO})_6$ with 0.3 torr of CO and 5 torr of Ar buffer at 21 °C. Depletion (increase in transmitted light intensity) of $\text{Cr}(\text{CO})_6$ is evident at ca. 2000 cm^{-1} (feature 1), illustrating that net photolysis has occurred. The positive absorptions (decrease in transmitted light intensity) at ca. 1980

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