

the yield of identifiable products ( $\text{AgS}_2^+$  and L) is unchanged.

### Conclusion

The very different coordination proclivities of silver(I) and silver(II) would appear to preclude the possibility of strong coordination of one multidentate, saturated amine ligand in both oxidation states. This is a somewhat perplexing conclusion, since it is not entirely obvious that macrocyclic or macrobicyclic polyamines as studied in the present work should not be able to adopt a configuration suited to, say, linear, trigonal, or tetrahedral coordination of silver(I). It is also obscure as to why open-chain polyamines, even ammonia itself, do not give rise to readily accessible silver(II) complexes although there is, of course, much empirical evidence of marked differences between the properties of macrocyclic ligands and their open-chain analogues.<sup>28</sup>

The development of a silver purification procedure based on silver(II) complexes of macrocyclic amines does not require that the silver(I) species produced by reduction in acetonitrile be a strong macrocyclic complex. Hence, it might be presumed that the cyclic process for silver purification outlined previously would be feasible provided photoreduction and acid generation leading to consumption of macrocyclic amine could be avoided. In a practical sense, however, it would seem that the purpose of sophisticated (and expensive) ligand design is at least partly

defeated if the ligand is not then involved in a robust and simple system. More specifically, the complex  $\text{Ag}(\text{TMC})^{2+}$  found to undergo most facile reduction by silver metal incorporates the least readily accessible ligand and is one of the most sensitive to photoreduction. It is therefore unlikely that an  $\text{Ag}(\text{TMC})^{2+}$ -based process could effectively compete with any such as  $\text{AgCl}$  purification through chloro complex formation in nonaqueous solvents based on less exotic procedures.

Whatever value the silver(II) complexes discussed herein may have as thermal oxidants, their photoredox behavior warrants further examination. The apparent lack of any ligand decomposition during their photoreactions in acetonitrile obviously suggests some potential for use in photoelectrochemical devices. Our current research is directed toward development of a more detailed understanding of the nature of the reactive excited state and a quantitative description of its redox kinetics.

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**Registry No.** TMT A, 92216-10-9; TMT B, 92216-11-0; tet a, 10368-90-8; tet b, 10368-91-9;  $[\text{Ag}(\text{cyclam})](\text{ClO}_4)_2$ , 41777-41-7;  $[\text{Ag}(\text{TMC})](\text{ClO}_4)_2$ , 41777-42-8;  $[\text{Ag}(\text{tet a})](\text{ClO}_4)_2$ , 41777-44-0;  $[\text{Ag}(\text{tet b})](\text{ClO}_4)_2$ , 38596-53-1;  $[\text{Ag}(\text{TMT A})](\text{ClO}_4)_2$ , 92096-40-7;  $[\text{Ag}(\text{TMT B})](\text{ClO}_4)_2$ , 92216-13-2;  $[\text{Ag}(\text{H}_2\text{diAMsar})](\text{ClO}_4)_4$ , 92096-43-0;  $[\text{Ag}(\text{H}_2\text{diAMsar})](\text{NO}_3)_4$ , 92096-45-2; Ag, 7440-22-4;  $\text{AgNO}_3$ , 7761-88-8; dimethyl sulfate, 77-78-1; silver perchlorate, 7783-93-9.

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## Effect of High Pressure on the Emission Spectrum of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ Single Crystals

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Investigations of the emission of  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  single crystals under high pressure are reported for the first time. The spectra are recorded at room temperature up to 52 kbar. The following pressure effects are observed: a very small red shift, a distinct sharpening of emission spectra, and a considerable decrease in emission intensity. Model conceptions are presented to account for the experimental results.

### Introduction

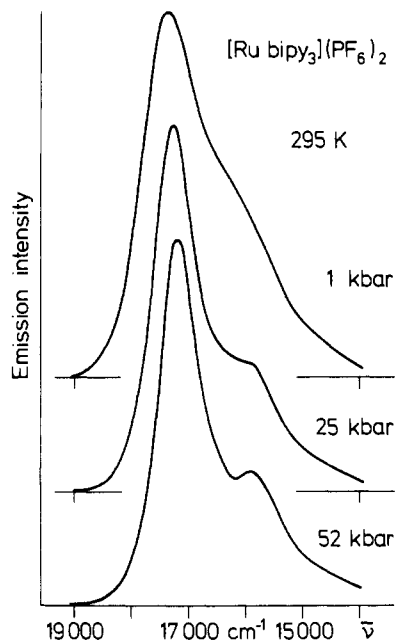
During the past decade, the photophysical as well as the photochemical properties of  $[\text{Ru}(\text{bpy})_3]^{2+}$  (bpy = 2,2'-bipyridine) have attracted widespread interest.<sup>1-3</sup> Most investigations of the excited states of  $[\text{Ru}(\text{bpy})_3]^{2+}$  were confined to fluid solutions,<sup>4,5</sup> glassy matrices,<sup>6-8</sup> or mixed crystals.<sup>9-11</sup> That is why only little is known about the spectroscopic properties of pure single crystals.<sup>12,13</sup> It has been demonstrated

that polarized spectroscopy with emphasis on the emission spectroscopy of single crystals is an especially effective technique for the investigation of excited-state properties.<sup>14</sup>

The existing theoretical models for the excited states of  $[\text{Ru}(\text{bpy})_3]^{2+}$  and related compounds are controversial. The Crosby model,<sup>15</sup> constructed to explain the emission behavior of  $[\text{Ru}(\text{bpy})_3]^{2+}$  at low temperature, has been contradicted recently by the electronic structure models of Kober and Meyer<sup>16</sup> and of Ferguson and Herren.<sup>17</sup> But the latter models are still too coarse to be capable of explaining the data obtained from emission spectroscopy. Moreover, there is disagreement concerning the symmetry of the complexes in their lowest excited states, which may be reduced from the  $D_3$  ground-state symmetry to  $C_2$ .<sup>8,18,19</sup> So further theoretical and experimental investigations have to be undertaken to come to a better un-

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**Figure 1.** Unpolarized emission spectra of single-crystal  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ . The normalized spectra are recorded at room temperature and at three different pressures. See ref 12 for the polarized emission spectra at standard conditions. The spectra at 1 bar and at 1 kbar are equivalent within the limits of experimental error.

understanding of the nature of the lowest excited states of  $[\text{Ru}(\text{bpy})_3]^{2+}$ .

In order to contribute to these investigations, we report in this paper the effects of high hydrostatic pressure on the emission spectrum of single-crystal  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  at room temperature.

### Experimental Section

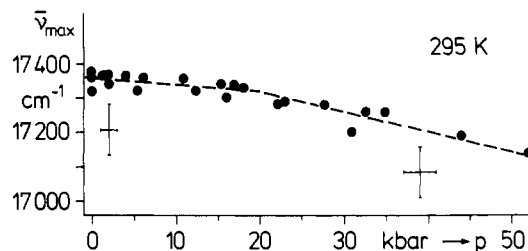
$[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  was synthesized as described previously.<sup>12</sup> Single crystals of  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  were grown by slow evaporation of ethanol-acetonitrile (1:1 v/v) solutions at room temperature.  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  crystallizes in hexagonal needles with the  $\bar{C}_3$  axis of the complex cation parallel to the needle axis ( $\equiv$  crystallographic  $\bar{c}$  axis).<sup>20</sup> Crystals suitable for emission spectroscopy were selected under a polarization microscope. The size of the crystals used in the high-pressure experiments was typically  $50 \mu\text{m} \times 50 \mu\text{m} \times 200 \mu\text{m}$ .

High-pressure studies were achieved by means of an optical high-pressure cell working according to Bridgman's gasket technique.<sup>21</sup> A metal gasket with a small concentric hole (0.5 mm), which forms the pressure chamber, was placed between two sapphire pistons. The pressure medium was chosen to be paraffin oil, which permits quasi-hydrostatic conditions up to about 50 kbar. The applied pressure was measured by utilizing the ruby luminescence method.<sup>22</sup>

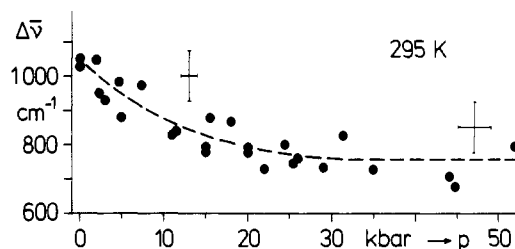
The samples in the high-pressure cell were excited with the focused, attenuated beam of an argon ion laser. Emission measurements were carried out with a spectrophotometer constructed especially for microcrystals.<sup>21,23</sup> Emission spectra were not corrected for the spectra response of the detection system.

### Results

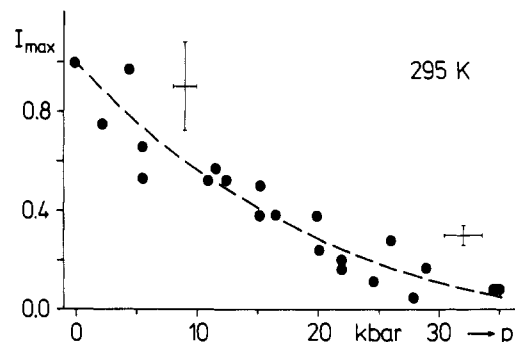
Figures 1–4 show the spectroscopic behavior of single-crystal  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  under high pressure at room temperature. The intensity of the emitted light with the electric field vector  $\vec{E}$  perpendicular to the crystallographic  $\bar{c}$  axis ( $\vec{E} \perp \bar{c}$ ) is at room temperature about a factor of 20 larger than the intensity of the  $\vec{E} \parallel \bar{c}$ -polarized component.<sup>12,13</sup> Consequently, unpolarized spectra represent in the limit of experimental errors the  $\vec{E} \perp$



**Figure 2.** Energy of the emission maximum ( $\bar{\nu}_{\text{max}}$ ) of single-crystal  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  as a function of pressure. The experimental points result from three different crystals. The dashed lines have slopes of  $\Delta\bar{\nu}_{\text{max}}/\Delta p \approx -2 \text{ cm}^{-1}/\text{kbar}$  for  $p < 20 \text{ kbar}$  and  $\Delta\bar{\nu}_{\text{max}}/\Delta p \approx -6 \text{ cm}^{-1}/\text{kbar}$  for  $p > 20 \text{ kbar}$ , respectively.



**Figure 3.** Pressure dependence of the half-width of the main peak ( $\Delta\bar{\nu}$ ) in the emission spectra of single-crystal  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ .  $\Delta\bar{\nu}$  was obtained as twice the energetic difference between the emission maximum and the point at half-maximum height on the blue-side flank of the spectrum. Experimental points are from three measurements on different crystals.



**Figure 4.** Maximum height ( $I_{\text{max}}$ ) of the emission spectra of single-crystal  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  as a function of pressure. The intensity is normalized to the emission intensity at atmospheric pressure. Experimental points result from measurements on three different crystals.

$\bar{c}$ -polarized spectra. The development of the  $\vec{E} \parallel \bar{c}$ -polarized component with pressure could not be registered, because depolarizing effects of the pressure cell windows mixed substantial  $\vec{E} \perp \bar{c}$  intensity into the very weak  $\vec{E} \parallel \bar{c}$  spectra. Emission spectra of  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  single crystals under pressure were found to be independent of the exciting wavelengths,  $\lambda_{\text{ex}} = 363.8, 457.9, 488.0 \text{ nm}$ .

The main effects of pressure on the emission spectrum (unpolarized or  $\vec{E} \perp \bar{c}$  polarized) of  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  single crystals are as follows:

(a) **Pressure-Induced Red Shift of the Emission Spectra.** As can be seen from Figure 2, the red shift of the emission maximum is very small for the first 20 kbar ( $\Delta\bar{\nu}_{\text{max}}/\Delta p \approx -2 \text{ cm}^{-1}/\text{kbar}$ ), whereas it takes a value of  $-6 \text{ cm}^{-1}/\text{kbar}$  for pressures  $p \gtrsim 20 \text{ kbar}$ .

(b) **Pressure-Induced Decrease of Half-Width.** In the low-pressure region ( $p \lesssim 20 \text{ kbar}$ ), the emission spectrum sharpens continuously and the resolution of the broad, structureless spectrum (at atmospheric pressure) is improved. A second peak on the low-energy side about  $1400 \text{ cm}^{-1}$  below the main peak can clearly be distinguished. For pressures above 20 kbar,

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the band shape does not change much (see Figure 1). This development is also demonstrated in Figure 3, where the half-width of the main peak (taken as twice the energy difference between the emission maximum and the point at half-maximum height on the blue side of the spectrum) is shown as a function of pressure. This plot again can be divided into two regions: for  $p \lesssim 20$  kbar, the half-width decreases substantially, whereas it remains nearly constant for  $p \gtrsim 20$  kbar.

**(c) Pressure-Induced Decrease of Emission Intensity.** For pressures up to 35 kbar, a continuous decrease of the height of the emission maximum by a factor of about 10 can be observed (see Figure 4). The decrease of the integrated intensity is still somewhat more pronounced, because of the pressure-induced sharpening of the emission spectrum.

Spectra recorded after pressure release exhibit the same energetic positions and half-widths as those found at 1 bar. Information concerning the reversibility of the intensity could not be obtained since the crystals broke through pressure release and consequently the comparability of the intensities was lost.

### Discussion

Polarized emission spectra of  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  single crystals at atmospheric pressure and at room temperature have already been published and group theoretically classified on the basis of crystallographically oriented but noninteracting  $[\text{Ru}(\text{bpy})_3]^{2+}$  centers.<sup>12</sup> A comparison of our single-crystal emission spectra with those obtained from  $[\text{Ru}(\text{bpy})_3]^{2+}$  doped into host matrices at low concentrations shows that the closer packing of  $[\text{Ru}(\text{bpy})_3]^{2+}$  centers in the pure single crystals does not produce any evident intermolecular solid-state interactions concerning the electronic properties. This result is not unexpected, as the distance between Ru centers in the pure  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  single crystals is greater than 10 Å.<sup>20</sup> Thus, the emission spectrum of pure single crystals is considered as a property of the  $[\text{Ru}(\text{bpy})_3]^{2+}$  complex alone. The crystal lattice only delivers a perturbational environment.

In ref 12 we argued that at least at room temperature a decision as to whether the complex symmetry of the ground-state  $D_3$  is reduced to  $C_2$  in the lowest excited states of  $[\text{Ru}(\text{bpy})_3]^{2+}$  (as actually is discussed<sup>8,18,19</sup>) cannot be given on the basis of our spectroscopic data. Consequently, the optical transitions were classified in the  $D_3'$  double group to take into account spin-orbit coupling. According to group-theoretical selection rules for electric dipole transitions, it was stated that the  $\vec{E} \perp \vec{c}$ -polarized emission spectrum at room temperature emerges from one or more  $E'$  states and the  $\vec{E} \parallel \vec{c}$ -polarized one comes from  $A_2'$ . We assume that the same states (mainly the  $E'$  states, because they carry about 95% of the emission intensity) are also responsible for the emission spectra at high pressure and further that no pressure-induced solid-state interactions gain a dominant influence.

The application of high pressure leads to a slight red shift of the  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  emission maximum with the values of  $\Delta\bar{\nu}_{\text{max}}/\Delta p \approx -2 \text{ cm}^{-1}/\text{kbar}$  for  $p \lesssim 20$  kbar and  $\Delta\bar{\nu}_{\text{max}}/\Delta p \approx -6 \text{ cm}^{-1}/\text{kbar}$  for  $p \gtrsim 20$  kbar, respectively. These are very small values, compared for example to the shifts of the phosphorescence of crystalline rare-earth chelates ( $\Delta\bar{\nu}_{\text{max}}/\Delta p \approx -30 \text{ cm}^{-1}/\text{kbar}$ <sup>24</sup>), of the absorption of crystalline Ni(II), Pd(II), or Pt(II) chelates ( $\Delta\bar{\nu}_{\text{max}}/\Delta p \approx -80$  to  $-160 \text{ cm}^{-1}/\text{kbar}$ <sup>25</sup>), or even of the luminescence of tetracyanoplatinates(II) ( $\Delta\bar{\nu}_{\text{max}}/\Delta p$  up to  $-380 \text{ cm}^{-1}/\text{kbar}$ <sup>14,21,26</sup>). Consequently, one is forced to explain the smallness of the pressure effect. This can be achieved by analogy to a model that has already been

discussed by Drickamer and co-workers for the behavior of the absorption bands of Fe complexes under pressure.<sup>27</sup>

The radiative transitions from the lowest excited states of  $[\text{Ru}(\text{bpy})_3]^{2+}$  are charge-transfer (CT) transitions between ligand  $\pi^*$  and metal 4d orbitals. Application of pressure will influence the d orbitals as well as the  $\pi^*$  orbitals. For simplicity, our first-order approach is given in the parentage group of  $O_h$  symmetry. The excited states of  $[\text{Ru}(\text{bpy})_3]^{2+}$  result from the promotion of an electron from a Ru  $t_{2g}$  orbital to a bpy  $\pi^*$  orbital. It is known that the  $\pi^*$  orbitals of aromatics and heterocyclics are lowered in energy under pressure.<sup>28</sup> The  $\pi-\pi^*$  transition of phen (=1,10-phenanthroline), whose electronic structure resembles that of bpy, shifts to the red continuously by  $-22 \text{ cm}^{-1}/\text{kbar}$ , this value being only slightly modified by complexation of phen in  $[\text{Fe}(\text{phen})_3]^{2+}$ .<sup>27</sup> Furthermore, on compression of the complex the overlap between the metal  $t_{2g}$  and the ligand  $\pi^*$  orbitals increases. As a consequence,  $\pi^*$  back-bonding is enhanced, and this leads to a stabilization of the  $t_{2g}$  orbitals. Thus, the net pressure effect is a reduced red shift for the CT transition compared to that for the  $\pi-\pi^*$  transition. Indeed, this has been found for the d- $\pi^*$  absorption bands of  $[\text{Fe}(\text{phen})_3]^{2+}$ .<sup>27</sup> Our results concerning the  $[\text{Ru}(\text{bpy})_3]^{2+}$  complex are in accordance with the foregoing conclusions.

In the low-pressure region ( $p \lesssim 20$  kbar), the emission spectra of  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  single crystal sharpen distinctly, but do not alter their shapes for higher pressure (Figure 1). This behavior can be explained by the effect of site homogenization. In a real crystal, there exist crystal lattice defects. Therefore, each  $[\text{Ru}(\text{bpy})_3]^{2+}$  molecule sees a slightly different environment, which influences the energies of the excited states. This site distribution (normally Gaussian) implies the inhomogeneous broadening of the emission spectra of crystals. We assume that under pressure crystal defects are removed to some extent and especially that molecules in extreme sites are influenced most. Thus, the site distribution is homogenized. As these extreme sites are removed, their contribution to the emission spectrum is missing and the inhomogeneous broadening is reduced. Consequently, emission bands get narrower (Figures 1 and 3). The spectrum therefore sharpens, and the vibronic peak (about  $1400 \text{ cm}^{-1}$  below the main peak) is clearly resolved. The importance of the inhomogeneous broadening could also be observed by the method of site-selective excitation of  $[\text{Ru}(\text{bpy})_3]^{2+}$  solutions at  $T = 2 \text{ K}$ . One finds a sharpening of the emission spectrum, too.<sup>13</sup>

The effect of pressure-induced sharpening seems to be finished at ca. 20 kbar, because no further reduction of the half-width occurs on pressure increase (Figure 3). Thus, below 20 kbar, applied pressure mainly leads to the compression of the crystal lattice. With further increasing pressure, the intramolecular compression apparently becomes significant. This is supported by the change in red shift at about 20 kbar from a very small value for  $p < 20$  kbar to a distinctly greater value (though still small) for  $p > 20$  kbar (Figure 2).

A drastic decrease in emission intensity is observed, when high pressure is applied to  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  single crystals (Figure 4). Such behavior is usually explained with increased thermal relaxation.<sup>28</sup> This is in agreement with the reduction of the emission lifetime, which has been observed to decrease from  $0.56 \mu\text{s}$  at 1 bar to  $0.51 \mu\text{s}$  at 2.3 kbar.<sup>29</sup> At present, it is difficult to give the physical reason for the pressure-induced reduction of the emission intensity. However, it is not unlikely that the process involved is coupled to an energy barrier. For  $[\text{Ru}(\text{bpy})_3]^{2+}$  solutions it has been found by

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temperature variation at atmospheric pressure that the radiationless relaxation of the emitting states is an activated process, the activation energies being dependent on the solvent, i.e. the second coordination sphere.<sup>3-5</sup> It is quite possible that the corresponding energy barrier is reduced by a pressure-induced deformation of the potential surfaces. It is worthwhile to mention that the main effect of intensity reduction occurs in a pressure range below 20-25 kbar, a region in which the complex environment (i.e. the crystal lattice, which also can be regarded as the second coordination sphere) is strongly influenced.

### Conclusion

High-pressure investigations on the emission spectrum of [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> single crystals have been reported for the first time. As the  $\vec{E} \parallel \vec{z}$ -polarized component carries only 5% of the emission intensity at room temperature, the  $\vec{E} \perp \vec{z}$ -polarized and the unpolarized spectra are comparable. A very small red shift of the emission spectrum is observed, which

is explained by the simultaneous stabilization of the ligand  $\pi^*$  and the metal  $t_{2g}$  orbitals. Under pressure the resolution of the emission spectra is enhanced and the emission bandwidth decreases by about 30% due to a reduction of the inhomogeneous broadening of the spectra. The pressure-induced intensity reduction is possibly coupled to the change of an energy barrier involved in the radiationless relaxation of the lowest excited states. From the pressure behavior of the band shape and of the red shift, two pressure regions can be distinguished. For pressures below about 20 kbar compression of the crystal lattice seems to be the dominant effect, whereas for higher pressures intramolecular compression gains a considerable influence on the pressure behavior of the emission spectra.

**Acknowledgment.** The authors express their thanks to Professor G. Glieman for support of this work. The Verband der Chemischen Industrie is acknowledged for financial support.

**Registry No.** [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub>, 60804-74-2.

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## Flash Photolysis Studies of Dinuclear Manganese Carbonyl Compounds<sup>1</sup>

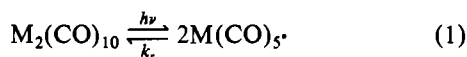
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Received April 26, 1984

The Mn(CO)<sub>4</sub>L• (L = CO, PR<sub>3</sub>; R = *n*-Bu, *i*-Bu, *i*-Pr, OPh) radicals have been observed directly as transient species following flash photolysis of Mn<sub>2</sub>(CO)<sub>8</sub>L<sub>2</sub> in hexane solution. The transient absorbance due to the radical disappears according to a second-order rate law. No difference in the decay behavior was noted when the experiments were conducted under an argon atmosphere as compared with CO. Earlier results from this laboratory in which a transient absorption was noted following flash photolysis of vacuum-degassed solutions of Mn<sub>2</sub>(CO)<sub>10</sub> are shown to have been due to an experimental artifact. There is no direct evidence in the flash photolysis experimental results for dissociative loss of CO from Mn(CO)<sub>4</sub>L•. In addition, under the conditions of flash photolysis, Mn(CO)<sub>4</sub>PR<sub>3</sub>• is not observed to undergo replacement of phosphine by CO when a CO atmosphere is employed. The spectral characteristics of the radicals have been measured. The bimolecular rate constants for recombination of Mn(CO)<sub>4</sub>PR<sub>3</sub>• radicals have been measured in hexane solution at 25 °C: P(*n*-Bu)<sub>3</sub>, 1 × 10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup>; P(*i*-Bu)<sub>3</sub>, 2 × 10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup>; P(*i*-Pr)<sub>3</sub>, 4 × 10<sup>6</sup> M<sup>-1</sup> s<sup>-1</sup>; PPh<sub>3</sub>, 1 × 10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup>; P(OPh)<sub>3</sub>, 9 × 10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup>. The recombination rates are lowest for phosphorus ligands of largest steric requirement.

### Introduction

It has been well established that irradiation of dinuclear metal carbonyl compounds at wavelengths corresponding to the  $\sigma-\sigma^*$  or  $d\pi-\sigma^*$  transitions results in efficient homolysis of the metal-metal bond. Studies of cross-coupling reactions of Mn<sub>2</sub>(CO)<sub>10</sub> and Re<sub>2</sub>(CO)<sub>10</sub> and of halogen atom abstraction reactions during irradiation show that metal-metal bond cleavage is homolytic, producing metal-centered radicals with 17-electron configurations.<sup>2-4</sup> Recombination of the radicals, eq 1, is bimolecular, with rate constant  $k_r$  near the diffu-



sion-controlled limit. In the case of Mn<sub>2</sub>(CO)<sub>10</sub>,  $k_r$ , defined by the rate law  $-d[\text{Mn}(\text{CO})_5\cdot]/dt = 2k_r[\text{Mn}(\text{CO})_5\cdot]^2$ , has been reported to have values of 3.9 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> at 20 °C in cyclohexane<sup>5</sup> and 9.5 × 10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup> at 22 °C in hexane.<sup>6</sup> Both

sets of results are based on flash photolysis results. For Re<sub>2</sub>(CO)<sub>10</sub>,  $k_r$  has the value of 3.7 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> at 22 °C in hexane.<sup>6</sup> Pulsed radiolysis studies yield similar values for recombination rates in ethanol as solvent.<sup>7</sup>

To properly interpret some of the observed chemical behavior of the radicals it is important to know how replacement of CO on the metal center by larger ligands such as phosphines affects the rates of recombination. We know in general that recombination rates should decrease as a result of such substitution. When the ligands on the metal are sufficiently large, metal-metal bond formation is no longer energetically favored and the resulting radicals are persistent. The properties of such persistent radicals, of the form Mn(CO)<sub>3</sub>L<sub>2</sub>•, where L is a bulky phosphine, have been reported.<sup>8-10</sup>

Aside from recombination, radicals may also undergo other reactions, notably substitution. There is substantial evidence that the radicals are highly labile. Whether that lability is related to a dissociative loss of CO from the radical, or to a

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