

expected not to grow large enough to remain in the low-spin state below the critical temperature and, therefore, to turn back to the high-spin state.

Additional single-crystal experiments are in progress to specify the mechanism of this spin transition, viz., (i) accurate measurements of the temperature dependence of the lattice parameters, to get further information about the correlation between the spin change and the structural reorganization, and (ii) determination

of the compressibility tensor, with the purpose of investigating the electron-phonon coupling.

**Supplementary Material Available:** Tables of calculated fractional positions and isotropic thermal parameters for hydrogen atoms and anisotropic thermal parameters for non-hydrogen atoms (2 pages); tables of observed and calculated structure factors at room temperature and 130 K (14 pages). Ordering information is given on any current masthead page.

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## Excited-State Raman Spectroscopy of $W(CO)_4(\alpha\text{-diimine})$ Complexes

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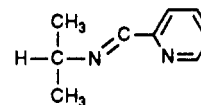
The Raman spectra of  $W(CO)_4(\text{diimine})$  complexes (diimine = 2,2'-bipyridine, 4,4'-dimethyl-2,2'-bipyridine, and pyridine-2-carbaldehyde isopropylimine) in the lowest tungsten to diimine charge-transfer excited state are reported. The excited-state peaks are assigned to ligand ring deformation modes and to carbonyl stretching modes. The effect of the electron transfer on 2,2'-bipyridine and 4,4'-dimethyl-2,2'-bipyridine ring mode frequencies is similar to that previously observed on the prototypical ruthenium compounds. The totally symmetric cis-carbonyl stretching mode in the charge-transfer excited state is about  $50\text{ cm}^{-1}$  higher in energy than that of the molecule in the ground electronic state. The increase is interpreted in terms of loss of metal-carbonyl  $\pi$  back-bonding in the charge-transfer excited state.

Raman spectroscopy of excited electronic states of transition-metal compounds is attracting increasing interest. Following the pioneering work of Woodruff and Dallinger,<sup>1,2</sup> a variety of metal complexes have been studied.<sup>3-15</sup> The primary area of interest has been the effect of the transfer of an electron to a ligand on the normal modes of the recipient ligand. More recently, several studies have probed the effect of electron transfer to a given ligand on the vibrational properties of other ligands in the molecule.<sup>11,15</sup> The latter area is the focus of this study.

A series of  $W(CO)_4L$  complexes ( $L = \text{diimine}$ ) were chosen for this study. The excited-state properties of these compounds have been studied both spectroscopically and photochemically by Oskam and co-workers.<sup>16-20</sup> These complexes have a low-lying metal-to-ligand charge-transfer transition in the visible region of the spectrum. The properties of the charge-transfer excited state were correlated with the energy of the  $\pi^*$  diimine ligand orbital.

The higher the energy of the  $\pi^*$  orbital, the larger the solvatochromism and the larger the intensity of the resonance Raman band for the cis-CO and the CN normal modes.

In this paper, we report the Raman spectra of a series of  $W(CO)_4(\alpha\text{-diimine})$  complexes in their metal-to-diimine charge-transfer excited states. Excited-state spectra were found for the complexes containing the 2,2'-bipyridine (bpy), 4,4'-dimethyl-2,2'-bipyridine ( $\text{Me}_2\text{bpy}$ ), and pyridine-2-carbaldehyde isopropylimine (pyca) ligands. The structure of the latter ligand is shown below.



Excited-state Raman spectra in the  $900\text{--}1600\text{-cm}^{-1}$  diimine ligand ring deformation region and in the CO stretching region are reported. The carbonyl bonding changes caused by the electron-transfer transition to the diimine ligands are discussed.

### Experimental Section

The excited-state Raman spectra of the title complexes were obtained by exciting and probing with  $406\text{-nm}$ ,  $10\text{-ns}$  pulses ( $0.4\text{--}2.0\text{ mJ/pulse}$ ) at a  $45\text{-Hz}$  repetition rate from an excimer pumped dye laser (Lambda Physik EMG 201 MSC and FL 2001). Dispersing prisms were used directly in front of the laser in order to reduce contributions from the background fluorescence from the dye laser. In addition, an iris diaphragm was used to block undesired frequencies from reaching the sample. The sample solutions ( $\sim 1 \times 10^{-3}\text{ M}$ ) were prepared by dissolving the title complexes in  $\text{CH}_3\text{CN}$ . The room-temperature solution was circulated by a peristaltic pump through a 20-gauge hypodermic needle to produce a jet stream. The flow rate was about  $0.3\text{ mL/s}$ . The laser beam was focused by using a plano-convex lens with  $150\text{-mm}$  focal length. The focus was adjusted to lie about  $5\text{--}8\text{ mm}$  behind the jet stream in order to minimize dielectric breakdown and the possibility of the stimulated Raman effect.<sup>21,22</sup> The Raman spectra were obtained by using a triple monochromator with an EG&G OMA III diode-array detector.

The ground-state Raman spectra of  $W(CO)_4(\text{Me}_2\text{bpy})$  were obtained by using argon ion laser excitation at  $488$  and  $514.5\text{ nm}$  with  $100\text{--}150\text{ mW}$  of power incident at a jet stream. The sample solutions ( $\sim 10^{-3}\text{ M}$ ) were prepared by dissolving the complex in  $\text{CH}_3\text{CN}$ . The title com-

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**Table I.** Ground-State and Excited-Electronic-State Raman Bands in the Spectra of  $W(CO)_4(\alpha\text{-diimine})$  and the Corresponding  $Ru(\alpha\text{-diimine})_3^{2+}$ <sup>a,b</sup>

$W(CO)_4(\text{bpy})$		$Ru(\text{bpy})_3^{2+}$ <sup>c</sup>		$W(CO)_4(\text{Me}_2\text{bpy})$		$Ru(\text{Me}_2\text{bpy})_3^{2+}$ <sup>c</sup>		$W(CO)_4(\text{pyca})$	
ground state <sup>d</sup>	excited state	ground state	excited state	ground state	excited state	ground state	excited state	ground state	excited state
1025	1027	1023	1029		985*		996	1010	1018
1175	1182	1170			1014*			1172	1178
	1225*		1211	1021	1029	1025	1026	1226	1232
1260	1265				1118*		1177	1243	1250
1278	1282	1274	1285	1203	1206	1201	1202	1280	1284
1315	1322	1314	1321		1223*			1409	1415
	1424*		1434	1256	1261	1258		1562	1561
1482	1489	1487	1504	1282	1284	1274	1282	1595	1596
1560	1562	1557	1564	1321	1324	1319	1321	1624	1625
1605	1606	1604	1624		1344*				1826
	1828						1445		1900
	1898			1484	1482	1482	1496	2012	2011
2010	2010				1513*				2062*
	2069*			1553	1553	1550			
					1580*		1572		
				1624	1619	1619	1624		
					1825				
				2010	1896				
					2007				
					2064*				

<sup>a</sup>The bands from the excited-state tungsten compounds are labeled with an asterisk. <sup>b</sup>All values are in units of  $\text{cm}^{-1}$ . <sup>c</sup>Reference 14. <sup>d</sup>Reference 23.

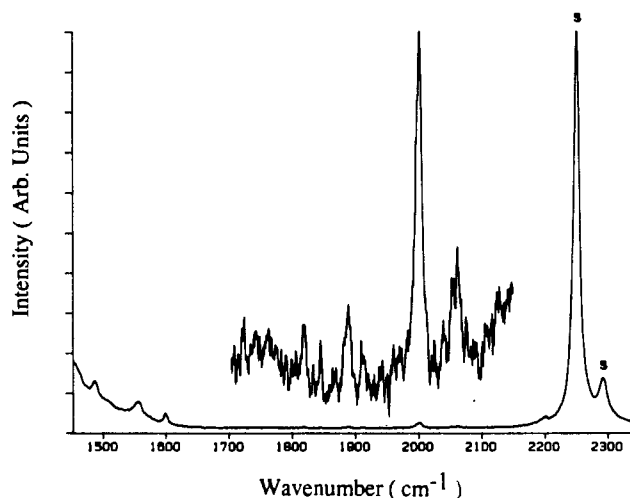
pounds were gifts from Professor A. Oskam.<sup>16-20</sup>

## Results

The ground-electronic-state Raman frequencies of the three compounds studied here are given in Table I.<sup>23</sup> The Raman signals in the  $900\text{--}1600\text{-cm}^{-1}$  region correspond to vibrational modes of the  $\alpha$ -diimine ligands. Only one peak is observed in the CO stretching region of these compounds. It has been assigned to the stretching mode of the CO ligand cis to the diimine ligand  $\nu_s(\text{CO}^{\text{cis}})$ .<sup>16,24,25</sup> This peak has been reported to show a pronounced resonance Raman enhancement. However the signals from the trans carbonyl,  $\nu_s(\text{CO}^{\text{trans}})$ , were not observed even though the exciting wavelength was within the charge-transfer absorption band and resonance enhancement would be expected to occur. The IR spectra of these compounds contain four peaks in the CO region. In order of increasing frequency, these peaks have been assigned to the  $B_2$  (trans-CO),  $A_1$  (trans-CO),  $B_1$  (cis-CO), and  $A_1$  (cis-CO) normal modes.<sup>24,25</sup>

The excited-state Raman spectra of  $W(CO)_4(\text{bpy})$  obtained by using the pulsed dye laser source show several new features in addition to residual ground state signals. The spectrum in the CO stretching region is shown in Figure 1. Three new peaks at  $1828$ ,  $1898$ , and  $2069\text{ cm}^{-1}$  appear in the spectrum as the laser pulse energy is increased. A fourth signal at  $2010\text{ cm}^{-1}$  is the ground-state cis-CO stretching mode. The excited-state Raman spectrum of the  $W(CO)_4(\text{bpy})$  complex in the  $\Delta\nu = 900\text{--}1600\text{-cm}^{-1}$  region is similar to those of  $Ru(\text{bpy})_3^{2+}$  and other bipyridine complexes.<sup>2,14</sup> The comparison with  $Ru(\text{bpy})_3^{2+}$  is summarized in Table I.

The excited-state Raman spectra were studied as a function of the laser pulse energy. The intensity of the ground-state Raman signals is proportional to the laser intensity, but the intensity of the excited-state Raman signals is proportional to the square of the laser intensity. The experimentally determined order of the multiphoton process is calculated from the slope of the log-log plot of the signal intensity as a function of laser intensity. The log-log plot of the excited-state Raman signal intensities versus the laser intensities ideally should be linear with a slope of 2 if no saturation or relaxation of the excited state occurs. Usually, the slope is slightly smaller than 2 due to relaxation processes. The peak at  $1225\text{ cm}^{-1}$  clearly shows a marked nonlinear laser pulse energy dependence. In order to quantify this effect, the log



**Figure 1.** Electronic excited-state Raman spectrum of  $W(CO)_4(\text{bpy})$  in the CO stretching region. The solvent ( $\text{CH}_3\text{CN}$ ) peaks are indicated with an "s".

of the intensity of the  $1225\text{ cm}^{-1}$  Raman peak was plotted versus the log of the laser pulse energy. The log-log plot was linear with a slope of  $1.7 \pm 0.3$ . The signal at  $2069\text{ cm}^{-1}$  also has a clearly measurable nonlinear power dependence. The log-log plot for this peak has a slope of  $1.6 \pm 0.3$ . It was not possible to obtain reliable log-log plots for the other excited-state Raman peaks due to low signal to noise ratios and/or the interference from the intense solvent signals in the diimine vibrational region.

The metal-ligand stretching region of the spectrum between  $300$  and  $800\text{ cm}^{-1}$  was carefully examined. Under the same experimental conditions with which the excited-state peaks in the high-frequency region of the spectrum were observed, no excited-state Raman signals in the metal-ligand stretching region could be found.

The excited-state Raman spectra of  $W(CO)_4(\text{Me}_2\text{bpy})$  obtained by using the pulsed dye laser are shown in Figure 2. The excited-state spectrum in the  $\Delta\nu = 900\text{--}1600\text{-cm}^{-1}$  region is similar to that of the comparison complex  $[Ru(\text{Me}_2\text{bpy})_3]^{2+}$ . Three new peaks appear in the excited-state spectrum in the CO stretching region at frequencies of  $1825$ ,  $1896$ , and  $2064\text{ cm}^{-1}$ . The ground-state peak is also seen at  $2007\text{ cm}^{-1}$ . The signal at  $2064\text{ cm}^{-1}$  in the excited state spectrum has a nonlinear power dependence. A plot of the log of the peak intensity versus the log of the laser power is linear with a slope of  $1.6 \pm 0.2$ . Reliable

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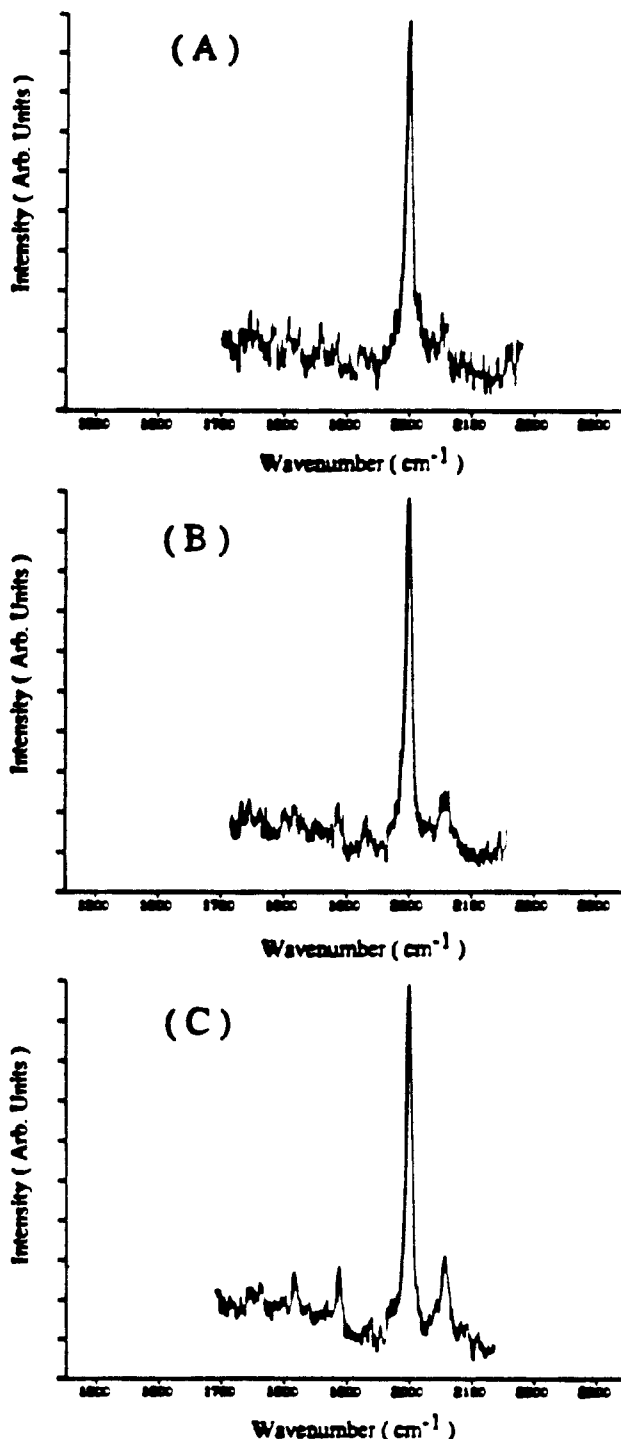


Figure 2. Power dependence of excited-state Raman spectra of  $W(CO)_4(Me_2bpy)$  in the CO region: (A) 0.5 mJ/pulse; (B) 0.8 mJ/pulse; (C) 1.4 mJ/pulse.

slopes could not be obtained for the other two peaks because the signal to noise ratio is too low.

The excited-state Raman spectrum of  $W(CO)_4(pyca)$  contains new peaks only in the CO stretching region. No new peaks are observed in the region between 200 and 1600  $cm^{-1}$  in the excited-state spectrum. The new CO stretching peaks are shown in Figure 3. The frequencies are 1826, 1900, and 2062  $cm^{-1}$ . The signal at 2011  $cm^{-1}$  is the ground-state cis-CO stretching mode. The peak at 2062  $cm^{-1}$  shows a nonlinear pulse energy dependence but the signal to noise ratio is too low to obtain a reliable slope from the log-log plot.

#### Discussion

**Excited-State Spectra and Assignments.** The new peaks that are observed in the Raman spectrum obtained at high laser pulse energy but are absent in the low pulse energy or CW spectra are

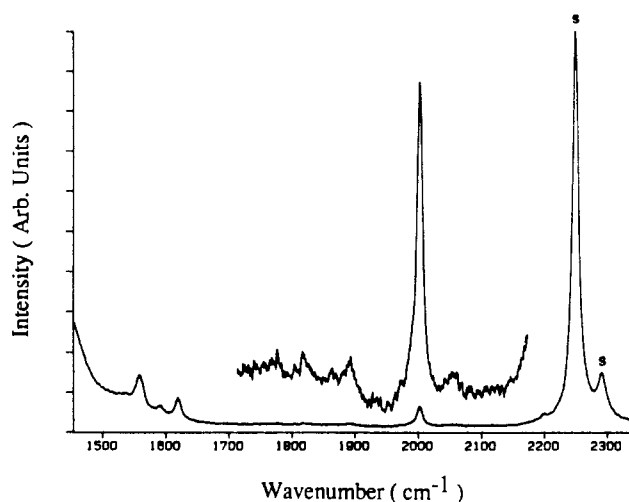


Figure 3. Excited-state Raman spectrum of  $W(CO)_4(pyca)$  in the 1500–2300- $cm^{-1}$  region. The solvent ( $CH_3CN$ ) peaks are indicated with an "s".

assigned to the molecule in its excited electronic state. It is easy to assign a peak to a normal mode of the molecule in its excited electronic state when the frequency of a peak in the spectrum obtained with high pulse energy is significantly different from those of peaks in the ground-state spectrum and when the dependence of the peak intensity on the laser pulse energy is nonlinear. However, it is possible that some of the frequencies of normal modes of the molecule in its excited electronic state differ by only a few wavenumbers from those of the molecule in its ground state. In this case, only the criterion of nonlinear dependence on the pulse energy can be used to definitively assign the peak. Unfortunately, in many cases the overlap of two peaks or a poor signal to noise ratio prevents unambiguous determination of a nonlinear dependence. Thus, in the case of real spectra such as those shown in Figures 1–3 where a large number of peaks appear and many of them are suspected of being excited-state peaks, only a small number can be unambiguously proven to arise from molecules in their excited electronic state. On the basis of the above stringent criteria, the peaks that are unambiguously assigned to normal modes of molecules in their excited electronic state are indicated by asterisks in the table.

The spectral region between 900 and 1600  $cm^{-1}$  is the most difficult to assign because of the large number of ground-state normal modes in this region and because of the interference by solvent bands. In the high pulse energy spectrum of  $W(CO)_4(bpy)$ , two peaks can be unambiguously assigned to the excited-state molecule. The peak at 1225  $cm^{-1}$  and the peak at 1424  $cm^{-1}$  are both assigned to ligand ring modes. It is interesting to note that the excited-state spectrum of  $Ru(bpy)_3^{2+}$  has peaks at 1211 and 1434  $cm^{-1}$ . In the ruthenium complex, the excited state peaks were correlated with the ground-state peaks at 1274 and 1487  $cm^{-1}$ , respectively. For the same reasons, the 1225- $cm^{-1}$  peak in the spectrum of the tungsten complex is correlated with the 1278- $cm^{-1}$  ground-state peak and that at 1424  $cm^{-1}$  is correlated with the 1482- $cm^{-1}$  ground-state peak. A recent normal coordinate analysis of  $Ru(bpy)_3^{2+}$  assigned both of the ground-state modes to ring skeletal stretches with large components of carbon–nitrogen stretches ( $\nu_{10}$  and  $\nu_7$  respectively).<sup>26</sup>

In the high pulse energy spectrum of  $W(CO)_4(Me_2bpy)^{2+}$ , seven peaks can be unambiguously assigned to the excited-state molecule. The peaks at 985, 1014, 1118, 1223, 1344, and 1513  $cm^{-1}$  are all assigned to ligand ring modes. The 1223- $cm^{-1}$  peak in the spectrum of the tungsten complex is probably correlated with the 1256- or 1282- $cm^{-1}$  ground-state peak and that at 1513  $cm^{-1}$  is probably correlated with the 1553- $cm^{-1}$  ground-state peak. These peaks arise from ring skeletal stretches with large components

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of carbon–nitrogen stretches. It is interesting to note that the excited-state spectrum of  $\text{Ru}(\text{Me}_2\text{bpy})_3^{2+}$  has peaks at 996, 1177, 1445, and 1572  $\text{cm}^{-1}$ .

All three complexes studied in this work have a peak in the CO stretching region of the spectrum obtained at high laser pulse energy that can be unambiguously assigned to molecules in an excited electronic state. This peak occurs about 50  $\text{cm}^{-1}$  to high energy of the highest ground state peak. In addition, it has a clear nonlinear laser pulse energy intensity dependence. The peak at 2069  $\text{cm}^{-1}$  in  $\text{W}(\text{CO})_4(\text{bpy})$ , 2064  $\text{cm}^{-1}$  in  $\text{W}(\text{CO})_4(\text{Me}_2\text{bpy})$ , and 2062  $\text{cm}^{-1}$  in  $\text{W}(\text{CO})_4(\text{pyca})$  is assigned to  $\nu(\text{CO}^{\text{cis}})$  in the excited state molecule.

Two additional peaks are found in the high pulse energy spectra of these complexes that are not observed in the ground-state Raman spectra. The frequencies of these peaks are almost identical with the ground-state trans-CO  $B_2$  mode and cis-CO  $B_1$  mode observed in the IR spectra of the molecules. The peaks are too weak to give good quality log–log plots to test for nonlinear power dependence. However, they qualitatively appear to have nonlinear behavior because they appear to be absent in the low pulse energy spectra (and in the ground-state resonance Raman spectra) but are observed in the high pulse energy spectra. The absence of a frequency change between the ground and excited electronic states could be coincidental. However, in keeping with the stringent criteria for assigning peaks to excited states, these CO stretching peaks are considered to arise from ground-state molecules.

**Interpretation of the CO Frequency Changes.** Both the direction and the relative magnitude of the shift of the CO stretching frequencies can be interpreted in terms of the nature of the excited electronic state. The lowest energy excited state in all of the molecules studied here is tungsten-to-diimine ligand charge transfer.<sup>27,28</sup> This excited state arises from the formal promotion of an electron from a  $d-\pi$  orbital on the metal to the lowest empty  $\pi$ -antibonding orbital on the conjugated ligand.

In the excited-state Raman spectra of all of the complexes studied, a new carbonyl ligand stretch at  $\sim 2065\text{-cm}^{-1}$  that shows a nonlinear power dependence is found. The energy shift from the ground state to the excited state is  $\sim 50\text{-cm}^{-1}$ . This increase in frequency indicates that the bond strength between the carbon and oxygen is increased after the metal-to-diimine charge-transfer

transition. This increase is explained as the result of the formal oxidation of the central metal atom and the corresponding reduction of the  $\pi$  back-bonding between the metal and the carbonyl ligands. A recent molecular orbital calculation on an analogous chromium compound suggested that an increase in  $\sigma$  donation and a decrease in back-donation occurs in the charge-transfer excited state.<sup>29</sup> The decrease in back-bonding increases the CO stretching frequency.

The trend in the magnitude of the increase of the frequency can be explained in terms of the relative magnitude of the metal-to-ligand charge-transfer character. The greater the diimine ligand character, the greater the formal charge on the metal, the greater the reduction in back-bonding to the carbonyl ligands, and the greater the increase in the CO stretching frequency. The observed increase in the CO stretching frequency is 50  $\text{cm}^{-1}$  for  $\text{W}(\text{CO})_4(\text{pyca})$ , 54  $\text{cm}^{-1}$  for  $\text{W}(\text{CO})_4(\text{Me}_2\text{bpy})$ , and 59  $\text{cm}^{-1}$  for  $\text{W}(\text{CO})_4(\text{bpy})$ . This trend follows that expected on the basis of previous spectroscopic studies.<sup>16</sup> The bpy ligand has the largest MLCT character as manifested by the large solvatochromism and the relatively high intensities of the resonance Raman bands for the cis-CO and the CN modes compared to those of the metal–ligand and ligand bending modes. In contrast, the pyca ligand gives a smaller MLCT character as evidenced by the small solvatochromism and the relatively low intensities for the resonance Raman bands of the cis-CO and CN modes relative to those for the metal–ligand and the ligand bending modes. These reported trends have been explained in terms of the decreasing energy of the ligand  $\pi$ -antibonding orbital from bpy to pyca.<sup>16</sup> These changes in charge-transfer character also account for the changes in the increases of the CO stretching frequencies in the excited-state Raman spectra. Because both the differences in the changes in vibrational frequencies in the series and the number of members in the series are small, it would not be worthwhile to further quantify the explanation.

**Note Added in Proof.** J. J. Turner et al. (private communication) have observed by transient IR spectroscopy an increase in the CO stretching frequency in the MLCT excited state of  $\text{ClRe}(\text{CO})_3(4,4'\text{-bpy})$ .

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