The synthetic cyanocycline A[14] was identical with an authentic sample in TLC behavior and spectroscopic properties.[15]

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Supplementary Material Available: Copies of NMR spectra of key intermediates and synthetic cyanocycline A (9 pages). Ordering information is given on any current masthead page.

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(13) All the other oxidation conditions we tried furnished no more than 25% yield of **1**.

(14) The yellow crystals started darkening at 140 °C and became a black mass by 160 °C without showing clear melting point.

(15) We are indebted to Professor Steven Gould, Oregon State University, for a sample of authentic cyanocycline A.

Dual Emission from an Ortho-Metalated Ir(III) Complex

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Several complexes of Ir(III) containing both the bidentate N-coordinating ligand 2,2′-bipyridine (bpy) and the N,C-ortho-metalating ligand 2-phenylpyridine (ppy) have recently been prepared; these include the two species Ir(ppy)$_2$(bpy)$^+$ (A) and Ir(ppy)(bpy)$_2$$^{2+}$ (B). The former was prepared from the dichloro-bridged dimer, [Ir(ppy)$_2$Cl]$_2$, by modification of the procedure of Nonoyama[1,2] while the latter was obtained by reaction[3] of *cis*-[Ir(bpy)$_2$(OSO$_2$CF$_3$)$_2$] [CF$_3$SO$_3$] with ppy in refluxing 2-ethoxyethanol. Both complexes were purified by column chromatography on Sephadex LH-20 using ethanol for elution. The purity of the complexes was monitored with thin-layer chromatography using silica gel plates and 1:1:1 acetone/methanol/water mixtures for elution. Samples of the complexes used in these studies showed only one component in thin-layer chromatography. While only one isomer of B is possible, there are three possible isomers of A. Data from ^{1}H and ^{13}C NMR experiments[4] indicate that A has C_2 symmetry. The NMR spectrum indicates, as does thin-layer chromatography, that only a single isomer of A is present with no detectable impurities due to a mixture of isomers. While X-ray structural data for A are lacking, structural data for related complexes[5-8] suggest that A is the isomer with cisoid metal–carbon bonds and bpy metal–nitrogen bonds transoid to the metal–carbon bonds. These species were prepared in order to probe further the effects of metal–carbon bonding on energy-transfer processes and electron-transfer reactions of metal complexes.[9,10] Emission spectroscopic studies reported here reveal unusual and distinct intramolecular energy-transfer behavior in these complexes. Whereas dual emission from the former is observed in glasses at 77 K, a single emission is observed in the latter.

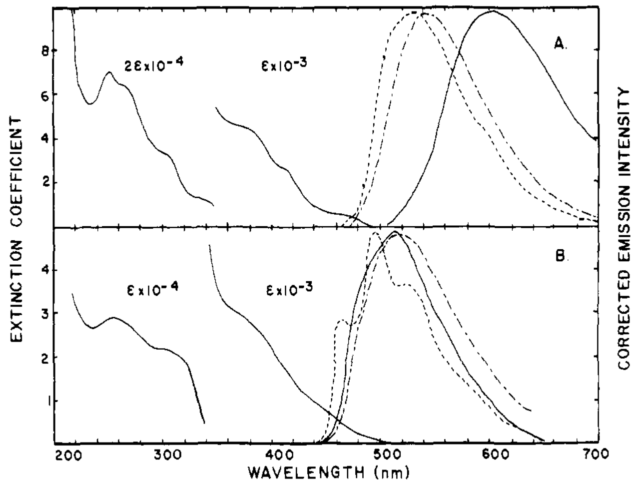

Figure 1. Absorption and emission spectra of Ir(ppy)$_2$(bpy)$^+$ (A) and of Ir(bpy)$_2$(ppy)$^{2+}$ (B). A: (—) absorption (left) and emission (right) in methanol at room temperature; (- - -) emission in ethanol/methanol (4:1 by volume) at 77 K; (-···-) emission in poly(methyl methacrylate) at room temperature. B: (—) absorption (left) and emission (right) in methanol at room temperature; (- - -) emission in ethanol/methanol (4:1 by volume) at 77 K; (-···-) emission in poly(methyl methacrylate) at room temperature.

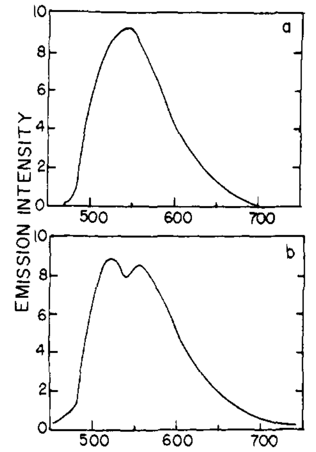

Figure 2. Time-resolved emission spectra of Ir(ppy)$_2$(bpy)$^+$ in ethanol/methanol (4:1 by volume) at 77 K excited at 336 nm with a pulsed nitrogen laser: (a) 100 ns after excitation; (b) 15 μs after excitation.

The absorption spectra of A and B at room temperature and their time-integrated emission spectra in fluid solutions at room temperature and in 77 K glasses are presented in Figure 1. The broad, structureless emission spectrum of A in 77 K glasses contrasts with the structured emission of B, as does the large red shift of the emission of A in fluid room temperature solutions relative to the small red shift of B. That this is largely a viscosity effect rather than a temperature effect is evidenced by observations of comparable red shifts in the emissions of A and B in 77 K and room temperature poly(methyl methacrylate) solutions.

The emission lifetimes of A and B are comparable in 77 K ethanol–methanol glasses (5.0 and 6.8 μs, respectively) and in fluid room temperature methanol solutions (0.35 and 1.1 μs, respectively). Luminescence decay curves of both complexes excited with the 337-nm fundamental of the N$_2$ laser at 77 K fit sufficiently well to a single exponential analysis to indicate that, if two components are emissive, their lifetimes are similar. Attempts to fit the luminescence decay data for A to a double-exponential

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function yielded components whose lifetimes differed by less than 2 μs, and no significant improvement over the single-exponential fits was obtained. However, following pulsed excitation at 337 nm, time resolution of the emission of A via boxcar averaging techniques reveals a structured emission at long delay times (>15 μs) with an origin at 520 nm (Figure 2), whereas time resolution of B indicates that its emission spectrum is independent of delay time. Pulsed excitation of A at 477 nm in 77 K glasses results in the same structured emission as that in Figure 2, and no further resolution of this structure is obtained by time resolution. Under these conditions, single-exponential analysis yields a 5-μs lifetime and double-exponential analysis again fails to give significant improvement to fits of the experimental data at any of the wavelengths throughout the emission spectrum. Furthermore, the same structured emission of A can be observed in its time-integrated emission spectrum under long-wavelength excitation (>460 nm) while the time-integrated emission spectrum of B is independent of excitation wavelength. The emission spectra of both A and B are independent of delay time and excitation wavelength in room temperature fluid solutions. The positions of the emission energies of both A and B were found to be dependent upon the solvent medium (blue shifts in more polar solvents). The magnitude of the luminescence lifetimes of A and B and the solvent dependence of their emission spectra are indicative of emission which originates in MLCT excited states.

Cyclic voltammetric analysis of A reveals a reversible oxidation wave at $E_{\mathrm{pa}} = +1.32$ V vs. SCE in acetonitrile while the first oxidation wave of B is anodically shifted to $E_{\mathrm{pa}} = +2.05$ V. The first reduction wave of A is also reversible at $E_{\mathrm{pc}} = -1.4$ V vs. SCE while the first reduction wave of B is observed at $E_{\mathrm{pc}} = -1.2$ V. These results are consistent with prior studies indicating that, relative to metal-nitrogen bonding in bpy species, metal-carbon bonding in ppy complexes facilitates metal oxidation.[10-13] Correlation of ΔE values ($\Delta E = E_{\mathrm{pa}}{}^{\mathrm{ox}} - E_{\mathrm{pc}}{}^{\mathrm{red}}$) for A and B (2.72 and 3.25 V, respectively) with their emission energies is consistent with a metal-centered oxidation and a bpy-centered reduction in both the optical and electrochemical processes.[14-18]

Several sources of a second emission evident in time-resolved luminescence of A should be considered. These include emission originating from impurities, such as a mixture of structural isomers or from ground-state association processes, and emission originating from a second, unequilibrated electronic excited state. The absence of evidence of impurities in TLC and NMR analyses and the adherance of solutions of A to Beer's law over the concentration range which was studied suggest that the dual emission of A is not due to impurities but rather is due to emission from unequilibrated excited states. The similarity in the lifetimes of the two emissions in the dual luminescence of A indicates contributions from a second MLCT excited state. While these two states are too similar in their lifetimes to differentiate in double-exponential fitting of their decay curves, their lifetimes are sufficiently different to show the types of changes in emission profile with time under 337-nm excitation that are illustrated in Figure 2. A MLCT state in which an electron is promoted to a π^* orbital of ppy (MLCT ppy) is expected to lie above the low-energy MLCT state in which an electron is promoted to a bpy π^* orbital (MLCT bpy) in both A and B. This type of MLCT ppy excited state may be responsible for the second component in the emission of A. The large red shift in emission from A in fluid solutions is indicative of a large distortion in the MLCT bpy excited state of A which does not occur in B. This type of distortion may give rise to a barrier to energy transfer from the MLCT ppy to the MLCT bpy state in A which is absent in B. When this complex is excited at wavelengths longer than about 460 nm, it appears possible to preferentially excited directly into the lower energy MLCT bpy state, thereby favoring emission from this state. Studies to further characterize the two emitting states of A and the origin of the large distortion of its MLCT bpy state are in progress.

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Synthesis, Structure, and Reactivity of Trimethylphosphine-Zirconocene Thioaldehyde Complexes

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Several thioaldehyde complexes of middle and late transition metals[1] have been reported. To our knowledge, however, no thioaldehyde complexes of early transition metals (groups 3-5) have been prepared. We now report a general, direct, and efficient synthesis of zirconocene thioaldehyde complexes **1** (Figure 1), which are stabilized by coordination of a trimethylphosphine ligand. These complexes have been characterized by ^{1}H, ^{13}C, and ^{31}P NMR, IR, and high-resolution mass spectrometry. In addition, complex **1a** has been characterized by X-ray crystallography and elemental analysis.

Our route to compounds **1a,b** (Scheme I) is related in appearance (and presumably also in mechanism) to the synthesis of zirconocene complexes of benzyne,[2a] cyclohexyne,[2b] and acyclic alkynes[2c] which we have recently reported and to the synthesis of tantalum-imine complexes reported by Bercaw.[2d] The requisite (alkylthio)(methyl)zirconocenes **2a,b** are available by treatment of chloro(methyl)zirconocene[3a] with a lithium thiolate or more simply by treatment of dimethylzirconocene[3b] with 1 equiv of a thiol. Heating compounds **2a,b** in the presence of trimethylphosphine leads to the formation of **1a,b** in high yield.

The X-ray crystal structure of **1a** is shown in Figure 2. Two enantiomeric, crystallographically independent, but chemically similar molecules are found in the asymmetric unit. As can be seen, the sulfur occupies the central zirconium orbital, reminiscent of the η^2-O-inside conformation seen for acyl(chloro)zirconocenes.[4] The C-S bond distances of 1.785 (11) and 1.739 (13) Å are shorter than typical C-S single bond distances of 1.805-1.825 Å,[5] indicating that while the predominant resonance form of **1a** is a

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