

# The Effect of the Diphosphine Basicity on the Excited-State Properties of *trans*-(N<sub>2</sub>)<sub>2</sub>W(R<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PR<sub>2</sub>)<sub>2</sub>: Identification of Near-Degenerate, Luminescent <sup>3</sup>MLCT and <sup>3</sup>LF Terms

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Absorption spectra (77 and 298 K), luminescence spectra (5–80 K), and luminescence lifetimes (5–80 K) for the title complexes have been correlated to increasing diphosphine basicity (R = 4-CF<sub>3</sub>-Ph < 4-H-Ph < 4-CH<sub>3</sub>O-Ph < Et). As a consequence, spectral peaks have been assigned to <sup>1,3</sup>MLCT (B<sub>1u</sub>, W → phosphorus) and <sup>1,3</sup>LF (B<sub>2g</sub>) terms. As the ligand basicity increases, the <sup>3</sup>MLCT bands observed in absorption blue-shift nearly 8000 cm<sup>-1</sup> and the vibrationally structured <sup>3</sup>LF bands observed in emission red-shift approximately 1300 cm<sup>-1</sup>. <sup>3</sup>LF terms lie lowest in energy in the 4-H-Ph, 4-CH<sub>3</sub>O-Ph, and Et compounds, and temperature-dependent lifetime data suggest emission from each be assigned to the equilibrated, spin-orbit split levels of the <sup>3</sup>LF term. The <sup>3</sup>LF and <sup>3</sup>MLCT excited-state terms lie close in energy in the 4-CF<sub>3</sub>-Ph compound, resulting in an emission band shape that is temperature-dependent. At 77 K, the emission band is broad and structureless and is assigned to arise primarily from the <sup>3</sup>MLCT term. As the temperature is lowered toward 5 K, the <sup>3</sup>MLCT emission diminishes in intensity accompanied by the development of a vibrational structure that is characteristic of emission from the <sup>3</sup>LF term. These excited-state terms satisfy the requirements (different orbital origins, near-degeneracy) for separation by a Franck–Condon energy barrier, resulting in simultaneous emission from both terms between 5 and 77 K.

## 1. Introduction

Much work continues to focus on the luminescent properties of nd<sup>6</sup> metal-centered complexes, with the goal of characterizing the states from which emission occurs and elucidating the dynamics of energy degradation following excitation. The nature of luminescence and its orbital origins can often be adjusted through careful choice of temperature, solvent polarity, excitation wavelength, and ligand modification. Most of the studies in the literature concerning luminescence “tunability” via ligand alteration have focused on mononuclear and dinuclear complexes containing metal ions coordinated to imine ligands.<sup>1–6</sup> The low-energy electronic excitations are generally associated with metal-localized transitions [LF; d → d], ligand-localized transitions [LL; π → π\*(imine)], or metal-to-ligand charge-transfer transitions [MLCT; d(metal) → π\*(imine)].<sup>5,6</sup> The energies of each type of transition can be adjusted by altering the nature of the chromophoric imine ligand,<sup>1,2</sup> the electron-

donating ability of nonchromophoric ligands,<sup>3</sup> or both.<sup>4</sup> For instance, as phosphine ligands replace imine moieties in a metal’s coordination sphere, the energies of the MLCT [d → π\*(imine)] excited terms are affected; generally, more π-accepting phosphines elevate the energy of the MLCT excited terms.<sup>3</sup> In some cases, ligand variations can lead to a reordering of the energy of the excited terms, resulting in significant changes in emission properties. For some complexes in which two excited terms lie close in energy, simultaneous emissions from both excited terms are observed.<sup>2</sup> Not only have these types of investigations aided

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in the characterization of the low-lying excited terms of  $nd^6$  metal complexes, but they are also contributing to the design of new complexes capable of photon-induced charge separation and energy transfer<sup>4d,7</sup> and luminescence on-off switching.<sup>8</sup>

Substantially fewer studies have dealt with luminescent complexes for which a phosphine (or diphosphine) is the chromophoric ligand.<sup>9–12</sup> This generally occurs for complexes in which only phosphine ligands make up the coordination sphere of the metal. Nearly all instances occur in complexes

containing  $nd^8$  or  $nd^{10}$  metal centers.<sup>11,12</sup> The nature of the proposed phosphine-based acceptor orbital either involves a  $\pi^*$  orbital of an aromatic ring or a  $\pi$ -acceptor orbital involving overlap of the  $(n + 1)p_z$  orbital on the metal with a phosphorus-based orbital of identical symmetry. For the latter case, the extent of participation of the phosphorus-based orbital varies depending on the complex in question; transitions involving this acceptor orbital have been described as either metal-centered or MLCT depending on the extent of this participation. Electronic transitions have variously been described as  $\pi \leftrightarrow \pi^*(\text{phenyl})$ ,  $\sigma(\text{M-P}) \leftrightarrow \pi^*(\text{phenyl})$ ,  $nd(\text{M}) \leftrightarrow \pi^*(\text{phenyl})$ , or  $nd(\text{M}) \leftrightarrow \pi(\text{M } p_z/\text{P } d)$ . Reviews of the excited-state properties of metal phosphine complexes have been provided by Kutal<sup>9</sup> and Vogler and Kunkely.<sup>10</sup>

Several investigations into the photophysical properties of the  $nd^6$  luminescent compounds  $trans\text{-}(\text{N}_2)_2\text{W}(\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2)_2$  ( $\text{R} = 4\text{-H-Ph}$ )<sup>13,14</sup> and  $trans\text{-}(\text{N}_2)_2\text{Mo}(\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2)_2$  ( $\text{R} = 4\text{-H-Ph}$  and  $\text{Et}$ )<sup>14,15</sup> have been reported. These complexes represent the only  $nd^6$  systems for which a phosphine is a chromophoric ligand. Caruana and Kisch<sup>13</sup> first measured the emission ( $\varphi = 0.08$ ,  $\tau = 19 \mu\text{s}$ , and  $\lambda_{\text{max}} = 17\,700 \text{ cm}^{-1}$ ) and absorption properties of  $trans\text{-}(\text{N}_2)_2\text{W}(\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2)_2$  ( $\text{R} = 4\text{-H-Ph}$ ). Brummer and Crosby<sup>14</sup> subsequently investigated the temperature dependence (2–100 K) of its luminescence and assigned it to an equilibrated manifold of emissive, near-degenerate  ${}^3\text{MLCT}$  ( $\text{W} \rightarrow \text{P } d$ ) and  ${}^3\text{LF}$  excited levels, with the latter lying  $\sim 200 \text{ cm}^{-1}$  above the MLCT levels. Simultaneous emissions from equilibrated  ${}^3\text{LF}$  and  ${}^3\text{MLCT}$  levels are unusual, yet little attention has been paid to this complex. To test these preliminary assignments and learn more about the photophysical properties of this complex, we have investigated the series  $trans\text{-}(\text{N}_2)_2\text{W}(\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2)_2$ , where  $\text{R} = 4\text{-CF}_3\text{-Ph}$ ,  $4\text{-H-Ph}$ ,  $4\text{-CH}_3\text{O-Ph}$ , and  $\text{Et}$ . By monitoring variations in emission and absorption properties as a function of the diphosphine basicity, we have demonstrated that near-degenerate  ${}^3\text{MLCT}$  and  ${}^3\text{LF}$  excited terms are present in the aryldiphosphine-substituted molecules. On the basis of our data, we propose revised assignments for the luminescence from  $trans\text{-}(\text{N}_2)_2\text{M}(\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2)_2$  ( $\text{M} = \text{Mo}$  and  $\text{W}$ ;  $\text{R} = 4\text{-H-Ph}$ ).

## 2. Experimental Section

All reactions and solution transfers were performed under dry nitrogen using standard Schlenk methods. Tetrahydrofuran (THF) was distilled under nitrogen from sodium benzophenone. 2-Methyltetrahydrofuran (2-MeTHF) was passed through an  $\text{Al}_2\text{O}_3$  column prior to distillation under nitrogen from calcium hydride. Benzene and methanol were distilled under nitrogen from sodium metal and magnesium methoxide, respectively. All absorption and emission measurements were measured on dilute ( $< 10^{-4} \text{ M}$ ) samples.

The ligands  $\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2$  ( $\text{R} = 4\text{-H-Ph}$  and  $\text{Et}$ ) were purchased from Strem Chemicals. The  $\text{R} = 4\text{-CF}_3\text{-Ph}$  and

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4-CH<sub>3</sub>O-Ph ligands were prepared following literature methods<sup>16</sup> as were all metal complexes.<sup>17</sup> Pure orange crystals of each complex were grown by slow diffusion of methanol into a solution of a crude compound dissolved in THF. Infrared, NMR, and elemental analysis data are provided in the Supporting Information. The characteristic asymmetric (vs) and symmetric (w) dinitrogen stretching frequencies matched those reported earlier.<sup>17</sup> A single NMR resonance was observed for each complex, indicating that the trans isomer is exclusively present in our samples. Peak energies matched those measured by previous workers.<sup>17</sup> No <sup>31</sup>P NMR resonances due to uncomplexed ligands were detected for any of the samples. C, H, and N elemental analyses for all complexes are close to calculated values.

Absorption spectra of samples dissolved in 2-MeTHF at 77 and 298 K were recorded with a Cary 300 Conc UV-visible spectrophotometer. Spectra at 298 K were also measured in various composition methanol/benzene (1:1, 1:2, and 0:1 by volume) mixed solvents. For the 77 K measurements, the samples were contained in a cylindrical Pyrex tube (2 cm i.d.) mounted in a Pyrex optical Dewar. The Dewar was then mounted in the sample beam of the spectrophotometer. Absorption spectra at 77 K versus air are reported as relative absorbance versus wavenumber.

Emission spectra for the ligands were measured using an Aminco-Bowman Series 2 luminescence spectrometer. Spectra for the complexes were recorded on a spectrometer constructed in the laboratory. A focused beam of light provided by a 100-W mercury lamp was passed through 12 cm of CuSO<sub>4</sub>(aq) and a Corning 7-60 band-pass filter before irradiation of the sample. The sample was contained in a cylindrical Pyrex tube (2 cm i.d.) mounted in a Pyrex optical Dewar containing liquid nitrogen. Emitted light was collected at right angles to the excitation by focusing it through 1/2 in. of 3 M NaNO<sub>2</sub>(aq) and onto the slits of a Photon Technology Inc. (PTI) 0.25-m monochromator. The dispersed light was detected by a cooled Hamamatsu R-935 photomultiplier tube, whose signal was fed to a Pacific Instruments 110 photometer. A computer controlled the monochromator through a stepping-motor drive. The photometer output was collected, digitized, and stored by the computer at every wavelength of a scan. Emission spectra are displayed as relative intensity versus reciprocal centimeters and are not corrected for wavelength variations of the detection system. Spectral resolution is sample-limited.

Emission lifetimes were excited using the 337-nm output of a PTI LN-1000 nitrogen laser. Emitted light was collected and detected as described in the previous paragraph. The photomultiplier output was passed through a resistor, and the resulting voltage versus time profiles were stored on a Hewlett-Packard digital oscilloscope and then transferred to a computer for analysis.

The following remote-sensing apparatus was utilized for making low-temperature (5–80 K) emission measurements in a 60-L CSMH-60 Cryofab liquid-helium storage Dewar containing a few inches of liquid helium. A copper sample block was mounted on the end of a hollow stainless steel tube (3/8 in. i.d.). The sample was contained in a depression in the block. This assembly was extended into the storage Dewar through a specially machined cap fitted to the Dewar's mouth. The cap not only secures the sample rod but also allows it to be lowered to varying depths inside the Dewar. Excitation was brought to the sample with a 4 m length of a 1.0 mm diameter fused-silica optical fiber (Fiberguide Industries SFS1000N; hard clad, nylon-jacketed) directed down the hollow

tube. Emission was directed out of the Dewar and to the detection system with an identical fiber. The ends of both fibers were positioned ~1 cm above the sample. The fibers were protected by encasement in stainless steel chromatography tubing. The temperature was monitored with a calibrated CryoCal CD-301 silicon diode temperature sensor positioned in the copper block next to the sample. By positioning the sample block at different heights above the liquid-helium bath, the sample's temperature could be varied between 5 and 80 K. The closer the sample block is to the helium bath, the better are the temperature resolution and stability. A weak, blue fluorescence was intrinsic to the optical fibers. The spectral range of this fluorescence (<520 nm) was outside the range of all of the complexes under investigation.

### 3. Results and Discussion

Assignment of absorption and emission bands to excited terms is facilitated by considering the relative basicities of the diphosphine ligands, R<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PR<sub>2</sub> (R = 4-CF<sub>3</sub>-Ph, 4-H-Ph, 4-CH<sub>3</sub>O-Ph, and Et). Streuli<sup>18</sup> has determined the basicities for the analogous substituted monophosphines, PR<sub>3</sub>, to increase in the order (pK<sub>a</sub> values relative to water in brackets) R = 4-H-Ph [2.73] < 4-CH<sub>3</sub>O-Ph [4.46] < Et [8.69]. Tolman<sup>19</sup> found this same ordering for PR<sub>3</sub> donor strength based on measurements of the CO (A<sub>1</sub>) stretching frequency in a series of Ni(CO)<sub>3</sub>PR<sub>3</sub> complexes. Although no data are available concerning P(4-CF<sub>3</sub>-Ph)<sub>3</sub>, it is likely less basic than P(4-H-Ph)<sub>3</sub>. On the basis of the monophosphine data, we assume the diphosphine basicity to increase in the order R = 4-CF<sub>3</sub>-Ph < 4-H-Ph < 4-CH<sub>3</sub>O-Ph < Et. Further evidence for this ordering comes from measurements of oxidation potentials for the complexes *trans*-(N<sub>2</sub>)<sub>2</sub>M(R<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PR<sub>2</sub>)<sub>2</sub> (M = Mo<sup>0</sup> or W<sup>0</sup>)<sup>17</sup> and Re<sup>I</sup>Cl(N<sub>2</sub>)(R<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PR<sub>2</sub>)<sub>2</sub>.<sup>16</sup> For each series of complexes, oxidation of the metal is more favorable in the order 4-CF<sub>3</sub>-Ph (least easily oxidized) < 4-H-Ph < 4-CH<sub>3</sub>O-Ph < Et. Therefore, ease of oxidation of the metal complexes correlated well with increasing electron-donating ability of the ligated diphosphine.

Bennett and co-workers<sup>20</sup> have measured the crystal structure of *trans*-(N<sub>2</sub>)<sub>2</sub>W(R<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PR<sub>2</sub>)<sub>2</sub> (R = 4-H-Ph) and found it to possess approximate D<sub>4h</sub> microsymmetry. On the basis of the similarity of the infrared spectrum of the 4-H-Ph complex to those for the other complexes investigated, we assume that all of the complexes possess D<sub>4h</sub> microsymmetry and will interpret our spectral data under this assumption. Further support for this assumption is provided by <sup>31</sup>P NMR spectra; all complexes, when dissolved in THF at 298 K, show a single resonance. We note that the infrared spectrum of each complex (Nujol mull) shows a weak band at ~2000 cm<sup>-1</sup> assigned to the symmetric N<sub>2</sub> stretching mode, suggesting some distortion from D<sub>4h</sub> microsymmetry.

To account for our spectroscopic data, we adopt the orbital ordering proposed previously:<sup>14</sup> d<sub>xz</sub>, d<sub>yz</sub> (e<sub>2g</sub>) < d<sub>xy</sub> (b<sub>2g</sub>) < d<sub>z</sub><sup>2</sup> (a<sub>1g</sub>) ~ π{M p<sub>z</sub>/P d (a<sub>2u</sub>)} < d<sub>x<sup>2</sup>-y<sup>2</sup></sub> (a<sub>1g</sub>). The ordering of

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**Table 1.** Absorption Band Energies (77 K), Extinction Coefficients (298 K), and Orbital and Term Assignments for the Complexes  $trans\text{-}(N_2)_2M(R_2PCH_2CH_2PR_2)_2$  ( $M = Mo$  and  $W$ )

		energy in $cm^{-1}$ ( $\epsilon$ in $M^{-1} cm^{-1}$ )					
		$^3LF\ b_{2g} \rightarrow a_{1g}$	$^1LF\ b_{2g} \rightarrow a_{1g}$	$^1LF\ e_g \rightarrow a_{1g}$	$^3MLCT\ b_{2g} \rightarrow a_{2u}$ group 1	$^1MLCT\ b_{2g} \rightarrow a_{2u}$ group 2	$^1MLCT\ e_g \rightarrow a_{2u}$ group 3
W Complexes							
4-CF <sub>3</sub> -Ph	NA <sup>a</sup>	NA	NA	NA	19 000 (2000)	21 000 (6000)	24 400 (12 500)
4-H-Ph	18 000–20 000 (tail) (<1000)	NA	NA	NA	20 700 (2500)	23 200 (6000)	25 700 (12 000)
4-CH <sub>3</sub> O-Ph	19 000 (250)	NA	NA	NA	22 000 (3500)	24 100 (7000)	26 500 (13 000)
Et	18 100 (60)	19 300 (700)	21 100 (650)	NA	27 000 (2000)	29 000 (5000)	NA
Mo Complexes							
4-H-Ph <sup>b</sup>	18 000–20 000 (tail) (<1000)	NA	NA	NA	NA	23 000 (5900)	25 450 (11 100)
Et <sup>c</sup>	18 800 <sup>d</sup> (<40)	20 580 (590)	21 980 (590)	NA	NA	27 550 (2840)	NA

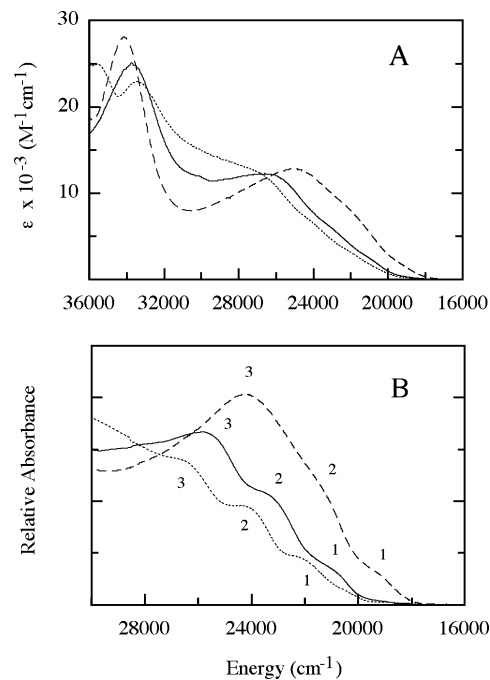
<sup>a</sup> NA = band not observed. <sup>b</sup> Data taken from ref 14. <sup>c</sup> Data taken from ref 15. Peak energies and extinction coefficients for the complex dissolved in heptane at 298 K. <sup>d</sup> A very weak, low-energy shoulder that overlaps strongly with the 20 580- $cm^{-1}$  band. Its value for  $\epsilon$  is an estimated upper limit.

the W-centered orbitals is well established for tetragonally distorted  $nd^6$  complexes under the assumption that diphosphine ligands exert a stronger ligand field than dinitrogen.<sup>21</sup> The  $\pi$  ( $a_{2u}$ ) acceptor orbital involves the appropriate symmetrized overlap of phosphorus 3d orbitals with a tungsten  $6p_z$  orbital. A similar acceptor orbital is involved in MLCT transitions observed for other  $D_{4h}$  molecules possessing diphosphine ligands.<sup>11</sup> The similarity of the absorption and emission properties for the molecules  $trans\text{-}(X)_2W(R_2PCH_2CH_2PR_2)_2$  ( $X = N_2$  or  $CO$ ;  $R = 4\text{-H-Ph}$ ) suggests that the acceptor  $\pi^*$  orbitals on  $N_2$  lie at high energies.<sup>13</sup>

**A. Absorption Measurements.** Table 1 gives absorption band energies, extinction coefficients, and term assignments for the W complexes. For all cases, peaks did not shift significantly in energy when measured in various composition methanol/benzene mixed solvents. Table 1 includes data measured previously for the analogous Mo complexes ( $R = 4\text{-H-Ph}$ <sup>14</sup> and  $Et$ <sup>15</sup>).

**(i) Absorption Spectra of the 4-CF<sub>3</sub>-Ph, 4-H-Ph, and 4-CH<sub>3</sub>O-Ph Complexes.** The 298 K absorption spectra of the complexes are shown in Figure 1A. Each complex displays better resolved spectra when cooled to 77 K. The lowest energy bands of the 77 K spectra are shown in Figure 1B. The absorption bands for each complex have similar shapes, with each being composed of three dominant overlapping peaks. The corresponding peaks for each compound are labeled 1–3 in Figure 1B. The lowest energy shoulder in the 4-CF<sub>3</sub>-Ph spectrum occurs at 19 000  $cm^{-1}$  (1), while the corresponding peaks in the spectra of the 4-H-Ph and 4-CH<sub>3</sub>O-Ph molecules occur at 20 700  $cm^{-1}$  (1) and 22 000  $cm^{-1}$  (1), respectively. Similar blue shifts occur for the peaks within groups 2 and 3. The regular nature of the energy shift within any particular peak grouping leads to the conclusion that these peaks arise from the same electronic transition whose energy is sensitive to the nature of the coordinated diphosphine.

These shifts can be understood if the bands are assigned to MLCT transitions involving a phosphorus-based acceptor orbital  $W\ p_z/P\ d\ (a_{2u})$  whose energy elevates with increasing diphosphine basicity. We assign the group 1 bands to  $^3MLCT$



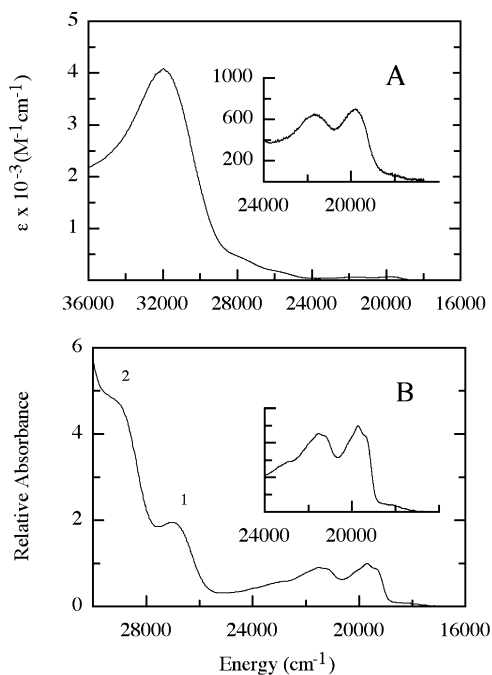
**Figure 1.** Absorption spectra of the 4-CF<sub>3</sub>-Ph (---), 4-H-Ph (—), and 4-CH<sub>3</sub>O-Ph (···) complexes at (A) 298 K and (B) 77 K. Peaks labeled with the same number arise from electronic transitions with the same orbital parentage.

( $^3B_{1u}, b_{2g} \rightarrow a_{2u}$ )<sup>22</sup> excited terms based on their being of lowest energy and intensity for each complex. This transition becomes allowed through spin-orbit coupling, which splits the  $^3B_{1u}$  term into  $B_{2u}$  and  $E_u$  components; transitions to the latter are dipole-allowed. It is significant that the complex  $trans\text{-}(N_2)_2Mo(R_2PCH_2CH_2PR_2)_2$  ( $R = 4\text{-H-Ph}$ )<sup>14,15</sup> does not show a distinct group 1 band but rather a diffuse, low-energy absorption tail ( $\epsilon < 1000\ M^{-1} cm^{-1}$ ), an observation that is consistent with the lesser importance of spin-orbit coupling in the Mo complexes ( $Mo^0, \xi_{SO} = 552\ cm^{-1}$ ;  $W^0, \xi_{SO} = 2089\ cm^{-1}$ ).<sup>23</sup> Our assignment for the group 1 bands differs from assignments made previously<sup>14</sup> for the 4-H-Ph complex. We emphasize that our assignments are consistent with all of the data presented in this account.

(21) Huheey, J. E. *Inorganic Chemistry: Principles of Structure and Reactivity*; Harper and Row Inc.: New York, 1972; p 322.

(22) Singlet and triplet spin designations are approximations due to the substantial spin-orbit coupling operative in these molecules.

(23) Griffiths, J. S. *The Theory of Transition Metal Ions*; Cambridge University Press: Cambridge, U.K., 1964; p 113.

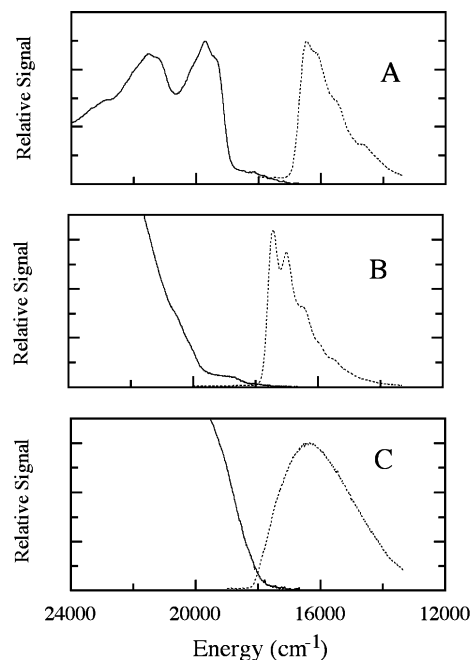


**Figure 2.** Absorption spectra of the Et complex at (A) 298 K and (B) 77 K. The inset of each figure shows an enlargement of the weak, low-energy bands.

We assign the more intense group 2 bands to  ${}^1\text{MLCT}$  ( ${}^1\text{B}_{1u}, b_{2g} \rightarrow a_{2u}$ ) terms. Finally, the most intense group 3 bands are assigned to  ${}^1\text{MLCT}$  ( ${}^1\text{E}_g, e_g \rightarrow a_{2u}$ ) terms. These latter bands are associated with electronic transitions that are both spin and orbitally allowed. The observation that the MLCT band energies are not solvent-sensitive is reasonable because the complexes are highly symmetrical and so probably possess small permanent dipole moments.<sup>24</sup> Our data (vid*o* infra) suggest that electron density changes accompanying the  ${}^{1,3}\text{MLCT}$  excitations are symmetrical, which translates into a small transition dipole for these excitations.

For the aryldiphosphine-substituted complexes, the more intense MLCT bands mask weaker LF bands. The onset of LF bands can be seen as low-energy absorption tails (18 000–20 000  $\text{cm}^{-1}$ ) for the 4-H-Ph and 4- $\text{CH}_3\text{O}$ -Ph complexes (Figure 1B). These two complexes contain the more basic aryldiphosphine ligands, and so their MLCT bands are shifted to higher energies compared with the MLCT bands for the 4- $\text{CF}_3$ -Ph complex. The 4- $\text{CH}_3\text{O}$ -Ph complex, containing the most basic of the three aryldiphosphine ligands, actually shows a well-resolved absorption shoulder at  $\sim 19\,000\text{ cm}^{-1}$  (Figure 3B). We assign this shoulder to a  ${}^3\text{LF}$  ( ${}^3\text{B}_{2g}, b_{2g} \rightarrow a_{1g}$ ) excitation (vid*o* infra) and assign the unstructured low-energy absorption tail for the 4-H-Ph complex to a similar origin. Significantly, the 4- $\text{CF}_3$ -Ph complex shows no low-energy absorption tail (Figure 3C), suggesting that the  ${}^3\text{MLCT}$  excited-state term lies lowest in energy for this complex.

**(ii) Absorption Spectrum of the Et Complex.** The 298 K absorption spectrum of the Et complex is shown in Figure 2A. Its shape and intensity are very different from those of its aryldiphosphine analogues. Among all of the complexes,



**Figure 3.** Overlap region of the lowest-energy 77 K absorption band (—) and 77 K emission band (⋯) for the (A) Et, (B) 4- $\text{CH}_3\text{O}$ -Ph, and (C) 4- $\text{CF}_3$ -Ph complexes.

the MLCT bands are expected to lie highest in energy for the Et complex. The bands at 27 000  $\text{cm}^{-1}$  (2000  $\text{M}^{-1}\text{ cm}^{-1}$ ) and 29 000  $\text{cm}^{-1}$  (5000  $\text{M}^{-1}\text{ cm}^{-1}$ ) are assigned to  ${}^3\text{MLCT}$  ( ${}^3\text{B}_{1u}, b_{2g} \rightarrow a_{2u}$ ) and  ${}^1\text{MLCT}$  ( ${}^1\text{B}_{1u}, b_{2g} \rightarrow a_{2u}$ ) terms, respectively, and are the analogues of the group 1 and 2 bands observed for the aryldiphosphine complexes. At lower energies, two low extinction bands are present at 19 300  $\text{cm}^{-1}$  ( $\epsilon = 700\text{ M}^{-1}\text{ cm}^{-1}$ ) and 21 100  $\text{cm}^{-1}$  ( $\epsilon = 650\text{ M}^{-1}\text{ cm}^{-1}$ ). Because of the large blue shift of the MLCT bands and the expected insensitivity of LF band energies to diphosphine substitution, we assign these weak bands to LF transitions. The small magnitude of their molar extinctions further supports LF assignments. The band at 19 300  $\text{cm}^{-1}$  is assigned to a  ${}^1\text{LF}$  ( ${}^1\text{B}_{2g}, b_{2g} \rightarrow a_{1g}$ ) term, while that at 21 100  $\text{cm}^{-1}$  is assigned to a  ${}^1\text{LF}$  ( ${}^1\text{E}_g, e_g \rightarrow a_{1g}$ ) term. The band at 19 300  $\text{cm}^{-1}$  has a low-energy shoulder centered at 18 100  $\text{cm}^{-1}$  ( $\epsilon = 60\text{ M}^{-1}\text{ cm}^{-1}$ ). Its unusually small molar extinction coefficient leads us to assign this band to a  ${}^3\text{LF}$  ( ${}^3\text{B}_{2g}, b_{2g} \rightarrow a_{1g}$ ) term. The magnitude of this shoulder's molar extinction is significantly smaller than that for  ${}^3\text{LF}$  absorption bands observed for other high-symmetry  $\text{W}^0$ -centered molecules.<sup>1d,2e,25–27</sup>

A nearly identical dramatic blue shift of MLCT bands, revealing weak  ${}^{1,3}\text{LF}$  bands, has been observed for *trans*-( $\text{N}_2$ ) $_2\text{Mo}(\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2)_2$  upon changing R from 4-H-Ph to Et.<sup>15</sup> Weak bands at 20 580  $\text{cm}^{-1}$  ( $\epsilon = 590\text{ M}^{-1}\text{ cm}^{-1}$ ) and 21 980  $\text{cm}^{-1}$  ( $\epsilon = 590\text{ M}^{-1}\text{ cm}^{-1}$ ) were assigned to a  ${}^1\text{LF}$  term for the Et complex. A very weak, poorly resolved shoulder at  $\sim 18\,800\text{ cm}^{-1}$  is associated with the 20 580  $\text{cm}^{-1}$

(24) Crosby, G. A. *Acc. Chem. Res.* **1975**, *8*, 231.

(25) Beach, N. A.; Gray, H. B. *J. Am. Chem. Soc.* **1968**, *90*, 5713.

(26) Wrighton, M. S.; Abrahamson, H. B.; Morse, D. L. *J. Am. Chem. Soc.* **1976**, *98*, 4105.

(27) (a) Wrighton, M.; Hammond, G. S.; Gray, H. B. *J. Am. Chem. Soc.* **1971**, *93*, 4336. (b) Moralego, C.; Langford, C. H.; Sharma, D. K. *Inorg. Chem.* **1989**, *28*, 2205.

**Table 2.** 77 K Emission Energies, Lifetimes, and Orbital and Term Assignments for *trans*-(N<sub>2</sub>)<sub>2</sub>M(R<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PR<sub>2</sub>)<sub>2</sub> (M = Mo and W)

R	$E_{\max}$ (cm <sup>-1</sup> )	$\tau$ ( $\mu$ s)	orbital and term assignments
W Complexes			
4-CF <sub>3</sub> -Ph	16 350 <sup>a</sup>	0.25	<sup>3</sup> MLCT ( <sup>3</sup> B <sub>1u</sub> , b <sub>2g</sub> ← a <sub>2u</sub> )
	18 000 <sup>b</sup> (5 K)	12	<sup>3</sup> LF ( <sup>3</sup> B <sub>2g</sub> , b <sub>2g</sub> ← a <sub>1g</sub> )
4-H-Ph	17 750 <sup>b</sup>	22	<sup>3</sup> LF ( <sup>3</sup> B <sub>2g</sub> , b <sub>2g</sub> ← a <sub>1g</sub> )
4-CH <sub>3</sub> O-Ph	17 400 <sup>b</sup>	36	<sup>3</sup> LF ( <sup>3</sup> B <sub>2g</sub> , b <sub>2g</sub> ← a <sub>1g</sub> )
Et	16 450 <sup>b</sup>	7	<sup>3</sup> LF ( <sup>3</sup> B <sub>2g</sub> , b <sub>2g</sub> ← a <sub>1g</sub> )
Mo Complexes			
4-H-Ph <sup>c</sup>	15 700 <sup>b</sup> (10 K)	28 (14 K)	<sup>3</sup> MLCT ( <sup>3</sup> B <sub>1u</sub> , b <sub>2g</sub> ← a <sub>2u</sub> )

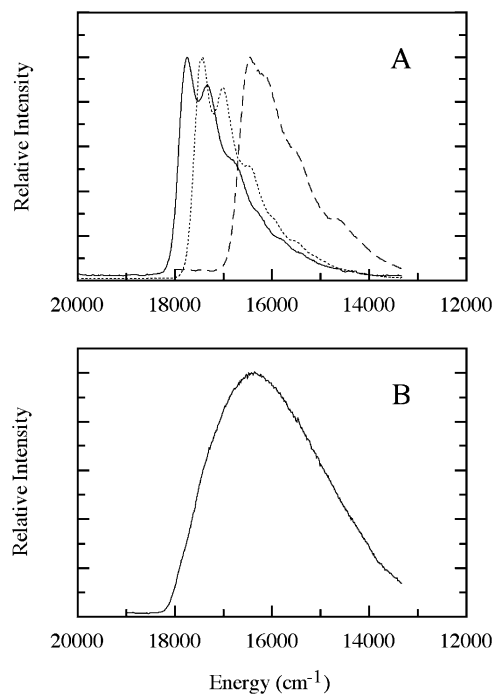
<sup>a</sup> Maximum of the emission band. <sup>b</sup> Apparent origin of the emission band. <sup>c</sup> Data taken from ref 14.

band and is likely the analogue of the 18 100 cm<sup>-1</sup> shoulder observed for *trans*-(N<sub>2</sub>)<sub>2</sub>W(Et<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PEt<sub>2</sub>)<sub>2</sub>. We assign this shoulder to a <sup>3</sup>LF (<sup>3</sup>B<sub>2g</sub>, b<sub>2g</sub> → a<sub>1g</sub>) excitation. Consistent with the diminished role of spin-orbit coupling in the Mo<sup>0</sup> complexes, its molar extinction (<40 M<sup>-1</sup> cm<sup>-1</sup>) is less than that for the <sup>3</sup>LF shoulder for the W<sup>0</sup> compound. This lowering in intensity parallels that noted previously for the <sup>3</sup>MLCT bands of the 4-H-Ph complexes of Mo and W.

When the Et complex is cooled to 77 K, its low-energy bands develop vibronic structure (Figure 2B) with (~500 ± 100) cm<sup>-1</sup> spacings. This is similar to the vibronic spacings observed on the 77 K emission band for this complex (Figure 3A). Figure 3 shows the band origin regions for the Et and 4-CH<sub>3</sub>O-Ph complexes. For the Et complex, there is a small Stokes shift (~1600 cm<sup>-1</sup>) between its 18 100 cm<sup>-1</sup> absorption shoulder and the spin-forbidden emission band ( $\tau_{em}$  = 7.0  $\mu$ s at 77 K). A nearly identical Stokes shift (~1500 cm<sup>-1</sup>) occurs between the 19 000 cm<sup>-1</sup> absorption shoulder and the spin-forbidden emission band ( $\tau_{em}$  = 36  $\mu$ s at 77 K) for the 4-CH<sub>3</sub>O-Ph complex. These observations support our <sup>3</sup>LF assignment for these low-energy absorption shoulders.

**B. Emission Measurements.** Table 2 gives the emission energies and emission lifetimes for the W complexes. The shape of the 77 K emission spectra did not change when excited at different wavelengths between 350 and 500 nm. Emission data measured previously<sup>14</sup> for *trans*-(N<sub>2</sub>)<sub>2</sub>Mo-(R<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PR<sub>2</sub>)<sub>2</sub> (R = 4-H-Ph) are also included in Table 2.

**(i) 77 K Emission from the Diphosphine Ligands.** Solutions of the R = 4-CF<sub>3</sub>-Ph, 4-H-Ph, and 4-CH<sub>3</sub>O-Ph ligands dissolved in 2-MeTHF glass at 77 K displayed blue emissions. Their emission spectra were broad and structureless with maxima at 458, 429, and 417 nm, respectively, a consistent blue shift with increasing electron-donating ability of the para substituent on the phenyl ring. The R = Et ligand was nonemissive under the same conditions. Emission from the ligands was comprised of short ( $\tau$  < 300 ns) and longer-lived components. The longer-lived emissions had lifetimes of 20, 30, and 40 ms, respectively. These observations are consistent with the emissions being assigned to an *n*(phosphorus) ←  $\pi^*$ (phenyl) transition, as previously proposed for the related monophosphine ligands (PR<sub>3</sub>).<sup>9,29</sup>

**Figure 4.** 77 K emission spectra for the (A) 4-H-Ph (—), 4-CH<sub>3</sub>O-Ph (⋯), Et (---) and (B) 4-CF<sub>3</sub>-Ph complexes.

The emission bands for the ligands lie at significantly higher energies than those for the W complexes and have very different shapes. In addition, their emission lifetimes are much longer than those for the complexes. These observations lead us to conclude that the 77 K emissions arise from the complexes and are not due to dissociated ligands.

**(ii) 77 K Emission Data for the 4-H-Ph, 4-CH<sub>3</sub>O-Ph, and Et Complexes.** The 77 K emission spectra for these molecules are given in Figure 4A. All possess similar vibronically structured band shapes with band origins of 17 750 (4-H-Ph), 17 400 (4-CH<sub>3</sub>O-Ph), and 16 450 (Et) cm<sup>-1</sup>, a red shift of ~1300 cm<sup>-1</sup> with increasing ligand basicity.

Figure 3 shows the band origin region for the Et and 4-CH<sub>3</sub>O-Ph complexes. On the basis of the small Stokes shift between the <sup>3</sup>LF absorption and emission bands for each complex and each compound's long emission lifetime (see Table 2), we assign luminescence from both complexes to a <sup>3</sup>LF (<sup>3</sup>B<sub>2g</sub>, b<sub>2g</sub> → a<sub>1g</sub>) excited-state term. Confirmation of these assignments resides in the observation that the ~900 cm<sup>-1</sup> difference between the <sup>3</sup>LF absorption bands for the 4-CH<sub>3</sub>O-Ph and Et complexes is nearly identical with the ~1000-cm<sup>-1</sup> difference between the <sup>3</sup>LF emission bands for the same two complexes. Because the 4-H-Ph molecule also possesses a long-lived emission decay and displays a similar emission band shape, its emission is also assigned to a <sup>3</sup>LF term. Because the Et ligand contains no aromatic rings, we conclude that the  $\pi$  systems of the 4-H-Ph and 4-CH<sub>3</sub>O-Ph complexes are not directly involved in the emissive transition.

The emission band origins red-shift ~1300 cm<sup>-1</sup> along the series 4-H-Ph, 4-CH<sub>3</sub>O-Ph, and Et. In contrast, the <sup>3</sup>MLCT band maxima observed in the absorption blue-shift

(28) Caruana, A. Ph.D. Thesis, Institut für Strahlenchemie im Max-Planck-Institut für Kohlenforschung.

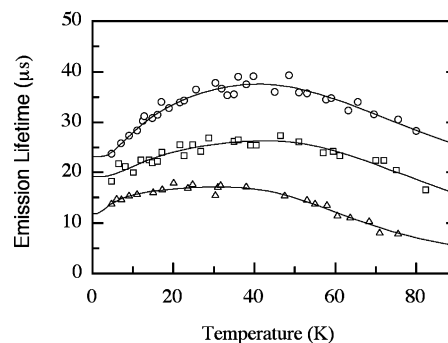
(29) Mataga, N. *Bull. Chem. Soc. Jpn.* **1963**, *36*, 654.

$\sim 8000\text{ cm}^{-1}$  along the same series. The reversal of energy trends and their different magnitudes supports our assignment of the dominant absorption bands (group 1–3 bands) and emission bands to transitions of different orbital parentage and is consistent with our  ${}^3\text{MLCT}$  and  ${}^3\text{LF}$  assignments. The red shift of the  ${}^3\text{LF}$  emission band origins with increasing diphosphine basicity can be understood using qualitative crystal field arguments. Because the  $d_{z^2}$  orbital is directed toward dinitrogen and away from the diphosphine ligands, its energy should be elevated less than that of the  $d_{xy}$  orbital as the diphosphine basicity is increased. Consequently, as the diphosphine basicity increases, the energy of the  $d_{xy} \leftrightarrow d_{z^2}$  transition decreases.

Our data require that emission from the 4-H-Ph, 4-CH<sub>3</sub>O-Ph, and Et complexes be assigned to a  ${}^3\text{LF}$  ( ${}^3\text{B}_{2g}, b_{2g} \rightarrow a_{1g}$ ) term. The peak spacings on the emission bands are irregular but, on average, lie in the range of  $500 \pm 100\text{ cm}^{-1}$ . This spacing is too high to be assigned to a W–P stretching mode but is similar to the  $555\text{-cm}^{-1}$  (Nujol mull) infrared band observed for each complex that has been assigned to a W–N stretching mode.<sup>17</sup> It is also similar to the totally symmetric resonance at  $525 \pm 3\text{ cm}^{-1}$  observed in the Raman spectrum of the 4-H-Ph complex (298 K, C<sub>6</sub>H<sub>6</sub>).<sup>14</sup> We tentatively assign the vibronic structure on the emission bands to a W–N stretching mode coupled to the  $b_{2g} \leftarrow a_{1g}$  electronic transition. This may also be the origin of the structure associated with the  ${}^1\text{LF}$  absorption bands of the Et complex (Figure 2B). The Franck–Condon-allowed band shape for the emissions suggests little geometrical distortion between the ground- and excited-state potential wells for the  ${}^3\text{LF}$  excitation. This is surprising because the electronic transition involves a tungsten-centered  $d_{z^2}$  orbital ( $\sigma$  antibonding, W–N; nonbonding, W–P) and a  $d_{xy}$  orbital ( $\pi$  bonding, W–N; nonbonding, W–P) and should formally result in a large distortion along the W–N stretching coordinate. We offer no rationalization for this discrepancy and emphasize that the data do not support an alternative to our  ${}^3\text{LF}$  assignment.

It was shown previously<sup>14</sup> that the 77 K emission from the 4-H-Ph complex consists of both a short-lived ( $\tau < 100\text{ ns}$ ) and longer-lived ( $\tau = 21\text{ }\mu\text{s}$ ) component. The short-lived emission has been attributed to the impurity *trans*-(N<sub>2</sub>)<sub>2</sub>W(R<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PR<sub>2</sub>)<sub>2</sub><sup>+</sup> and was found to contribute less than 5% to the overall emission at 77 K.<sup>28</sup> Although the impurity emission occurs within the spectral range of the long-lived emission from *trans*-(N<sub>2</sub>)<sub>2</sub>W(R<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PR<sub>2</sub>)<sub>2</sub>, its band shape is very different. Because we have not performed time-resolved experiments, we cannot definitively eliminate the possibility that emission from the Et, 4-CH<sub>3</sub>O-Ph, and 4-CF<sub>3</sub>-Ph complexes may also have a contribution from an analogous impurity. We believe that any impurity emission is insignificant for the Et and 4-CH<sub>3</sub>O-Ph complexes because their emission decays are exponential at all temperatures (5–80 K) and their emission band shapes are similar to that of the 4-Ph-H complex.

**(iii) Temperature-Dependent Emission Properties for the 4-H-Ph, 4-CH<sub>3</sub>O-Ph, and Et Complexes.** Our data indicate that the LF excited term lies well below the MLCT



**Figure 5.** Emission lifetime versus temperature data for the 4-H-Ph (□), 4-CH<sub>3</sub>O-Ph (○), and Et (△) complexes. The curves are fits of the data to eq 1.

excited term in the Et complex. On the other hand, these terms appear to lie close in energy in the 4-H-Ph and 4-CH<sub>3</sub>O-Ph complexes. We decided to probe the manifold of emissive, excited triplet levels by measuring the emission band shapes and emission lifetimes of these three complexes as a function of temperature between 5 and 80 K. Brummer and Crosby<sup>14</sup> found the emission band shape and lifetime of the 4-Ph-H complex to be temperature-dependent (2–100 K). They assigned emission to an equilibrated manifold of three emissive, near-degenerate  ${}^3\text{MLCT}$  and  ${}^3\text{LF}$  levels. The vibronically structured 8 K emission band was assigned primarily to the E<sub>u</sub> component of the  ${}^3\text{MLCT}$  ( ${}^3\text{B}_{1u}$ ) term. As the temperature was raised toward 100 K, they observed a weak, broad, unstructured band growing into the emission spectrum and assigned it to a level derived from a  ${}^3\text{LF}$  ( ${}^3\text{B}_{2g}$ ) term. From an analysis of the lifetime versus temperature data, they placed this emissive  ${}^3\text{B}_{2g}$  level approximately 200  $\text{cm}^{-1}$  above the E<sub>u</sub> level. Our data necessitate that for the 4-H-Ph, 4-CH<sub>3</sub>O-Ph, and Et compounds the levels derived from the  ${}^3\text{B}_{2g}$  term lie lowest in the equilibrated manifold of levels.

If levels deriving from a  ${}^3\text{MLCT}$  term are involved in the manifold of equilibrated levels, then their energy relative to the  ${}^3\text{LF}$  levels should be highly sensitive to the diphosphine basicity. To test this premise, the emission lifetimes for the 4-H-Ph, 4-CH<sub>3</sub>O-Ph, and Et complexes were measured between 5 and 80 K. Decay curves were exponential for at least three lifetimes for each complex at every temperature. Lifetime versus temperature profiles for the three complexes are shown in Figure 5. Data for the 4-Ph-H complex agree with those measured previously by Brummer and Crosby.<sup>14</sup> Following their analysis, we assume that luminescence emanates from a manifold of three levels whose populations are governed by the Boltzmann distribution law. This model predicts the following form for the temperature-dependent emission lifetime:

$$\tau(T) = \frac{1 + \exp(-\Delta E_{1,2}/kT) + \exp(-\Delta E_{1,3}/kT)}{k_1 + k_2 \exp(-\Delta E_{1,2}/kT) + k_3 \exp(-\Delta E_{1,3}/kT)} \quad (1)$$

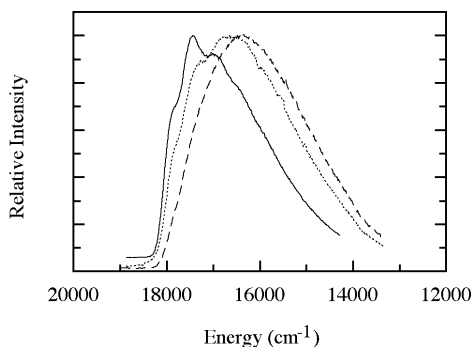
$k_1$ ,  $k_2$ , and  $k_3$  are temperature-independent, first-order rate constants for excited-state decay from each of the three levels in the manifold.  $\Delta E_{1,2}$  and  $\Delta E_{1,3}$  are the energy gaps between the lowest level and the second and third levels, respectively.



**Table 3.** Energy Gaps and Rate Constants That Characterize the Equilibrated Manifold of Luminescent Levels in 4-H-Ph, 4-OCH<sub>3</sub>-Ph, and Et Complexes<sup>a</sup>

R	$\Delta E_{1,2}$ (cm <sup>-1</sup> )	$\Delta E_{1,3}$ (cm <sup>-1</sup> )	$k_1$ ( $\mu\text{s}^{-1}$ )	$k_2$ ( $\mu\text{s}^{-1}$ )	$k_3$ ( $\mu\text{s}^{-1}$ )
4-CF <sub>3</sub> -Ph	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
4-H-Ph	12	230	0.050	0.015	2.1
4-CH <sub>3</sub> O-Ph	10	170	0.040	0.001	0.44
Et	3	210	0.10	0.020	9.0

<sup>a</sup> See text for parameter definitions. <sup>b</sup> No data because emission decay curves were highly nonexponential below 50 K.

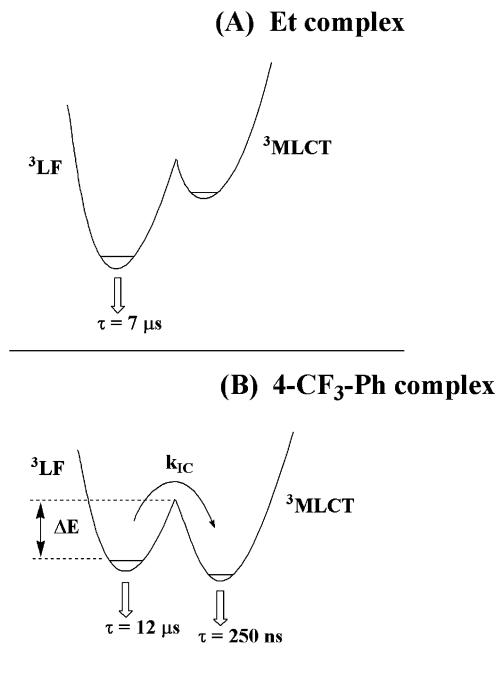
**Figure 6.** Emission spectra of the 4-CF<sub>3</sub>-Ph complex at 5.0 K (—), 32 K (⋯), and 77 K (---).

We emphasize that only a three-level manifold is required to fit our data. The fitted curves are shown in Figure 5, and the resulting parameters are summarized in Table 3. The values for  $\Delta E_{1,2}$  and  $\Delta E_{1,3}$  do not vary appreciably among the three complexes. Any minor variations do not reflect either the  $\sim 8000$  cm<sup>-1</sup> blue shift for their <sup>3</sup>MLCT absorption bands or the  $\sim 1300$  cm<sup>-1</sup> red shift for their <sup>3</sup>LF emission bands as the ligand basicity increases. We conclude that none of the levels in the equilibrated manifold are of <sup>3</sup>MLCT parentage but are rather due solely to levels derived from the <sup>3</sup>LF excited term.

The temperature dependence of the luminescence band shape for the 4-CH<sub>3</sub>O-Ph and Et complexes is similar to that chronicled for the 4-H-Ph complex. Specifically, at low temperatures, the band origins of the vibronically structured spectra (Figure 4) carry the most intensity, with the other members of the progression carrying diminishingly less intensity. As the temperature is raised, the origin gradually loses intensity while the second member of the progression gains intensity. This subtle intensity shift has been attributed to a weak, broad emission growing into the spectrum at high temperatures and is consistent with our model of an equilibrated manifold of luminescent levels. We interpret this effect to arise strictly from population redistribution among emissive levels derived from the spin-orbit split <sup>3</sup>LF term.

Figure 7A is a qualitative diagram depicting the relative disposition of potential wells for the Et complex. Emission emanates only from the <sup>3</sup>LF term between 5 and 80 K because the energy of the <sup>3</sup>MLCT term is too high to allow its thermal population. The same situation pertains for the 4-H-Ph and 4-CH<sub>3</sub>O-Ph complexes.

**(iv) 77 K Emission Data for the 4-CF<sub>3</sub>-Ph Complex.** The 77 K emission spectrum of this complex is given in Figure 4B. It is broad and structureless with a maximum at

**Distortion Coordinates****Figure 7.** Qualitative diagram showing the distribution of potential wells for the <sup>3</sup>LF and <sup>3</sup>MLCT terms in the (A) Et and (B) 4-CF<sub>3</sub>-Ph complexes.  $\Delta E$  is the energy barrier, and  $k_{\text{IC}}$  is the rate constant for interconfigurational transition. Lifetime data are for 77 K.

16 350 cm<sup>-1</sup>. The 77 K emission decay is biexponential and is comprised of a short component ( $\tau \sim 250$  ns) and a longer component ( $\tau = 12 \mu\text{s}$ ). These emission characteristics are much different from those displayed by the other compounds. It is expected that the <sup>3</sup>MLCT term will lie closest in energy to the <sup>3</sup>LF term in the 4-CF<sub>3</sub>-Ph complex because it possesses the least basic diphosphine ligand. In addition, the 77 K absorption spectrum for the 4-CF<sub>3</sub>-Ph complex shows evidence of only MLCT bands (Figure 1), with the low-energy <sup>3</sup>MLCT band overlapping the compound's emission band (Figure 3C). For these reasons, the 77 K luminescence from the 4-CF<sub>3</sub>-Ph molecule is assigned to arise primarily from a short-lived <sup>3</sup>MLCT (<sup>3</sup>B<sub>1u</sub>) term. For reasons to be discussed in the next section, we assign the longer-lived emission to emanate from a <sup>3</sup>LF term.

The broad, unstructured emission band of the 4-CF<sub>3</sub>-Ph complex has a Stokes shift of  $\sim 2900$  cm<sup>-1</sup>, suggesting that a significant geometrical distortion accompanies the <sup>3</sup>MLCT excitation, at least compared to that accompanying the <sup>3</sup>LF excitation discussed previously. Because the MLCT absorption and emission band energies are insensitive to solvent variations, we conclude that any distortion must be symmetrical in nature, thereby resulting in little change in the dipole moment. The <sup>3</sup>MLCT excitation involves a phosphorus-based acceptor orbital (nonbonding, W-N;  $\pi$  bonding, W-P) and a tungsten-based d<sub>xy</sub> orbital (nonbonding, W-N;  $\pi$  bonding, W-P). This transition should result in distortion along the W-P stretching coordinate. Because the <sup>3</sup>MLCT emission shows no W-N vibronic structure, we speculate that transitions to this term are coupled to W-P bond stretching within the WP<sub>4</sub> plane. A similar structureless



emission band has been observed for emission from the analogous  $^3\text{MLCT}$  terms for the square-planar species  $\text{M}(\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2)_2^+$  ( $\text{M} = \text{Rh}^{\text{I}}$  and  $\text{Ir}^{\text{I}}$ ;  $\text{R} = 4\text{-H-Ph}$ ).<sup>11</sup> Clearly, the degree and nature of the geometrical distortion differs for the  $^3\text{LF}$  and  $^3\text{MLCT}$  excitations.

Another possible origin for the 77 K emission from the 4- $\text{CF}_3$ -Ph complex is intramolecular exciplex formation via stacking of phenyl rings from the same diphosphine ligand. This type of emission was observed from crystalline samples of the tetrahedral species  $\text{Au}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2\text{PF}_6$  as well as samples of the salt dispersed in poly(methyl methacrylate).<sup>15</sup> The exciplex emission has a broad, structureless band shape maximizing at 600 nm. Significantly, the crystal structure of this complex clearly shows close-range stacking of phenyl rings. The crystal structure of the 4-H-Ph complex<sup>20</sup> shows no evidence of phenyl stacking. Because the  $\text{CF}_3$  substituent lies para to phosphorus in the 4- $\text{CF}_3$ -Ph complex, there is no reason to expect steric factors to develop that would promote phenyl stacking in this complex. We, therefore, eliminate exciplex formation as the source of emission from the 4- $\text{CF}_3$ -Ph compound.

**(v) Temperature-Dependent Emission Properties for the 4- $\text{CF}_3$ -Ph Complex.** The 5, 32, and 77 K emission spectra for this complex are shown in Figure 6. As the temperature is lowered toward 5 K, the emission band narrows and develops a vibrational structure similar to that associated with the  $^3\text{LF}$  bands observed for the other compounds. At each temperature, the overall emission decays with a fast component that we assign to a  $^3\text{MLCT}$  term and a slower component that we assign to a  $^3\text{LF}$  term. As the temperature is varied, the lifetime of the  $^3\text{MLCT}$  emission varies in the range 200–300 ns while the lifetime of the longer-lived  $^3\text{LF}$  emission stays relatively constant at  $12 \pm 3 \mu\text{s}$ . At lower temperatures, the longer emission contributes more to the overall emission intensity. The precision of our data does not allow us to perform a lifetime versus temperature fit for either component.

The  $^3\text{LF}$  and  $^3\text{MLCT}$  terms lie close in energy for the 4- $\text{CF}_3$ -Ph complex. We assign luminescence below 80 K to a superposition of emissions from these two terms. Emission from the longer-lived  $^3\text{LF}$  term dominates at 5 K, while emission from the shorter-lived  $^3\text{MLCT}$  term grows in intensity as the temperature is raised toward 80 K. At 77 K, emission arises primarily from the  $^3\text{MLCT}$  term. Significantly, the 5 K spectrum displays a vibronic structure reminiscent of that seen for the  $^3\text{LF}$  emissions from the other three complexes, while the 77 K spectrum is unstructured. Because the emission decay of the complex is nonexponential at all temperatures, the levels belonging to the two terms cannot be thermally equilibrated.

The data suggest that an energy barrier ( $\Delta E$ ) exists between the  $^3\text{LF}$  and  $^3\text{MLCT}$  terms, with the former yielding population to the latter as the temperature increases. Figure 7B shows the qualitative disposition of energy wells for these terms in the 4- $\text{CF}_3$ -Ph complex.  $k_{\text{IC}}$  is the temperature-dependent rate constant for interconfigurational transition. The  $^3\text{LF}$  term preferentially emits at 5 K. Raising the temperature increases  $k_{\text{IC}}$ , causing thermal population of the

shorter-lived  $^3\text{MLCT}$  term. Watts and Missimer<sup>2d</sup> and Striplin and Crosby<sup>20</sup> have discussed the factors that favor the existence of a thermally accessible Franck–Condon energy barrier between excited-state terms. Two conditions are important: (1) the terms must lie close in energy and (2) the terms must arise from different orbital origins, resulting in significant geometrical distortion relative to one another. Both conditions appear to be satisfied for the  $^3\text{LF}$  and  $^3\text{MLCT}$  terms of the 4- $\text{CF}_3$ -Ph complex.

An alternative explanation for the observed temperature-dependent emission is that the rates at which the  $^3\text{LF}$  and  $^3\text{MLCT}$  terms are populated from their respective  $^1\text{LF}$  and  $^1\text{MLCT}$  terms are temperature-dependent. This model requires no thermal communication between the triplet terms and predicts a temperature-dependent emission band shape. The fact that we observe no band shape changes for the 4- $\text{CF}_3$ -Ph complex at 77 K upon excitation at different wavelengths between 350 and 500 nm causes us to reject this alternate model.

**C. Reexamination of the Emission from *trans*-( $\text{N}_2$ )<sub>2</sub>Mo( $\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2$ )<sub>2</sub> ( $\text{R} = 4\text{-H-Ph}$ ).** This complex emits weakly at 77 K in 2-MeTHF.<sup>14</sup> Its emission band is broad and structureless with a maximum at  $15\,700 \text{ cm}^{-1}$  (10 K), and its emission lifetime is  $28 \mu\text{s}$  (14 K). Luminescence was previously assigned to a  $^3\text{LF}$  ( $^3\text{B}_{2g}, b_{2g} \rightarrow a_{1g}$ ) term.<sup>14</sup> As outlined below, our data suggest that emission be assigned to a  $^3\text{MLCT}$  ( $^3\text{B}_{2u}, b_{2g} \rightarrow a_{2u}$ ) term.

Evidence for our alternate assignment resides in the observation that the onset of the  $^3\text{LF}$  band occurs at higher energies for *trans*-( $\text{N}_2$ )<sub>2</sub>Mo( $\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2$ )<sub>2</sub> ( $18\,800 \text{ cm}^{-1}$ ) relative to that of *trans*-( $\text{N}_2$ )<sub>2</sub>W( $\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2$ )<sub>2</sub> ( $18\,100 \text{ cm}^{-1}$ ). This shift, coupled with the expectation of a  $\sim 1300 \text{ cm}^{-1}$  blue shift of the  $^3\text{LF}$  bands in progressing from the Et complex to the 4-H-Ph complex, would place the lowest-energy  $^3\text{LF}$  band for *trans*-( $\text{N}_2$ )<sub>2</sub>Mo( $\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2$ )<sub>2</sub> ( $\text{R} = 4\text{-H-Ph}$ ) at  $\sim 20\,100 \text{ cm}^{-1}$ . This band should, therefore, lie at the high-energy extreme of its low-energy absorption tail ( $18\,000\text{--}20\,000 \text{ cm}^{-1}$ ). We conclude that this absorption tail is likely due to weak MLCT bands and that luminescence from this complex likely arises from a  $^3\text{MLCT}$  term. Further support for this assignment arises from the observation that the emission band shape for *trans*-( $\text{N}_2$ )<sub>2</sub>Mo( $\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2$ )<sub>2</sub> ( $\text{R} = 4\text{-H-Ph}$ ) is nearly identical with that for the  $^3\text{MLCT}$  emission from *trans*-( $\text{N}_2$ )<sub>2</sub>W( $\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2$ )<sub>2</sub> ( $\text{R} = 4\text{-CF}_3\text{-Ph}$ ), with both being broad and unstructured.

#### 4. Conclusions

The dominant  $^1\text{MLCT}$  absorption bands for the complexes blue-shift  $\sim 8000 \text{ cm}^{-1}$  as the diphosphine basicity increases ( $4\text{-CF}_3\text{-Ph} < 4\text{-H-Ph} < 4\text{-CH}_3\text{O-Ph} < \text{Et}$ ). This shift uncovers poorly resolved, low-extinction absorption tails for the 4- $\text{CH}_3\text{O-Ph}$  and 4-H-Ph complexes that are assigned to  $^3\text{LF}$  excitations. The shift of the  $^1\text{MLCT}$  bands is so dramatic for the Et complex that well-resolved  $^1\text{LF}$  bands are revealed, with the lowest-energy shoulder being assigned to a  $^3\text{LF}$  excited term. By contrast, the vibronically structured emission bands for the 4-H-Ph, 4- $\text{CH}_3\text{O-Ph}$ , and Et complexes red-shift  $\sim 1300 \text{ cm}^{-1}$  as the diphosphine basicity

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increases and are assigned to  $^3\text{LF}$  terms. Their luminescence is temperature-dependent, with exponential emission decays at all temperatures. Temperature-dependent lifetime data indicate that emission originates solely from the levels of the spin-orbit split  $^3\text{LF}$  term. Luminescence decay from the  $4\text{-CF}_3\text{-Ph}$  complex is biexponential at all temperatures. At 77 K, it displays a broad, structureless emission band arising mainly from a short-lived  $^3\text{MLCT}$  term with a minor contribution from a longer-lived  $^3\text{LF}$  term. As the complex is cooled toward 5 K, its emission band develops a vibrational structure reminiscent of that seen on the emission bands for the other three complexes. The total luminescence at 5 K appears to be composed of simultaneous emission from near-

degenerate  $^3\text{MLCT}$  and  $^3\text{LF}$  terms, with emission from the latter being dominant.

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**Supporting Information Available:** Listings of infrared,  $^{31}\text{P}$  NMR, and elemental analysis data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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