61 methyl in cyt *c*-551, but not for the Met 80 methyl in horse heart cyt *c*. For both cytochromes, additional broad proton peaks in the low-frequency region did not give rise to correlation peaks above the spectral noise level. There are only a few of these however, and they are believed to be protons on the ligand methionine and histidine side chains that are very close to the iron. From the detail in Figure 4, it is clear that much remains to be done. One-dimensional ^1H spectra of paramagnetically shifted resonances in hemoproteins and iron–sulfur proteins have long been used to probe the active-site region. The dispersion of carbon resonances adds a new dimension and adds new probe resonances that may be followed during ligand changes, spin-state changes, and conformational changes in the active-site region.

A detailed interpretation of the contact and pseudocontact shifts for the heme or proteins is beyond the present scope. Several excellent reviews of theory have been given.[23] It has long been known, and is highlighted by comparing Tables I and II, that free heme and hemoproteins are very different because of the influence of the protein. The addition of carbon chemical shift data to the analysis may afford a better description of the electronic environment at the protein active site.

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Registry No. Cytochrome *c*-551, 9048-77-5; cytochrome *c*, 9007-43-6; dicyanoheme *b*, 130523-00-1; protoporphyrin IX, 553-12-8.

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Photophysical Properties of a Series of $(CO)_5Re–Re(CO)_3(\alpha,\alpha'\text{-diimine})$ Compounds

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The electronic absorption and emission spectra of a series of $(CO)_5Re–Re(CO)_3(\alpha,\alpha'\text{-diimine})$ compounds as powders and 2-methyltetrahydrofuran glasses at temperatures ranging from 4.2 K to room temperature are reported. The lowest energy absorption band from these compounds is assigned to a composite band of the lowest metal to $\pi_1^*(\alpha,\alpha'\text{-diimine})$ charge-transfer (MLCT) transitions. Emission from these compounds is assigned to a MLCT excited state. $Re_2(CO)_8(2,2'\text{-bpy})$, $Re_2(CO)_8(4,4'\text{-}Me_2bpy)$, $Re_2(CO)_8(1,10\text{-phen})$, and $Re_2(CO)_8(\text{isopr-Pyca})$ exhibit both fluorescence and phosphorescence from this excited state, whereas only phosphorescence is observed from $Re_2(CO)_8(\text{isopr-DAB})$ and $Re_2(CO)_8(\text{ptol-DAB})$.

Introduction

Excited-state properties of metal-metal-bonded compounds are the subject of continuing interest. The most extensive studies of metal-metal-bonded compounds have involved investigations of their photochemical reactivities.[1,2] Luminescence[3,4] and resonance Raman spectroscopy[5–7] have also been used to characterize the excited states.

The series of bimetallic compounds of the type $M(CO)_5M'(CO)_3(\alpha,\alpha'\text{-diimine})$ (M,M′ = Mn, Re), where two carbonyls of the parent decacarbonyl compound have been replaced by a bidentate diimine ligand, are of particular relevance to the work in this paper. A variety of these compounds have been synthesized and studied.[5,8] This series of compounds exhibits intense low-energy metal to α,α'-diimine ligand charge-transfer (MLCT) bands in the visible region of the electromagnetic spectrum.[3,5,8] Although, in general, MLCT excited states are unreactive, irradiation into the MLCT band of these compounds causes splitting of the metal-metal bond as well as CO loss.[3,9–12] Under certain conditions metal–nitrogen bond breaking has also been observed.[9] Relatively little is known about the luminescence properties of metal-metal-bonded species with low-lying MLCT excited states. The emission spectrum of $Re_2(CO)_8(1,10\text{-phen})$ was measured by Morse and Wrighton in EPA at 77 K.[3] Exciting into the MLCT band yielded emission with a maximum at about 14 500 cm^{-1} and a lifetime of 95 μs. The emission was independent of excitation wavelength. The long lifetime is consistent with emission from a ^3MLCT excited state.

In this paper, the luminescence and absorption spectra of a series of $Re_2(CO)_8L$ (L = α,α'-diimine) compounds from powders and from 2-methyltetrahydrofuran (2-MeTHF) glasses at temperatures ranging from 4.2 K to room temperature are reported. The compound structure and the α,α'-diimine ligands are shown in Chart I. For clarity, only the nitrogen atoms of the α,α'-diimine ligand are shown in the structure of the metal compound. The ligands are (a) 2,2′-bipyridine (2,2′-bpy), (b) 4,4′-dimethyl-2,2′-bipyridine ($4,4'\text{-}Me_2bpy$), (c) 1,10-phenanthroline (1,10-phen), (d) R-pyridine-2-carbaldehyde imine (R = isopropyl, isopr-Pyca), and (e) R-1,4-diaza-1,3-butadiene (R = isopropyl, isopr-DAB; R = *p*-tolyl, ptol-DAB). Multiple emission bands are observed. Single-crystal absorption spectra of $Re_2(CO)_8(2,2'\text{-bpy})$ are examined in detail. The emission and lowest energy absorption bands are assigned and the emission lifetimes, temperature and excitation wavelength dependences, and medium effects are discussed.

Experimental Section

Synthesis. The ligands[13] and binuclear metal compounds[3,8] were synthesized according to published methods. A mixture of 2 mmol of $Re(CO)_5^-$ and 1.8 mmol of $Re(CO)_3(\alpha,\alpha'\text{-diimine})Br$ in 40 mL of THF was stirred for 2 days. The solvent was evaporated under vacuum and the product purified by column chromatography. Chromatographic separations were carried out with silica gel as the stationary phase. The silica gel was dried, deoxygenated, and activated before use by heating

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[†] University of California.

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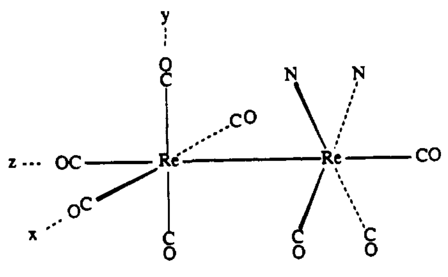
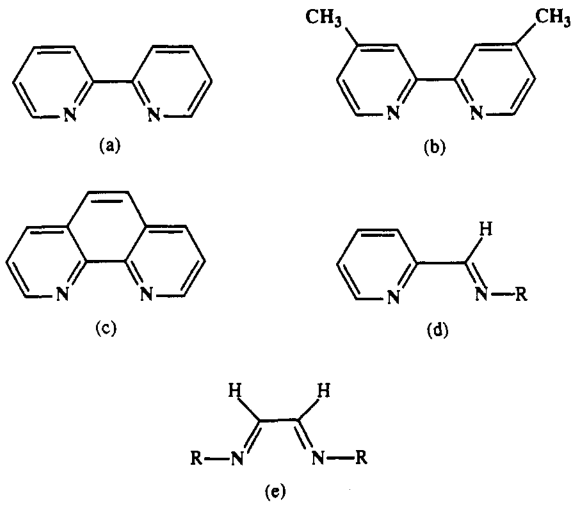
Chart I



Molecular Stucture of $Re_2(CO)_8(\alpha,\alpha'$-diimine) Compounds



α,α'-diimine Ligands

under vacuum. Extreme care was taken to keep the column under a nitrogen atmosphere. The purity of the compounds was checked by IR and NMR spectroscopy. $Re_2(CO)_8(2,2'\text{-bpy})$, $Re_2(CO)_8(4,4'\text{-}Me_2bpy)$, $Re_2(CO)_8(1,10\text{-phen})$, $Re_2(CO)_8(\text{isopr-Pyca})$, and $Re_2(CO)_8(\text{isopr-DAB})$ are dark red compounds, while $Re_2(CO)_8(\text{ptol-DAB})$ is dark blue.

Preparation of $Re_2(CO)_8(2,2'\text{-bpy})$ Single Crystals. Thin single crystals of $Re_2(CO)_8(2,2'\text{-bpy})$ for polarized absorption spectra measurements were grown between two small round quartz plates by evaporation from a solution of the compound in 2-MeTHF. The sample was shielded from light during crystal growth.

Spectroscopic Measurements. The visible emission spectra of $Re_2(CO)_8(2,2'\text{-bpy})$, $Re_2(CO)_8(4,4'\text{-}Me_2bpy)$, $Re_2(CO)_8(1,10\text{-phen})$, and $Re_2(CO)_8(\text{isopr-Pyca})$ were taken by using an argon ion laser excitation source with the samples mounted inside a Displex closed-cycle helium refrigerator unit equipped with a thermocouple and a heater. The signal was collected, passed through a Spex Model 1702 0.75-m single monochromator, and then detected with an RCA C31034 photomultiplier tube. The signal from the photomultiplier tube was fed into an EG&G Model 1105 photon counter and then stored digitally with an Apple II computer. Emission spectra for these complexes were obtained for both solid samples and 2-MeTHF glasses (10^{-3} M). The solid samples were in the form of microcrystalline powders and will be referred to as powder samples. 2-MeTHF was purified immediately prior to use by refluxing it over CaH_2 followed by distilling under dry nitrogen. Sample solutions were prepared quickly and shielded from light during preparation.

The near-infrared emission spectra of powder samples of $Re_2(CO)_8(\text{isopr-DAB})$ and $Re_2(CO)_8(\text{ptol-DAB})$ were measured at 4.2 K with the samples mounted inside a liquid-helium dewar. The 457.9-nm line of an argon ion laser chopped at 110 Hz was used to excite the samples. The signal was collected, sent through a PTi $^1/_4$-m monochromator, and then detected with a germanium IR detector. The signal from the detector was processed through a Princeton Applied Research Model 121 lock-in amplifier and stored digitally with a PC Prime 88 computer. All emission spectra were corrected for the system response.

Emission lifetimes were determined for the powder samples of all of the compounds at 15 K. The samples were mounted inside the Displex refrigeration unit and excited with 406-nm pulsed light from a XeCl excimer pumped dye laser (DPS in *p*-dioxane). A 1-cm cell containing a saturated aqueous $K_3Fe(CN)_6$ solution was used in the optical path to filter out the laser line from the emission signal. The signal was passed through a Spex Model 1702 single monochromator, detected by an RCA C31034 photomultiplier tube, and then digitally stored by a Tektronix RTD 710 transient digitizer interfaced to an IBM-PC/XT computer. The limiting system response time was 20 ns. Emission lifetimes were reproducible to within ±10% unless otherwise indicated.

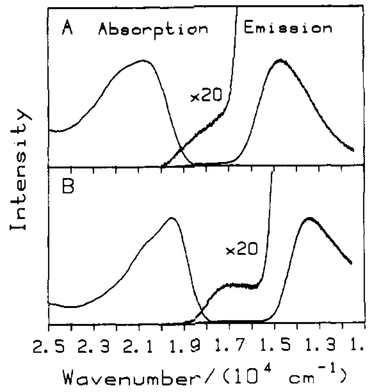


Figure 1. Normalized absorption (left) and emission (right) spectra of (A) $Re_2(CO)_8(2,2'\text{-bpy})$ and (B) $Re_2(CO)_8(\text{isopr-Pyca})$ in 2-MeTHF. The absorption and emission spectra were measured at 77 and 20 K, respectively. The wavelength of excitation was 457.9 nm.

Table I. Lowest Energy Electronic Absorption Maxima for the $Re_2(CO)_8L$ Compounds in 2-MeTHF at 293 and 77 K^a

	max/cm^{-1} (log ϵ/M^{-1} cm^{-1})^b		
L	293 K	77 K	Δ^c
2,2'-bpy	19 500 (3.62)	20 800 21 600 (sh)	+1300
4,4'-Me$_2$bpy	19 600 (3.69)	20 800 21 600 (sh)	+1200
1,10-phen	19 200 (3.73)	20 300 21 900 (sh)	+1100
isopr-Pyca	18 600 (3.88)	19 600 20 800 (sh)	+1000
isopr-DAB	19 600 (4.03)	20 100 21 200 (sh)	+500
ptol-DAB	18 000 (4.06)	18 100	+100

^{a}sh = shoulder. ^{b}±3%. $^c\Delta$ = [max(77 K) − max(293 K)] in cm^{-1}.

The excitation spectrum of a powder sample of $Re_2(CO)_8(2,2'\text{-bpy})$ was recorded by using a Spex Fluorolog spectrometer with the sample mounted inside of a liquid-nitrogen dewar. The spectrum was corrected for variations in the exciting lamp intensity.

Solution electronic absorption spectra were recorded on a Cary 219 UV/vis spectrophotometer. Spectra were obtained from 2-MeTHF solutions at both room temperature and at 77 K. Low-temperature (20 K) single-crystal electronic absorption spectra were recorded by using a previously described apparatus.[14]

Results

Electronic Absorption Spectra. The electronic absorption spectra of all of the compounds in 2-MeTHF at room temperature and at 77 K contain an intense low-energy transition (ϵ = 4000–12 000 M^{-1} cm^{-1}) between 18 000 and 21 000 cm^{-1}. Representative spectra are shown in Figure 1. On cooling, this band blue shifts in all cases and a high-energy shoulder is resolved for all of the compounds except for $Re_2(CO)_8(\text{ptol-DAB})$. Table I lists the lowest energy absorption band maxima and the log of the extinction coefficient at room temperature. Also listed in Table I are the lowest energy absorption band maxima at 77 K and the shifts in the band maxima observed upon cooling.

The single-crystal polarized absorption spectra of $Re_2(CO)_8(2,2'\text{-bpy})$ at 20 K are shown in Figure 2A. Spectrum I was taken with the incident light polarized along one extinction direction, and spectrum II, with the incident light polarized in the orthogonal direction. The orientation of the molecular axes with respect to the polarized light is unknown. The spectra show a strongly polarized, extremely broad absorption band from 17 500 to 22 500

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Table II. Emission Maxima for the $Re_2(CO)_8L$ Compounds at Low Temperture[a]

	max/cm^{-1}					
	powder sample		2-MeTHF glass		Δ[c]	
L	fluor[b] (HE)	phos (LE)	fluor[b] (HE)	phos (LE)	fluor (HE)	phos (LE)
2,2'-bpy[g]	15 800	13 400	17 900	14 700	+2100	+1300
4,4'-Me_2bpy[g]	15 800	13 600	*d*	14 800		+1200
1,10-phen[g]	16 300	13 600	17 400	14 400	+1100	+800
isopr-Pyca[e,g]	16 700 (I), 15 000 (II)	13 200	17 000	13 500	+300	+300
isopr-DAB[h]	*d*	12 600	*f*	*f*		
ptol-DAB[h]	*d*	11 400	*f*	*f*		

[a] The excitation wavelength was 457.9 nm. Spectra were corrected for the system response. HE = high-energy and LE = low-energy emission. [b] The fluorescence band appears as a shoulder on the phosphorescence band. [c] Δ = [max(2-MeTHF) − max(powder)] in cm^{-1}. [d] Fluorescence was not observed. [e] Three bands were observed in the powder spectrum, whereas only two were observed in the 2-MeTHF glass spectrum; Δ for the fluorescence band was calculated by using the maximum of the highest energy band at 16 700 cm^{-1} in the powder spectrum. See text for details. [f] Spectra not measured. [g] T = 20 K. [h] T = 4.2 K.

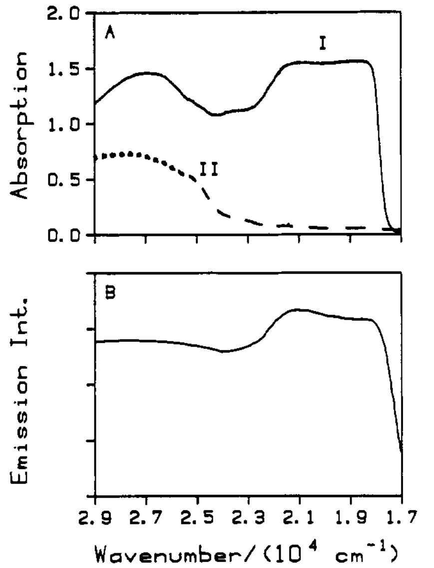

Figure 2. (A) Single-crystal polarized absorption spectra of $Re_2(CO)_8$(2,2'-bpy) at 20 K. Spectrum I was taken with the incident light polarized along one extinction direction. Spectrum II was taken with the incident light polarized along the orthogonal direction. (B) Excitation spectrum of a powder sample of $Re_2(CO)_8$(2,2'-bpy) at 77 K. The spectrum was measured by monitoring the emission at 735 nm.

cm^{-1}, which is intense along one polarization direction (spectrum I) but absent in the orthogonal direction (spectrum II). Two shoulders are observed at higher energies (23 600 and 25 000 cm^{-1}) in both spectra. Additional broad bands are found at 27 000 cm^{-1} in spectrum I and at 27 800 cm^{-1} in spectrum II.

Emission Spectra. Low-Temperature (4.2 and 20 K) Emission Spectra. At low temperature all of the powder samples exhibit an intense low-energy (LE) emission band. Representative spectra are shown in Figures 3 and 4. The isopr-DAB and ptol-DAB compounds emit further to the red than the others, peaking well into the near-infrared region of the electromagnetic spectrum. Also, the LE emission bands from $Re_2(CO)_8$(isopr-DAB) and $Re_2(CO)_8$(ptol-DAB) have smaller widths than the LE emission bands of the other compounds. The LE emission bands in the powder spectra of $Re_2(CO)_8$(isopr-DAB) and $Re_2(CO)_8$(ptol-DAB) at 4.2 K have full widths at half-maximum (fwhm) of 1500 and 1300 cm^{-1}, respectively, while the fwhm of the LE bands in the powder emission spectra of the other four compounds at 20 K are in the range 2100–3100 cm^{-1}. The LE emission band is also observed in the 20 K 2-MeTHF glass spectra of the 2,2'-bpy, 4,4'-Me_2bpy, 1,10-phen, and isopr-Pyca compounds (Figure 1). In each case, the LE band is blue shifted in the glass spectrum with respect to the spectrum of the powder sample taken under the same conditions. Table II lists the emission maxima for both the powder and the glass samples at low temperature along with the shifts in the band maxima between the powder and the glass spectra. Glass spectra were not measured for $Re_2(CO)_8$(isopr-DAB) and $Re_2(CO)_8$(ptol-DAB).

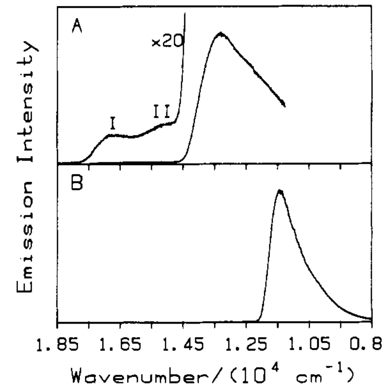

Figure 3. Low-temperature emission spectra from powder samples of (A) $Re_2(CO)_8$(isopr-Pyca), T = 20 K, and (B) $Re_2(CO)_8$(ptol-DAB), T = 4.2 K. The wavelengths of excitation were (A) 488.0 and (B) 457.9 nm.

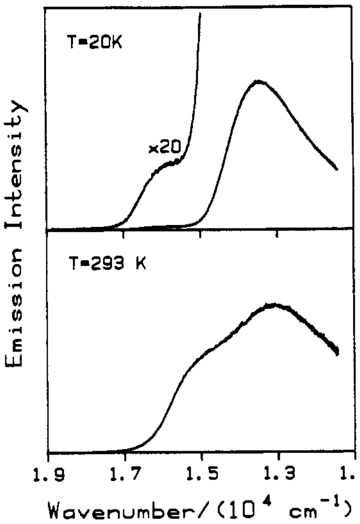

Figure 4. Temperature dependence of the emission spectrum from a powder sample of $Re_2(CO)_8$(2,2'-bpy). The sample was excited at 488.0 nm.

All of the compounds except for $Re_2(CO)_8$(isopr-DAB) and $Re_2(CO)_8$(ptol-DAB) exhibit a relatively weak emission band at higher energies than the LE emission in their powder emission spectra at low temperature, as shown in Figures 3 and 4. This high-energy (HE) emission band is also observed in the low-temperature 2-MeTHF glass spectra of $Re_2(CO)_8$(2,2'-bpy), $Re_2(CO)_8$(1,10-phen), and $Re_2(CO)_8$(isopr-Pyca) (Figure 1). Analogous to the LE emission, the HE emission is blue shifted in the glass spectra compared to the powder spectra taken under the same conditions. Only the LE emission was observed in the glass spectrum of $Re_2(CO)_8$(4,4'-Me_2bpy) at 20 K.

The HE emission band of $Re_2(CO)_8$(isopr-Pyca) contains two observable components in its 20 K powder spectrum. The two components are labeled I and II in Figure 3 and Table II.

Table III. Temperature Dependence of the Fluorescence and Phosphorescence Band Maxima for Powder Samples of the Re$_2$(CO)$_8$L Compounds[a]

L	λ_{ex}/nm	max/cm^{-1}			
		20 K		293 K	
		fluor[b] (HE)	phos (LE)	fluor[b] (HE)	phos (LE)
2,2′-bpy	488.0	15 800	13 500 (45)	14 900	13 100 (1.5)
4,4′-Me$_2$bpy	488.0	15 800	13 600 (52)	14 600	13 500 (1.1)
1,10-phen	457.9	16 300	13 600 (41)	15 400	12 400 (8)
isopr-Pyca[c]	488.0	16 700, 15 100 (1.4)	13 300 (94)	15 200	12 400 (11)

[a] Emission spectra were corrected for the system response. HE = high-energy and LE = low-energy emission. The values in parentheses are the relative intensities of the fluorescence and phosphorescence bands within each individual spectrum with the fluorescence band normalized to one; for the isopr-Pyca complex the highest energy band at 16 700 cm^{-1} was normalized to one. [b] The fluorescence band appears as a shoulder on the phosphorescence band. [c] Two emission bands were observed at 293 K, whereas three were observed at 20 K. See text for details.

Table IV. Emission Lifetimes for Powder Samples of the Re$_2$(CO)$_8$L Compounds at 15 K[a]

L	τ(HE band)	τ(LE band)
2,2′-bpy	<20 ns	<20 ns, 19.8 μs
4,4′-Me$_2$bpy	<20 ns	<20 ns, 24.6 μs
1,10-phen	<20 ns, 1.9 μs[b]	<20 ns, 34.4 μs
isopr-Pyca[c]	<20 ns (I), <20 ns, 0.3 μs[b] (II)	<20 ns, 8.7 μs
isopr-DAB	*d*	8.0 μs
ptol-DAB	*d*	3.1 μs

[a] Emission lifetimes, unless otherwise indicated, were reproducible to within ±10%. [b] The longer lived emission was weak, and its lifetime was estimated from where the decay curve went to 1/*e* of I_0; reproducible to within ±20% (see text for the definition of I_0). [c] I is the emission at 16 700 cm^{-1} and II is the emission at 15 000 cm^{-1} (see Table II and Figure 3). [d] The HE band was not observed.

However, as shown in Figure 1, only one component is resolved in the 20 K 2-MeTHF glass spectrum.

Temperature Dependence. As the temperature of the powder samples is raised from 20 to 293 K, the emission maxima red shift and the spectra broaden. Additionally, the intensity of the low-energy band decreases relative to the intensity of the high-energy band. Figure 4 compares the 20 and 293 K powder emission spectra for Re$_2$(CO)$_8$(2,2′-bpy). In the case of Re$_2$(CO)$_8$(isopr-Pyca), although two HE bands are observed in its powder spectrum at 20 K, only one HE band is observed in its powder spectrum at 293 K. Table III lists the peak positions and relative intensities of the HE and LE emission bands for the 2,2′-bpy, 4,4′-Me$_2$bpy, 1,10-phen, and isopr-Pyca compounds at the two temperatures with the HE band normalized to one in each spectrum. For Re$_2$(CO)$_8$(isopr-Pyca) the highest energy HE band (band I in Figure 3A) was normalized to one for the spectrum taken at 20 K. A HE emission band was not observed for Re$_2$(CO)$_8$(isopr-DAB) and Re$_2$(CO)$_8$(ptol-DAB) even upon raising the temperature to 293 K.

Excitation Wavelength Effects. The excitation wavelength dependence of the emission spectra for powder samples of Re$_2$(CO)$_8$(2,2′-bpy), Re$_2$(CO)$_8$(4,4′-Me$_2$bpy), Re$_2$(CO)$_8$(1,10-phen), and Re$_2$(CO)$_8$(isopr-Pyca) was studied. The emission maxima were independent of the wavelength of excitation within the experimental uncertainty. The relative intensities of the HE and LE band maxima for the 2,2′-bpy and 4,4′-Me$_2$bpy compounds varied by about 10–30% when the wavelength of excitation was changed. Given the low intensity of the HE band, this amount of fluctuation is considered to be within experimental uncertainty. However, for Re$_2$(CO)$_8$(1,10-phen) and Re$_2$(CO)$_8$(isopr-Pyca), the relative intensities of the bands varied in excess of 100%.

Excitation Spectra. The excitation spectrum of a powder sample of Re$_2$(CO)$_8$(2,2′-bpy) at 77 K is shown in Figure 2B. The spectrum was measured by monitoring the emission at 735 nm, close to the band maximum for the low-energy emission from this compound. The excitation spectrum exhibits a broad band from 17 500 to 22 500 cm^{-1}. A second broad maximum is found at about 27 700 cm^{-1}. Note the similarity between the Re$_2$(CO)$_8$(2,2′-bpy) single-crystal absorption spectrum (Figure 2A, spectrum I) and the excitation spectrum. Excitation spectra could not be measured for the HE emission band of this compound because it was too weak.

Emission Lifetimes. Emission lifetimes, obtained for both the HE and LE emission emission bands of the powder samples at 15 K, are listed in Table IV. For all of the compounds studied, the LE band has a component with a lifetime on the order of microseconds and the HE band has a component with a lifetime that is less than the limiting system response time of 20 ns. In addition to the microsecond lifetime component, the 2,2′-bpy, 4,4′-Me$_2$bpy, 1,10-phen, and isopr-Pyca compounds exhibit a short-lived component (<20 ns) within their LE emission band. Also, the HE band for the 1,10-phen and isopr-Pyca compounds exhibits a longer lived component in addition to the short-lived component. Results for the LE emission bands will be discussed in detail followed by a discussion of the results for the HE bands.

Low-Energy Emission Band. The LE emission band for all of the compounds contains a component with a lifetime on the order of microseconds. For Re$_2$(CO)$_8$(isopr-DAB) and Re$_2$(CO)$_8$(ptol-DAB), the LE emission decay curve was measured on the high-energy side of the emission band due to the loss of detector sensitivity where the emissions from these two compounds maximize in the red and near-infrared regions of the electromagnetic spectrum. The LE emission from both of these compounds exhibited a linear ln (intensity) versus time plot over at least 3 decay lifetimes, and the emission lifetimes were calculated from a least-squares fit to the ln (intensity) versus time data. The remainder of the compounds showed two components in the decay curve of their LE emission band. The emission lifetime of the LE band for each of these four compounds was measured at wavelengths near the emission maximum and on the low-energy side of the band. At each wavelength, the emission decay curve resolved into a short-lived component (<20 ns) and a long-lived component, but the decay intensity was dominated by the long-lived component. The intensity of the short-lived component relative to the long-lived component decreased at the higher wavelengths of measurement for Re$_2$(CO)$_8$(2,2′-bpy) and Re$_2$(CO)$_8$(4,4′-Me$_2$bpy). For Re$_2$(CO)$_8$(1,10-phen) and Re$_2$(CO)$_8$(isopr-Pyca), the relative intensities of the two components were essentially the same when measured at the low-energy side of the emission band as compared to the band maxima. For these four compounds, the lifetime of the long-lived component was calculated from a least-squares fit to the ln (intensity) versus time data from a point where the short-lived component had fully decayed out to 2 complete decay lifetimes of the long-lived component. In this region the ln (intensity) versus time plots were linear.

High-Energy Emission Band. The high-energy emission band observed from Re$_2$(CO)$_8$(2,2′-bpy) and Re$_2$(CO)$_8$(4,4′-Me$_2$bpy) exhibits one short-lived (<20 ns) component throughout the band. The HE band for Re$_2$(CO)$_8$(1,10-phen) resolved into two components. These included a short-lived (<20 ns) component and a long-lived component, with the short-lived component dominating the decay curve. The long-lived component tended to be more intense relative to the short-lived component at lower wavelengths of measurement within the HE emission band (i.e. 5800 Å compared to 6022 Å). The weak intensity of the long-lived component precluded calculation of its lifetime from a ln (intensity) versus time plot. The lifetime was thus estimated from where the decay curve went to 1/*e* of I_0, where I_0 was chosen as a point at which the short-lived component had fully decayed, and its value is,

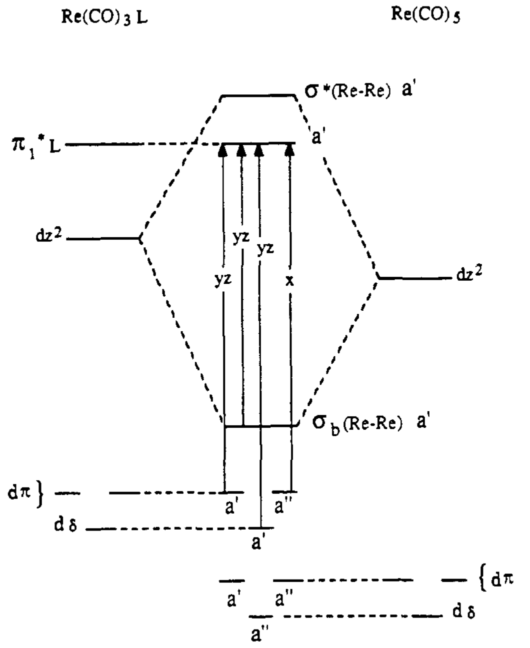

Figure 5. Schematic molecular orbital diagram for $Re_2(CO)_8L$ (L = α,α'-diimine).

therefore, less certain (±20%) than the lifetimes obtained from a least-squares analysis of the ln (intensity) versus time data. $Re_2(CO)_8$(isopr-Pyca) showed two energetically resolved bands in its high-energy emission band. The highest energy emission band, labeled I in Figure 3A, contains only one short-lived (<20 ns) component. The second band, labeled II in Figure 3A, exhibits a short-lived (<20 ns) and a long-lived component. The long-lived component within this band was slightly more intense relative to the short-lived component at higher wavelengths of measurement (i.e. 6800 Å compared to 6300 Å). Analogous to the long-lived component in the HE emission band of $Re_2(CO)_8$(1,10-phen), the long-lived component within this emission band of $Re_2(CO)_8$(isopr-Pyca) was weak and its lifetime was determined in the same manner as discussed above from the decay curve. For both the 1,10-phen and the isopr-Pyca compounds, the long-lived HE emission has an emission lifetime on the order of microseconds, but it is not as long-lived as the long-lived LE emission. Therefore, its lifetime is intermediate between the short-lived HE emission and the long-lived LE emission lifetimes and it will be referred to as the intermediate lifetime component within the HE emission band.

Discussion

The electronic absorption and emission spectra of the $Re_2(CO)_8(\alpha,\alpha'$-diimine) compounds will be discussed in terms of the molecular orbital diagram shown in Figure 5.[15] The ligands of the two Re fragments are staggered, giving the molecule a local C_s symmetry about the metal atoms.[5] The metal–metal bond axis is defined as the molecular z axis, and the yz plane is chosen as the mirror plane of symmetry bisecting the α,α'-diimine ligand. The metal dπ and dδ orbitals associated with the $Re(CO)_3L$ fragment are destabilized with respect to the orbitals on the $Re(CO)_5$ fragment due to the substitution of two carbonyl ligands by the more poorly back-bonding α,α'-diimine.[15] There are two low-energy dπ type orbitals and one dδ type orbital on each fragment. On the basis of the photoelectron spectroscopic studies, the Re–Re bonding orbital, σ_b(Re–Re), is higher in energy than the dπ and dδ type orbitals in the diagram and the dδ orbital is lower in energy than the dπ orbitals on each fragment.[15] The HOMO and LUMO are the σ_b(Re–Re) orbital and the lowest π^* orbital on the α,α'-diimine ligand (π_1^*), respectively. The lowest energy transitions are metal to ligand charge transfer in nature. The four lowest energy, one-electron transitions are symmetry-allowed, three in yz polarization and one in x polarization.

Electronic Absorption Spectroscopic Assignments. The intense lowest energy absorption band observed for each of the compounds is assigned to a superposition of the lowest energy MLCT transitions, including the two lowest d$\pi \rightarrow \pi_1^*$ transitions and the lowest d$\delta \rightarrow \pi_1^*$ transition. The σ_b(Re–Re) $\rightarrow \pi_1^*$ transition is most probably less involved, since the resonance Raman spectra for $[(CO)_5M\text{–}M'(CO)_3$(isopr-DAB)] (M, M' = Mn, Re) show only a weak resonance effect for the metal–metal stretching vibration within the lowest energy MLCT absorption band.[5] However, these Raman results do not mean that the σ_b(Re–Re) $\rightarrow \pi_1^*$ transition is not within the low-energy absorption band but rather that it is not expected to be a major contributor to the intensity. Both the high intensity and the blue shift of the band upon freezing of the 2-MeTHF solvent is consistent with the charge-transfer assignment.[16] The latter "rigidochromic" effect has been previously documented for molecules possessing similar charge-transfer excited states.[17,18]

The multiple components within the lowest energy absorption band begin to resolve in the low-temperature spectra. In 2-MeTHF at 77 K a high-energy shoulder appears for all of the compounds except for $Re_2(CO)_8$(ptol-DAB). These results are consistent with the absorption data of a series of $[(CO)_5Mn\text{–}M'(CO)_3$(R-DAB)] (M' = Mn, Re) compounds, where the band was assigned to a composite of the three lowest energy d $\rightarrow \pi_1^*$ transitions.[8]

The single-crystal polarized absorption spectra of $Re_2(CO)_8$(2,2'-bpy), shown in Figure 2A, support the assignment of the lowest energy absorption band to a composite of the lowest energy MLCT transitions. This band was allowed in one polarization (spectrum I) but disappeared completely in the orthogonal direction (spectrum II). The unusual broad shape of the allowed band in spectrum I is caused by the superposition of several transitions, and it is thus assigned to a composite of the dπ(a') $\rightarrow \pi^*_1$, d$\delta \rightarrow \pi_1^*$, and possibly the σ_b(Re–Re) $\rightarrow \pi_1^*$ transitions, all of which are yz polarized. The orthogonal polarization direction is then the molecular x direction. The x-polarized, low-energy, dipole-allowed dπ(a") $\rightarrow \pi_1^*$ transition is not distinctly observed in spectrum II. The weak shoulder at about 23 600 cm^{-1} could possibly be this transition, but it is not in the correct position energetically and cannot be definitely assigned to it.[15] Thus, the dπ(a") $\rightarrow \pi_1^*$ transition, although dipole allowed, is apparently weak in the single-crystal absorption spectrum.

Emission Spectroscopic Assignments. High-Energy, Short-Lived Emission. The lowest energy one-electron transitions of the $Re_2(CO)_8(\alpha,\alpha'$-diimine) compounds are MLCT transitions from the Re d orbitals to the α,α'-diimine π_1^* orbital.[15] The short-lived HE emission from the 2,2'-bpy, 4,4'-Me_2bpy, 1,10-phen, and isopr-Pyca compounds is thus assigned to a spin-allowed transition from an MLCT excited state. The MLCT assignment is supported by its sensitivity to the medium,[16] and the lifetime of the emission is characteristic of fluorescence. The electronic origin of the fluorescence from the 20 K 2-MeTHF glass spectra of $Re_2(CO)_8$(2,2'-bpy), $Re_2(CO)_8$(1,10-phen), and $Re_2(CO)_8$(isopr-Pyca) overlaps with the electronic origin of the corresponding absorption spectrum at 77 K. In addition, the origins of the low-temperature single-crystal absorption and powder emission spectra of $Re_2(CO)_8$(2,2'-bpy) overlap.

The isopr-DAB and ptol-DAB compounds do not fluoresce from their MLCT excited state, resulting in a separation of about 5000 cm^{-1} between the electronic origins of the 77 K 2-MeTHF glass absorption spectrum and the 4.2 K powder emission spectrum. Because these two compounds do not show extensive medium effects for their MLCT excited-state energies,[5] this large gap cannot be simply attributed to medium effects caused by the

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differing conditions under which the absorption and emission spectra were taken.

Low-Energy, Long-Lived Emission. The LE long-lived emission observed from all of the compounds is assigned to phosphorescence from an MLCT excited state. The microsecond lifetimes are characteristic of spin-forbidden transitions. Consistent with the charge-transfer assignment, the phosphorescence bands shift to higher energies in the 2-MeTHF glass spectra compared to the spectra of the powder samples taken under the same conditions. In addition, the temperature-dependence studies are consistent with the fluorescence and phosphorescence assignments. As the temperature of the powder samples of $Re_2(CO)_8(2,2'$-bpy), $Re_2(CO)_8(4,4'$-Me_2bpy), $Re_2(CO)_8$(1,10-phen), and $Re_2(CO)_8$(isopr-Pyca) was raised from 20 to 293 K, phosphorescence quenching was observed; the relative intensity of the phosphorescence to that of the fluorescence decreased (Table III and Figure 4).

The excitation spectrum of the phosphorescence from a powder sample of $Re_2(CO)_8(2,2'$-bpy) at 77 K, shown in Figure 2B, is very similar to the single-crystal absorption spectrum (Figure 2A, spectrum I), indicating that all the transitions within the broad, low-energy visible absorption band contribute to the phosphorescence from this compound and that the phosphorescence is not simply an impurity emission. Efficient deactivation down to the lowest energy excited state is consistent with the previous photochemical results, which show that the lowest energy excited state is responsible for the observed photochemistry of these compounds.[3]

Additional Emissions. The intermediate lifetime component found within the fluorescence bands of the 1,10-phen and isopr-Pyca compounds is assigned to an impurity emission. The excitation wavelength dependence studies are consistent with this assignment. The relative intensities of the fluorescence to the phosphorescence bands for these two compounds vary greatly with excitation wavelength. However, the 2,2′-bpy and the 4,4′-Me_2bpy compounds, which do not exhibit an intermediate lifetime component within their fluorescence emission bands, do not show such a variation. An alternative interpretation for the intermediate lifetime component can be made. The component could be attributed to emission from a metal-centered excited state. High-energy and low-energy emission bands were observed in the spectra of analogous mononuclear $M(CO)_4(\alpha,\alpha'$-diimine) (M = Cr, Mo, W) compounds.[19-22] The high-energy band contained two different lifetime components, one of which was assigned to a triplet ligand field excited state.[21] However, the intermediate lifetime emission in the rhenium dimers, if metal-centered, should have also been observed from the 2,2′-bpy, 4,4′-Me_2bpy, isopr-DAB, and ptol-DAB compounds. Since it was not observed for these four compounds, and since the excitation wavelength studies are also consistent with its assignment as an impurity emission, the metal-centered assignment was not adopted.

The short-lived component observed in the LE emission band of $Re_2(CO)_8(2,2'$-bpy), $Re_2(CO)_8(4,4'$-Me_2bpy), $Re_2(CO)_8$(1,10-phen), and $Re_2(CO)_8$(isopr-Pyca) is also assigned to an impurity emission. Alternatively, it could be assigned to emission from different components within the lowest energy MLCT manifold.[21] However, the isopr-DAB and ptol-DAB compounds would then be expected to exhibit similar behavior, but they do not. Therefore, the short-lived emission within the phosphorescence band is assigned to an impurity emission.

Comparisons with Other Work. Photochemical studies show that homolytic splitting of the metal-metal bond occurs upon irradiation into the intense low-energy MLCT absorption band of $(CO)_5M–M'(CO)_3(\alpha,\alpha'$-diimine) (M, M′ = Mn, Re).[3,9] Moreover, the photochemical quantum yields for the disappearance of $M_2(CO)_8$(1,10-phen) (M = Mn, Re) were wavelength independent and photochemistry occurred with good quantum efficiency even at the lowest energies of excitation.[9] Thus, photochemistry occurs from the lowest excited state. Assignment of the lowest excited state to the σ_b(Re–Re) → π_1^* MLCT, where the metal–metal bond is weakened in the transition by depopulation of the σ_b(Re–Re) orbital, is consistent with the observed photochemistry. Alternatively, the lowest energy excited state along the reaction coordinate could be a nonemitting strongly repulsive $\sigma\sigma^*$ state that is populated by energy transfer and that leads to homolytic metal–metal bond cleavage.

Assignment of the broad, intense, low-energy absorption band of the $Re_2(CO)_8(\alpha,\alpha'$-diimine) compounds to a composite of the lowest energy MLCT transitions is consistent with previous interpretations of resonance Raman excitation profiles and MCD spectra of the related $M(CO)_4(\alpha,\alpha'$-diimine) (M = W, Mo) monomers. The Raman and MCD experiments showed the existence of several transitions within the lowest energy MLCT absorption band of these monomers.[22,23]

The energy difference between the Re 5d metal orbitals and the π_1^* orbital on the α,α'-diimine ligand depends upon the identity of the ligand. Quantum chemical investigations of α,α'-diimines show that the energy of the π_1^* level decreases in the order 2,2′-bpy > R-Pyca > R-DAB.[24] The energies of the low-temperature powder sample emission follow this trend. On the basis of the energies of the phosphorescence band maxima, the energy difference between the Re d and the π_1^* orbitals decreases in the order 1,10-phen = 4,4′-Me_2bpy > 2,2′-bpy > isopr-Pyca > isopr-DAB > ptol-DAB. Thus, the energy splitting is dominated by the energy of the π_1^* orbital. The lowest energy absorption band maxima are more difficult to interpret in this way because they are composite bands, and therefore their maxima depend upon the relative intensities of the individual components.

The extent of electron transfer in the metal to ligand charge-transfer transitions for the series of $Re_2(CO)_8(\alpha,\alpha'$-diimine) compounds is related to the energy separation of the π_1^* and the d orbitals. The amount of mixing between the metal d orbitals and the π_1^* orbital on the diimine depends, in part, on this separation. The smaller the separation, the greater the mixing. An increase in mixing will result in a decrease in metal to ligand charge-transfer character. In the limit of complete mixing, the transition will lose its charge-transfer character and become more of a metal–ligand bonding to anti-bonding transition. The magnitude of the blue shift in the lowest energy absorption band observed upon freezing is, to some extent, a measure of its charge-transfer character.[5] The greater the shift, the greater the charge-transfer character. From the data in Table I, it can be concluded that the charge-transfer character is greatest for the bipyridine and phenanthroline compounds and smallest for the diazabutadiene compounds. The isopr-Pyca compound lies intermediate between these two extremes. The same trend in charge-transfer character was found from resonance Raman studies of related monomers.[22] Thus, the splitting of the π_1^* and the Re d orbitals is greatest for the bipyridine and phenanthroline compounds and smallest for the diazabutadiene compounds. This trend is consistent with the quantum mechanical calculations and with the energies of the emission maxima.

Fluorescence from MLCT excited states is not common for heavy-metal complexes. The absence of fluorescence is generally attributed to strong spin–orbit coupling effects, which provide an efficient nonradiative decay mechanism from singlet to triplet excited states. However, the exact nature of such effects is not fully understood.[25] The absence of fluorescence from $Re_2(CO)_8$(isopr-DAB) and $Re_2(CO)_8$(ptol-DAB) indicates that nonradiative decay from singlet to triplet MLCT excited states is more efficient in these compounds than in the others studied. Differences in the CT character of the excited state will cause

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differences in the efficiencies of this decay due to differences in the amount of metal character present in the excited state. The smaller the CT character, the stronger the spin–orbit coupling effects and the more efficient the decay. Nonradiative decay pathways in the complexes showing both fluorescence and phosphorescence are more complicated. However the trend in the phosphorescence lifetimes for the compounds studied reflects the predicted trend in the CT character of the emitting state. The compounds with the largest CT character have the longest phosphorescence lifetimes.

Summary

The electronic absorption and emission spectra of a series of $Re(CO)_8(\alpha,\alpha'\text{-diimine})$ compounds under various conditions were measured and analyzed. The broad, intense, lowest energy absorption band from these compounds is assigned to a composite of several metal to $\pi_1^*(\alpha,\alpha'\text{-diimine})$ charge-transfer transitions including two $d\pi \rightarrow \pi_1^*$ transitions, a $d\delta \rightarrow \pi_1^*$ transition, and possibly a $\sigma_b(\text{Re–Re}) \rightarrow \pi_1^*$ transition. Emission from these compounds, is assigned to a Re $d \rightarrow \pi_1^*$ MLCT excited state. $Re_2(CO)_8$(2,2′-bpy), $Re_2(CO)_8$(4,4′-Me_2bpy), $Re_2(CO)_8$(1,10-phen), and $Re_2(CO)_8$(isopr-Pyca) exhibit both fluorescence and phosphorescence from this excited state, whereas only phosphorescence is observed from $Re_2(CO)_8$(isopr-DAB) and $Re_2(CO)_8$(ptol-DAB).

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Registry No. $Re_2(CO)_8$(2,2′-bpy), 130404-88-5; $Re_2(CO)_8$(4,4′-Me_2bpy), 130327-18-3; $Re_2(CO)_8$(1,10-phen), 130404-89-6; $Re_2(CO)_8$(isopr-Pyca), 130327-19-4; $Re_2(CO)_8$(isopr-DAB), 97698-45-8; $Re_2(CO)_8$(*p*-tol-DAB), 99791-93-2.

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pH Control of the Photophysical Properties of Ruthenium Complexes Containing 3-(Pyrazin-2-yl)-1,2,4-triazole Ligands

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A new series of $[Ru(bpy)_2(L)](PF_6)_2$ complexes, where bpy = 2,2′-bipyridine and L = 3-(pyrazin-2-yl)-1,2,4-triazole (HL0), 1-methyl-3-(pyrazin-2-yl)-1,2,4-triazole (L1), 1-methyl-5-(pyrazin-2-yl)-1,2,4-triazole (L2), and 3-methyl-5-(pyrazin-2-yl)-1,2,4-triazole (HL3), have been prepared and characterized. ^1H NMR spectroscopy has been used to analyze the coordination modes of the ligands, while UV–vis absorption, emission, and resonance Raman spectroscopies, together with electrochemistry, have been used to study the properties of the complexes in their ground and excited states. Electrochemical data and resonance Raman experiments show that in the compounds containing protonated or *N*-methyl-substituted pyrazinyltriazole ligands the lowest π^* levels are pyrazinyltriazole based, while for the complexes with deprotonated ligands the lowest π^* levels are located on the bpy ligands. Furthermore, the emission data (lifetimes and maxima) suggest that the emitting states can be changed from bpy to pyrazinyltriazole based upon lowering the pH for $[Ru(bpy)_2(L0)]^+$ and $[Ru(bpy)_2(L3)]^+$. Another interesting feature is that the absorption and emission maxima of $[Ru(bpy)_2(L0)]^+$ and $[Ru(bpy)_2(L3)]^+$ do not change to a large extent when the pH is lowered.

Introduction

Much work carried out in the field of ruthenium coordination chemistry has revealed that ruthenium compounds with nitrogen-containing ligands have interesting electrochemical, photophysical, and photochemical properties. In particular, compounds such as $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) and $[Ru(bpz)_3]^{2+}$ (bpz = 2,2′-bipyrazine) have been investigated in detail and have been suggested as potential catalysts for the conversion of solar energy.[1-3]

We are at present investigating the effect of asymmetry in bidentate ligands on the physical properties of ruthenium and osmium compounds, and in earlier papers we reported ruthenium compounds containing 3-(pyridin-2-yl)-1,2,4-triazoles.[4,5] By the combination of a six- and a five-membered ring into a bidentate ligand, two different kinds of coordinating nitrogen atoms are created. As it is known that five-membered rings, as for example 1,2,4-triazoles, pyrazoles, and imidazoles, are strong σ-donor ligands and weak π-acceptor ligands compared to 2,2′-bipyridine, it is anticipated that asymmetric bidentate ligands of this kind may produce ruthenium compounds with unusual excited-state properties. This paper describes both the preparation of some novel pyrazinyltriazole ligands and the physical properties of a series of ruthenium bis(bipyridine) complexes containing these ligands.

From experiments described in the literature,[6] it is known that bipyrazine has weaker σ-donor capacities and stronger π-acceptor properties than bipyridine. It is, therefore, expected that there will be substantial differences between the photophysical properties of the compounds containing pyridyltriazoles and pyrazinyltriazoles. Of particular interest to us is the nature of the lowest unoccupied molecular orbital (LUMO) in these compounds. An additional feature of pyrazine-containing ligands is the possibility of protonation of the noncoordinating pyrazine atom in strong acidic media.[7-9]

Experimental Section

Physical Methods. ^1H NMR spectra were obtained on a JEOL JNM-FX 200 MHz spectrometer, while the COSY ^1H NMR spectra were recorded on a Bruker 300-MHz spectrometer, as reported previously.[10] The measurements of the ligands were carried out in $CDCl_3$,

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