

(values for  $\text{Ru}_3(\text{CO})_{12}$ ). Only in the latter case was simultaneous agreement for all three  $E'$  bands reached. Hence we have a very strong indication that in metal carbonyl intensity studies the angles formed with the CO vectors, rather than those with the MC ones, should be used in the geometrical terms of the equations.

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**Registry No.**  $\text{Ru}_3(\text{CO})_{12}$ , 15243-33-1;  $\text{Os}_3(\text{CO})_{12}$ , 15696-40-9.

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## Synthesis and Spectroscopic Characterization of Ruthenium and Osmium Complexes with Sterically Hindering Ligands. 3. <sup>1</sup> Tris Complexes with Methyl- and Dimethyl-Substituted 2,2'-Bipyridine and 1,10-Phenanthroline

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Metal complexes of the type  $[\text{M}(\text{L})_3]\text{Cl}_2$ , where  $\text{M} = \text{Ru}(\text{II})$  and  $\text{Os}(\text{II})$  and  $\text{L} = 6\text{-methyl-}2,2'\text{-bipyridine}$ ,  $6,6'\text{-dimethyl-}2,2'\text{-bipyridine}$ ,  $2\text{-methyl-}1,10\text{-phenanthroline}$ , and  $2,9\text{-dimethyl-}1,10\text{-phenanthroline}$ , have been prepared and isolated. Absorption spectra, emission spectra, luminescence quantum yields, and lifetimes of these complexes have been measured, and values of the radiative and nonradiative rate constants have been calculated. Although the positions of absorption and emission bands are hardly affected by the methyl substituents, the molar extinction coefficients, emission quantum yields, and lifetimes are decreased in value compared to complexes of the parent 2,2'-bipyridine or 1,10-phenanthroline ligands. Quantum yield and lifetime changes are greater for the dimethyl-substituted complexes of ruthenium, while methyl and dimethyl substitution produces about the same change for osmium complexes. Possible causes of the decrease in quantum yield are discussed.

### Introduction

The excited state properties of the tris(2,2'-bipyridine)ruthenium(II) ion have been the subject of a large number of experimental studies in recent years. In particular the luminescence,<sup>2</sup> photosensitization of energy- and electron-transfer processes of both organic and inorganic acceptors,<sup>3</sup> and photochemical<sup>4</sup> and photophysical<sup>5</sup> processes have been extensively studied. There has also been much interest in this ion and related complexes as catalysts in the photochemical decomposition of water.<sup>6</sup>

A few studies have delineated the effects of ligand substituents on the optical properties and excited states of tris(2,2'-bipyridine)ruthenium(II) and tris(1,10-phenanthroline)ruthenium(II) complexes,<sup>7</sup> but little work has

been reported on complexes with substituents in sterically hindering positions or with analogous complexes of osmium(II). In a previous paper we reported significant red shifts in the absorption and luminescence spectra of ruthenium(II) and osmium(II) complexes with the sterically hindering benzo-substituted 2,2'-bipyridine ligands: 2-(2'-pyridyl)quinoline and 2,2'-biquinoline.<sup>1a</sup>

In the present work we report the synthesis of ruthenium(II) and osmium(II) complexes with sterically hindering methyl-substituted 2,2'-bipyridine and 1,10-phenanthroline ligands and the effect of these substituents on the luminescence quantum yields, lifetimes, and emission and absorption spectra of the complexes.

### Experimental Section

**General Information.** All syntheses were carried out by using reagent grade materials. 2,9-Dimethyl-1,10-phenanthroline was used as obtained from Aldrich Chemical Co. Elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz., and the results are listed in Table I. The abbreviations  $\text{bpy} = 2,2'\text{-bipyridine}$ ,  $6\text{-Me}(\text{bpy}) = 6\text{-methyl-}2,2'\text{-bipyridine}$ ,  $6,6'\text{-Me}_2\text{bpy} = 6,6'\text{-dimethyl-}2,2'\text{-bipyridine}$ ,  $\text{phen} = 1,10\text{-phenanthroline}$ ,  $2\text{-Me}(\text{phen}) = 2\text{-methyl-}1,10\text{-phenanthroline}$ , and  $2,9\text{-Me}_2\text{phen} = 2,9\text{-dimethyl-}1,10\text{-phenanthroline}$  are used in the text.

**Preparation of 6-Me(bpy).** A 25-g sample of 2,2'-bipyridine in 200 mL of diethyl ether was added under nitrogen to 300 mL of a 1.3 N solution of methylithium prepared by the method of Gilman et al.<sup>8</sup> The orange mixture was refluxed with stirring until a deep red solution was obtained and then stirred at room temperature for 4 h. The mixture was added to a slush of 300 g of ice and 60 mL of 12 M HCl. After being warmed to room temperature, the solution

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Table I. Analytical Results

compd	% C		% H		% N	
	calcd	found	calcd	found	calcd	found
6-Me(bpy)	77.62	76.19	5.92	6.00	16.46	16.25
6,6'-Me <sub>2</sub> bpy	78.94	78.94	6.52	6.59	15.21	15.01
2-Me(phen)	80.39	79.76	5.19	4.81	14.42	14.26
[Ru(6-Me(bpy)) <sub>3</sub> ]Cl <sub>2</sub> ·4H <sub>2</sub> O	52.52	53.17	5.08	4.68	11.14	10.79
[Ru(6,6'-Me <sub>2</sub> bpy) <sub>3</sub> ]Cl <sub>2</sub> ·H <sub>2</sub> O	58.22	58.02	5.16	5.35	11.31	11.16
[Ru(2-Me(phen)) <sub>3</sub> ]Cl <sub>2</sub> ·2H <sub>2</sub> O	59.24	59.42	4.33	4.56	10.63	11.13
[Ru(2,9-Me <sub>2</sub> phen) <sub>3</sub> ]Cl <sub>2</sub> ·H <sub>2</sub> O	61.91	61.85	4.70	5.18	10.31	10.53
[Os(6-Me(bpy)) <sub>3</sub> ]Cl <sub>2</sub> ·4H <sub>2</sub> O	46.97	46.69	4.54	4.22	9.96	9.91
[Os(6,6'-Me <sub>2</sub> bpy) <sub>3</sub> ]Cl <sub>2</sub> ·2H <sub>2</sub> O	50.88	50.43	4.74	4.74	9.89	9.79
[Os(2-Me(phen)) <sub>3</sub> ]Cl <sub>2</sub> ·5H <sub>2</sub> O	50.15	49.99	4.32	4.03	9.00	9.42
[Os(2,9-Me <sub>2</sub> phen) <sub>3</sub> ]Cl <sub>2</sub> ·3H <sub>2</sub> O	53.67	53.35	4.50	4.03	8.94	9.85

was made basic with 20% NaOH and the yellow oil which separated was collected. The solution was extracted with ether, and the combined extracts were distilled to remove 85% of the ether. The remaining ether solution was combined with the yellow oil and steam distilled. After removal of the ether, 2.5 L of distillate was collected along with 10 mL of yellow oil. The oil was separated and converted to the picrate. The picrate was dissolved in a minimum amount of concentrated ammonia, and the liberated product extracted with CHCl<sub>3</sub>. Evaporation of the CHCl<sub>3</sub> gave 4.84 g (18%) of an amber oil.

**Preparation of 6,6'-Me<sub>2</sub>bpy.** Freshly distilled 2-methylpyridine (250 g) and a 5% Pd on charcoal catalyst (10 g, which had previously been degassed under a vacuum at 100 °C for 5 h) were refluxed for 120 h and filtered, and 90% of the excess 2-methylpyridine was removed by distillation. The remaining solution was poured into 500 mL of warm water, stirred, and cooled. The white solid which formed was collected and recrystallized from petroleum ether (bp 60–110 °C) to give 2.51 g (1% yield); mp 88–90 °C (lit.<sup>9</sup> mp 89–90).

**Preparation of 2-Me(phen).** The 2-Me(phen) was prepared by the method of Madeja.<sup>10</sup> The black oil obtained by this procedure was fractionally distilled to produce 2-methylphenanthroline as a viscous orange liquid, bp 180–185 °C (2 mm), which solidified upon standing. The product was recrystallized first from octane then from petroleum ether (bp 60–110 °C) to produce pale yellow crystals, mp 84–85 °C (lit.<sup>16</sup> 84–86 °C).

**Preparation of [Ru(6-Me(bpy))<sub>3</sub>]Cl<sub>2</sub>·4H<sub>2</sub>O and [Ru(6,6'-Me<sub>2</sub>bpy)<sub>3</sub>]Cl<sub>2</sub>·H<sub>2</sub>O.** A blue solution of ruthenium(II) chloride in methanol was prepared by the hydrogen (2 atm) reduction<sup>12</sup> of RuCl<sub>3</sub>·xH<sub>2</sub>O (Engelhard Industries). Ten milliliters of this solution containing 1 mmol of Ru(II) was added slowly under a nitrogen atmosphere to a solution of 4 mmol of 6-Me(bpy) or 6,6'-Me<sub>2</sub>bpy in 15 mL of ethylene glycol which had been deoxygenated by heating under a stream of N<sub>2</sub>. After distillation of the methanol solvent, the reaction mixture was refluxed under N<sub>2</sub> for 12 h during which time the solution changed to a deep brown-red. The solution was then cooled, 40 mL of water was added, and the solution was extracted with 50 mL of petroleum ether (bp 60–110 °C). Water and 75% of the ethylene glycol were removed by distillation at 2 mmHg. The resulting residue was diluted to 20 mL with MeOH and passed through a column (4.5 × 45 cm) of Sephadex LH-20 (Pharmacia Fine Chemicals). The center rust-red band was collected and the solvent removed by evaporation to obtain a red solid. The product was dissolved in MeOH and then passed through a longer Sephadex LH-20 column (2.5 × 96 cm). The product was collected and diluted with water, and the solvent was allowed to evaporate at room temperature. The red solid was collected and vacuum dried for 24 h over P<sub>4</sub>O<sub>10</sub> to yield 0.33 g (44%) of [Ru(6-Me(bpy))<sub>3</sub>]Cl<sub>2</sub>·4H<sub>2</sub>O or 0.041 g (5.5%) of [Ru(6,6'-Me<sub>2</sub>bpy)<sub>3</sub>]Cl<sub>2</sub>·H<sub>2</sub>O.

**Preparation of [Ru(2-Me(phen))<sub>3</sub>]Cl<sub>2</sub>·2H<sub>2</sub>O and [Ru(2,9-Me<sub>2</sub>phen)<sub>3</sub>]Cl<sub>2</sub>·H<sub>2</sub>O.** To 4 mmol of ligand dissolved in 15 mL of deoxygenated ethyl alcohol was added dropwise with stirring under N<sub>2</sub> 1 mmol of Ru(II) (from the H<sub>2</sub> reduction of RuCl<sub>3</sub> as above) in 10 mL of EtOH, and the solution was refluxed (with 2-Me(phen) for 2 h and with 2,9-Me<sub>2</sub>phen for 30 h). The EtOH was evaporated, the solid was extracted with MeOH, and the solution was filtered and passed down a Sephadex LH-20 column (4.5 × 45 cm). The main

band was collected, reduced in volume, and passed down a longer Sephadex column (2.5 × 96 cm). The middle portion of the orange or deep red band was collected and diluted with water, and the solution was allowed to evaporate slowly. The solid was collected and vacuum dried for 24 h over P<sub>4</sub>O<sub>10</sub> to yield 0.178 g (23%) of [Ru(2-Me(phen))<sub>3</sub>]Cl<sub>2</sub>·2H<sub>2</sub>O or 0.034 g (4.2%) of [Ru(2,9-Me<sub>2</sub>phen)<sub>3</sub>]Cl<sub>2</sub>·H<sub>2</sub>O.

**Preparation of [Os(6-Me(bpy))<sub>3</sub>]Cl<sub>2</sub>·4H<sub>2</sub>O and [Os(6,6'-Me<sub>2</sub>bpy)<sub>3</sub>]Cl<sub>2</sub>·2H<sub>2</sub>O.** These complexes were prepared by adding 0.75 mmol (0.39 g) of K<sub>2</sub>OsCl<sub>6</sub>·2H<sub>2</sub>O (Research Organic/Inorganic Chemical Corp.) to 3 mmol of ligand (0.51 g of 6-Me(bpy) or 0.55 g of 6,6'-Me<sub>2</sub>bpy) dissolved in 20 mL of deoxygenated ethylene glycol. The reaction was refluxed under N<sub>2</sub> (6 h with 6-Me(bpy) or 24 h with 6,6'-Me<sub>2</sub>bpy) producing a dark green solution. About 75% of the solvent was removed by distillation at 2 mmHg and the residue diluted with 20 mL of MeOH. The resulting solutions were run on a column (4.5 × 45 cm) of Sephadex LH-20. The dark green band was collected and a solid product obtained by addition of acetone and heptane to the MeOH after about 90% of the MeOH had been removed in the roto-vac. The product was vacuum dried for 24 h over P<sub>4</sub>O<sub>10</sub> to yield 0.34 g (54%) of [Os(6-Me(bpy))<sub>3</sub>]Cl<sub>2</sub>·4H<sub>2</sub>O or 0.050 g (7.8%) of [Os(6,6'-Me<sub>2</sub>bpy)<sub>3</sub>]Cl<sub>2</sub>·2H<sub>2</sub>O.

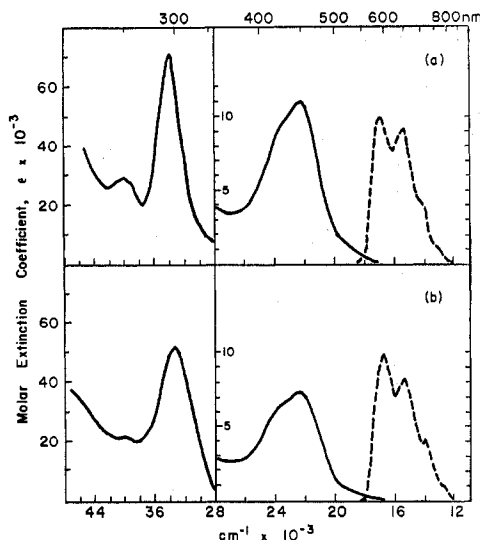
**Preparation of [Os(2-Me(phen))<sub>3</sub>]Cl<sub>2</sub>·5H<sub>2</sub>O and [Os(2,9-Me<sub>2</sub>phen)<sub>3</sub>]Cl<sub>2</sub>·3H<sub>2</sub>O.** The complexes were prepared by the method of Burstall et al.<sup>13</sup> for [Os(bpy)<sub>3</sub>]Cl<sub>2</sub>. The product was purified by dissolving it in MeOH and passing it successively through two columns (4.5 × 45 cm and 2.5 × 96 cm) of Sephadex LH-20. The center portion of the dark green band was collected and diluted with water, and the solution allowed to evaporate to dryness. The solid residue was collected and vacuum dried for 24 h over P<sub>4</sub>O<sub>10</sub> to produce [Os(2-Me(phen))<sub>3</sub>]Cl<sub>2</sub>·5H<sub>2</sub>O (34% yield) or [Os(2,9-Me<sub>2</sub>phen)<sub>3</sub>]Cl<sub>2</sub>·3H<sub>2</sub>O (5.6% yield).

**Spectroscopic Measurements.** Absorption spectra were measured by using a Cary 14 or a Beckman Acta III spectrophotometer with 1-cm quartz cells at room temperature. All luminescence measurements were made with an American Instrument Co. Aminco-Bowman spectrophotofluorometer previously described.<sup>14</sup> The complexes were dissolved in methanol-ethanol 1:4 (v/v) solutions and frozen to rigid glasses at 77 K by immersion of 12-mm Pyrex sample tubes in liquid nitrogen. Concentrations ((1–6) × 10<sup>-5</sup> M) were low enough to avoid the necessity for reabsorption corrections. Emission spectra and quantum yields were obtained by using 436-nm excitation from a Xe-Hg lamp isolated by the monochromator and passed through a 436-nm narrow band-pass filter (Sargent-Welch S-75603). The excitation band-pass was 22 nm for emission spectra and 11 nm for quantum yields. For emission spectra stray light was reduced by placing Optical Industries standard color filter GG475 (ruthenium complexes) or GG475 and OG515 (osmium complexes) in front of the PM tube. Both filters were also used for all quantum yield measurements.

To calibrate the detector system of the spectrophotofluorometer, we followed the procedure of Parker and Rees.<sup>15</sup> Light from a standard lamp<sup>16</sup> (operating at 6.50 V) was reflected off a MgO screen into the entrance slit of the emission monochromator. The Xe lamp

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(16) A secondary standard lamp kindly supplied by G. A. Crosby.



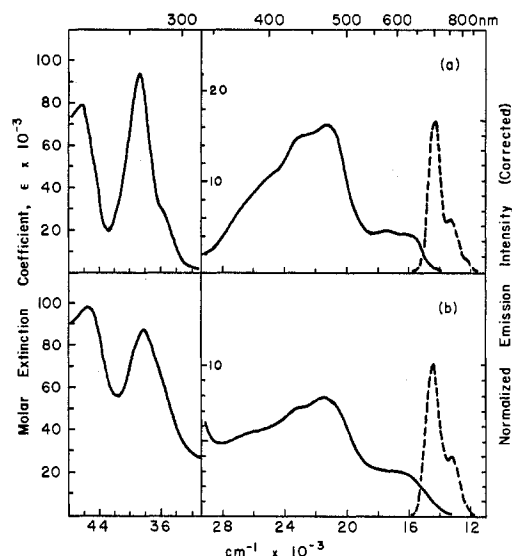
**Figure 1.** Absorption and luminescence spectra of representative ruthenium complexes (a)  $[\text{Ru}(6\text{-Me}(\text{bpy}))_3]\text{Cl}_2$  and (b)  $[\text{Ru}(6,6'\text{-Me}_2\text{bpy})_3]\text{Cl}_2$ ; (—) absorption spectra in methanol at room temperature; (---) luminescence spectra in methanol-ethanol glass (1:4 v/v) at 77 K.

housing was removed, and a solid sample accessory with three 1.0-mm slits was used to reduce the light level. The PM tube slit was set at 0.1 mm. The response of the R446S PM tube was then recorded, and correction factors were obtained by dividing the observed signal into the known lamp output at 10-nm intervals. Since the corrections must be made on a large number of points for each complex, the FORTRAN program of Drushel, Sommers, and Cox<sup>17</sup> was adapted for use in our laboratory by adding the capacity to locate local maxima and to plot the corrected spectra on an ordinary line printer. Band maxima, area under the curve, and the normalization factor were printed out for each emission spectrum.

Quantum yields were measured by the method of Parker and Rees<sup>15</sup> using their technique for obtaining the emission area under the actual quantum yield conditions. In a separate experiment the ratio of the corrected emission area to the uncorrected peak height was obtained. For the quantum yield measurement the emission intensity of the compound was then recorded at its peak height. The product of the ratio defined above and the measured uncorrected intensity at the peak height gives the corrected emission area. The emission intensities for the unknown and standard were measured in a very short period of time (20–30 s) to eliminate long-term instrumental drift. The absorbances of the two solutions (unknown and standard) were adjusted to be very close in value at the exciting wavelength and were kept below 0.05/cm. Sample solutions were prepared and cooled to 77 K immediately prior to quantum yield determinations. No evidence of dissociation or photodecomposition of the complexes was observed. Blanks were run in all measurements.

$[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  (G. Frederick Smith Chemical Co.) was used as the quantum yield standard by assuming a value of 0.376.<sup>28</sup> Our measured values for  $\text{Ru}(\text{phen})_3\text{Cl}_2$ ,  $0.600 \pm 0.035$ ,  $\text{Os}(\text{bpy})_3(\text{ClO}_4)_2$ ,  $0.0324 \pm 0.015$ , and  $\text{Os}(\text{phen})_3\text{Cl}_2$ ,  $0.125 \pm 0.010$ , are in good agreement with the values for these complexes reported by Demas and Crosby:<sup>28</sup>  $0.584 \pm 0.065$ ,  $0.0348 \pm 0.0020$ , and  $0.126 \pm 0.009$ , respectively. Absolute accuracy can be no better than the  $\pm 30\%$  estimated for  $\text{Ru}(\text{bpy})_3\text{Cl}_2$ .<sup>28</sup>

For the lifetime measurements a laser luminescence decay time apparatus was constructed as described by Demas and Flynn.<sup>18</sup> The complexes dissolved in methanol-ethanol glasses at 77 K in the Pyrex tubes used for emission spectra were irradiated with about 1-kW, 4-ns, 337-nm pulses from a Phase R N21 nitrogen laser. The light output was monitored by an RCA C7164R photomultiplier and displayed on a Tektronix 5441 storage oscilloscope. Decays were photographed on Polaroid positive/negative film, Type 665, and the negatives were projected onto graph paper with a photographic enlarger and traced



**Figure 2.** Absorption and luminescence spectra of representative osmium complexes (a)  $[\text{Os}(2\text{-Me}(\text{phen}))_3]\text{Cl}_2$  and (b)  $[\text{Os}(2,9\text{-Me}_2\text{phen})_3]\text{Cl}_2$ ; (—) absorption spectra in methanol at room temperature; (---) luminescence spectra in methanol-ethanol glass (1:4 v/v) at 77 K.

**Table II.** Absorption and Emission Spectral Data for  $[\text{RuL}_3]\text{Cl}_2$

L	absorptn <sup>a</sup>		emissn <sup>b</sup> $\lambda_{\text{max}}$ , nm
	$\lambda_{\text{max}}$ , nm	$10^{-3}\epsilon$ , $\text{M}^{-1}\text{cm}^{-1}$	
bpy	454	14.6	584, 628
	286, 244	79.2, 25.6	
6-Me(bpy)	448	11.1	585, 630
	293, 247	71.3, 29.3	
6,6'-Me <sub>2</sub> bpy	446	7.44	589, 636
	297, 248	51.8, 21.5	
phen	446, 417	19.0, 18.1	568, 609
	263, 224	113, 80.3	
2-Me(phen)	446	14.4	576, 615
	267, 224	104, 95.3	
2,9-Me <sub>2</sub> phen	501	2.58	588, 631
	270, 232	81.6, 132	

<sup>a</sup> In methanol at room temperature. <sup>b</sup> In methanol-ethanol (1:4, v/v) rigid glass at 77 K.

with a pencil with grid data also being included. Mean decay times were determined by a linear least-squares fit of  $\ln$  intensity vs. time.

## Results

The absorption and luminescence spectra of the substituted (bipyridine)ruthenium and (phenanthroline)osmium complexes are shown in Figures 1 and 2 and are representative for all eight compounds. The positions of the absorption maxima and the corresponding molar absorptivities as well as the positions of the emission maxima for all the ruthenium(II) and osmium(II) complexes are summarized in Tables II and III, respectively. The data on the unsubstituted complexes have been reported previously<sup>2,19</sup> but have been included here for purposes of comparison.

Table IV lists the quantum yields and lifetimes for all the complexes in rigid glasses at 77 K. The ratio of the measured lifetime,  $\tau_m$ , to the quantum yield,  $Q$ , has been tabulated as the radiative lifetime,  $\tau_r$ .<sup>28</sup> The radiative rate constant,  $k_r = 1/\tau_r$ , and the nonradiative rate constant,  $k_n = \tau_m^{-1} - \tau_r^{-1}$ , have also been calculated and tabulated in Table IV. Quantum yields and lifetimes for the unsubstituted complexes of ruthenium and osmium have been previously published,<sup>28</sup> and

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Table III. Absorption and Emission Spectral Data for  $[\text{OsL}_3]\text{Cl}_2$ 

L	absorptn <sup>a</sup>		emissn <sup>b</sup> $\lambda_{\text{max}}$ , nm
	$\lambda_{\text{max}}$ , nm	$10^{-3}\epsilon$ , $\text{M}^{-1}\text{cm}^{-1}$	
bpy	(~640), <sup>c</sup> 579	3.27	710, 773
	478, 436	11.1, 10.7	
	385, 368	9.02, 9.55	
	290, 244	77.3, 27.4	
6-Me(bpy)	(~645), <sup>c</sup> 600	3.22	707, 767
	472, 434	11.7, 10.4	
	377	8.37	
	295, 251	75.2, 20.2	
6,6'-Me <sub>2</sub> bpy	(~644), <sup>c</sup> 588	2.70	711, 775
	482, 410	9.04, 7.80	
	302, 251	57.0, 3.64	
	phen	(~625), <sup>c</sup> (~570) <sup>c</sup>	
476, 427	17.0, 18.2		
264, 221	99.7, 76.3		
2-Me(phen)	(~624), <sup>c</sup> 574	4.27	696, 756
469, (~437) <sup>c</sup>	16.5		
268, 223	94.0, 79.3		
2,9-Me <sub>2</sub> phen	(~600) <sup>c</sup>		
466, (~435) <sup>c</sup>	7.80		
270, 226	87.4, 98.4		

<sup>a</sup> In methanol at room temperature. <sup>b</sup> In methanol-ethanol (1:4, v/v) rigid glass at 77 K. <sup>c</sup> Shoulder.

our values are in good agreement with the earlier studies.

### Discussion

**Synthesis of the Complexes.** We have found it convenient to synthesize the ruthenium complexes using deep blue solutions containing Ru(II).<sup>12</sup> Ethylene glycol was the preferred solvent for bipyridine complexes because its boiling point permits a higher reaction temperature than is possible in ethanol. Ethanol was satisfactory for ruthenium phenanthroline complexes, but melts of the ligands were more successful for osmium phenanthroline compounds. As would be expected the product yields were lowest for the most sterically hindering dimethyl-substituted ligands with the rigid ring system of phenanthroline giving lower yields than bipyridine.

**Absorption Spectra.** The intense visible absorption band of  $\text{Ru}(\text{bpy})_3^{2+}$  has been assigned<sup>2</sup> to spin-allowed charge transfer from the metal d orbitals to the  $\pi^*$  orbitals of the ligand (CTTL), while the bands below 200 nm and at 285 nm have been assigned to intraligand  $\pi-\pi^*$  transitions by comparisons with the spectrum of the protonated bipyridine.<sup>2f</sup> Similar assignments have been made for the  $\text{Ru}(\text{phen})_3^{2+}$  complex<sup>2b</sup> and for analogous compounds of osmium. In addition the osmium complexes exhibit low-energy bands, 550–700 nm, which have been assigned to the principally spin-forbidden singlet-triplet metal-to-ligand charge-transfer absorption.<sup>20</sup> Owing to the similarities in the spectra of the methyl-substituted complexes, the same band assignments can be made for the complexes reported here.

Inspection of Tables II and III shows that, although the positions of the absorption maxima are not markedly affected by substitution, the intensities of the bands decrease as the number of methyl substituents increases (except for the 225-nm band in phenanthroline complexes which increases in intensity). The band structure also becomes less pronounced with methyl substitution.

Such behavior can be contrasted with the results for ruthenium and osmium complexes in which methyl substituents are present on the bipyridine and phenanthroline ligands but are not in a hindering position.<sup>7a,c,21</sup> Results of those studies

indicate that the charge-transfer absorption bands also shift only slightly with methyl substitution and that the intensities of the bands remain about the same in most complexes but increase significantly in complexes of ruthenium with 4,7-Me<sub>2</sub>phen and 3,4,7,8-Me<sub>4</sub>phen ligands.<sup>21</sup> Phenyl substitution was also found to increase the charge-transfer band intensity<sup>7b</sup> while benzo substitution in a sterically hindering position decreased intensity and caused a significant red shift in the band maxima.<sup>1a</sup> Less data are available for the  $\pi-\pi^*$  transitions, but they indicate that for bipyridine complexes of osmium, methyl substitution in the nonhindering 4,4'-positions increases rather than decreases the intensity of the 286-nm band,<sup>7a</sup> as opposed to the decrease in intensity in the complexes reported here.

**Emission Spectra.** It is generally agreed that the low-temperature emission from ruthenium and osmium complexes arises from a charge transfer to ligand (CTTL) excited state,<sup>26,22</sup> although because of strong spin-orbit coupling it is not appropriate to assign a spin multiplicity.<sup>23</sup> Crosby and co-workers<sup>7c</sup> have shown that the CTTL excited state actually consists of three closely spaced levels with symmetries  $A_1$ ,  $E_1$ , and  $A_2$  in order of increasing energy. Further it is estimated that at 77 K 90% of the photoluminescence arises from the  $A_2$  electronic level.

The luminescence spectra of the ruthenium(II) and osmium(II) complexes of the methyl-substituted ligands reported here are strikingly similar to those of the corresponding complexes of the unsubstituted ligands. The vibrational progression, indicative of a charge-transfer luminescence, is clearly displayed. As in the case of other ligand-substituted complexes of ruthenium, the energies of the emission bands are not markedly changed, although a slight red shift is observed. Apparently methyl substitution, even in a hindering position, does not appreciably alter the energy of the lowest excited levels. This behavior is in sharp contrast to the large red shifts produced by benzo substitution<sup>1a</sup> or deprotonation of the unsymmetrically substituted  $\text{Ru}(\text{phen})_2(4,7-(\text{OH})_2\text{phen})^{2+}$  complex.<sup>7f</sup>

**Lifetimes.** Investigations of ruthenium complexes containing various substituted bipyridine and phenanthroline ligands have shown that the lifetimes of the emitting CTTL states are sensitive to ligand substitution, but only a relative minor variation in the lifetime is produced. In both room-temperature fluid<sup>21</sup> and low-temperature glass emission lifetimes are longer for the phenanthroline systems than for the bipyridine. At 77 K both phenyl and methyl substitution on bipyridine and phenanthroline produce a decrease in the luminescence lifetime.<sup>7b,c,e</sup> In line with these observations we see from Table IV that substitution of methyl groups in sterically hindering positions of bipyridine and phenanthroline also leads to a decrease in the observed lifetimes. It is further noted that for the ruthenium complexes the lifetime of the dimethyl complexes is decreased about twice as much as for the monomethyl complex.

The osmium emission lifetimes are shorter than the values for the corresponding ruthenium complexes, but it is also observed that lifetimes are longer for the phenanthroline system than for the bipyridine. Less information is available for osmium complexes, but the previous results<sup>24</sup> show that in fluid solution methyl substitution on both bipyridine and phenanthroline decreases the emission lifetime. Our results at 77 K also show a decrease in the lifetime upon methyl substitution; however, in contrast to ruthenium complexes, the values for

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Table IV. Quantum Yields, Lifetimes, and Rate Constants for Ruthenium and Osmium Complexes<sup>a</sup>

compd	$Q^b$	$\tau_m,^c \mu s$	$\tau_r,^d \mu s$	$k_r,^e \mu s^{-1}$	$k_n,^f \mu s^{-1}$
Ru(bpy) <sub>3</sub> Cl <sub>2</sub>	0.376 ± 0.036 <sup>g</sup>	5.3 ± 0.4	14	0.071	0.12
Ru(6-Me(bpy)) <sub>3</sub> Cl <sub>2</sub>	0.0968 ± 0.005	4.1 ± 0.3	42	0.024	0.22
Ru(6,6'-Me <sub>2</sub> bpy) <sub>3</sub> Cl <sub>2</sub>	0.0176 ± 0.009	2.5 ± 0.4	140	0.0070	0.39
Ru(phen) <sub>3</sub> Cl <sub>2</sub>	0.600 ± 0.035	9.8 ± 0.3	16	0.061	0.041
Ru(2-Me(phen)) <sub>3</sub> Cl <sub>2</sub>	0.172 ± 0.018	5.9 ± 0.1	34	0.029	0.14
Ru(2,9-Me <sub>2</sub> phen) <sub>3</sub> Cl <sub>2</sub>	0.0479 ± 0.014	2.3 ± 0.4	48	0.021	0.41
Os(bpy) <sub>3</sub> (ClO <sub>4</sub> ) <sub>2</sub>	0.0324 ± 0.015	0.83 ± 0.08	26	0.039	1.2
Os(6-Me(bpy)) <sub>3</sub> Cl <sub>2</sub>	0.0226 ± 0.0017	0.65 ± 0.11	30	0.034	1.5
Os(6,6'-Me <sub>2</sub> bpy) <sub>3</sub> Cl <sub>2</sub>	0.0362 ± 0.012	0.71 ± 0.11	20	0.051	1.4
Os(phen) <sub>3</sub> Cl <sub>2</sub>	0.125 ± 0.010	2.4 ± 0.3	19	0.052	0.36
Os(2-Me(phen)) <sub>3</sub> Cl <sub>2</sub>	0.0788 ± 0.005	1.7 ± 0.2	22	0.046	0.54
Os(2,9-Me <sub>2</sub> phen) <sub>3</sub> Cl <sub>2</sub>	0.0695 ± 0.009	1.8 ± 0.3	26	0.039	0.52

<sup>a</sup> Measured in methanol-ethanol (1:4, v/v) at 77 K. <sup>b</sup> Excited at 436 nm. <sup>c</sup> Excited at 337 nm. <sup>d</sup> Calculated from  $\tau_m/Q$ . <sup>e</sup> Calculated from  $1/\tau_r$ . <sup>f</sup> Calculated from  $\tau_m^{-1} - \tau_r^{-1}$ . <sup>g</sup> Value from ref 2g.

the methyl and dimethyl substituted complexes are about the same.

**Quantum Yields.** Of the spectroscopic properties discussed thus far the greatest effect of methyl substitution in a sterically hindering position is in the luminescence quantum yields of the complexes. In sharp contrast to previous studies on ruthenium complexes of 4,4'-Me<sub>2</sub>bpy, 4,7'-Me<sub>2</sub>phen, and 5,6-Me<sub>2</sub>phen where relatively slight changes in the quantum yields are observed,<sup>7c</sup> we see in Table IV large decreases in the quantum yields when the methyl substituents are in the 6,6' positions of bipyridine or the 2,9 positions of phenanthroline in ruthenium compounds. Single methyl substitution decreases the yield about 72% while dimethyl substitution decreases the yield about 92%. By contrast 4,4'-dimethyl substitution on bipyridine decreases the yield about 10% while 4,7-dimethyl substitution on phenanthroline leads to an increase in the quantum yield.<sup>7c</sup> Decreases are also observed in the luminescence quantum yields of osmium complexes, but the amount of decrease is less. The single exception is the increase in quantum yield observed for Os(6,6'-Me<sub>2</sub>bpy)<sub>3</sub><sup>2+</sup>.

Inspection of Table IV shows that the calculated radiative lifetimes ( $\tau_r$ ) increase (except for Os(6,6'-Me<sub>2</sub>bpy)<sub>3</sub>Cl<sub>2</sub>) as one methyl or two methyl groups are added in sterically hindering positions. Assuming that the methyl substituents increase the metal to ligand distance, we have the result that the radiative lifetimes of a ligand to metal electronic transition increases as the ligand is forced further away from the metal ion.

The quantum yield for the radiative decay of the emitting state can be expressed by eq 1 where  $k_r$  is the rate constant

$$Q = k_r / (k_r + k_n) \quad (1)$$

for the radiative decay and  $k_n$  is the rate constant for the nonradiative decay of the level. The nonradiative rate constants,  $k_n$ , are also listed in Table IV. Methyl substitution produces an increase of  $k_n$  for all the complexes, but the values for the methyl and dimethyl osmium complexes are of comparable magnitude. From eq 1 we see that the observed decrease of the luminescence quantum yield is due to both the decrease in  $k_r$  and the increase in  $k_n$ . The relative contributions of these two factors to the decrease in the quantum yield are illustrated in Figure 3. The line on the left in each diagram represents the quantum yield of the unsubstituted complex while the line on the right represents the observed quantum yield of the methyl-substituted complex. The line in the middle represents the hypothetical quantum yield that the substituted complex would have if only a change in the radiative rate constant ( $\Delta k_r$ ) were caused by the methyl substituents.  $\Delta k_n$  represents the change in quantum yield due to the change in the nonradiative rate constant. The figure shows that, except for the osmium dimethylbipyridine complex, both factors contribute about equally to the decrease in observed quantum yields for substituted bipyridine complexes, while for the

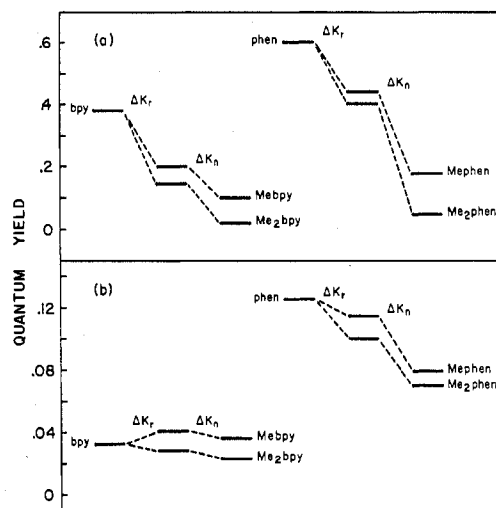


Figure 3. Methyl-induced changes in quantum yield resolved into radiative ( $\Delta k_r$ ) and radiationless ( $\Delta k_n$ ) factors: (a) ruthenium complexes, RuL<sub>3</sub><sup>2+</sup>; (b) osmium complexes, OsL<sub>3</sub><sup>2+</sup>.

substituted phenanthroline complexes the decrease in quantum yield is due more to the increase in the nonradiative rate constant.

Inspection of space-filling models of the methyl-substituted complexes reported here reveals that there is considerable steric hindrance between the methyl group(s) on one ligand interfering with the ring system on an adjacent ligand. Such interference can be relieved by an increase in the metal-ligand bond distances which would lead to a decrease in the strength of the ligand field. Such a decrease would cause a lowering of the excited dd state ( $t_{2g}^5 e_g$ ) and could result in its interaction with the  $t_{2g}^5 \pi^*$  excited state to produce the lower quantum yields.<sup>25</sup> The effect would be greater for the dimethyl complexes than for monomethyl complexes as is experimentally observed. Also twisting of the bipyridine ligands can relieve some of the steric hindrance, but the rigid phenanthroline ring system prevents twisting and would lead to a greater effect. The larger Os(II) ion should also relieve some of the steric hindrance, producing smaller changes for osmium complexes than for ruthenium complexes. These expectations are in general agreement with the observed decreases in the measured quantum yields of the complexes.

Other complexes of ruthenium and osmium with sterically hindering ligands are presently being synthesized, and it is hoped that a study of their spectroscopic properties will help to elucidate the pathway of radiationless deactivation and clarify the relative importance of each steric factor contributing

(25) This explanation was suggested by a reviewer.

to the decrease in quantum yield.

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**Registry No.** 6-Me(bpy), 56100-22-2; 6,6'-Me<sub>2</sub>bpy, 4411-80-7; 2-Me(phen), 3002-77-5; [Ru(6-Me(bpy))<sub>3</sub>]Cl<sub>2</sub>, 73396-22-2; [Ru-

(6,6'-Me<sub>2</sub>bpy)<sub>3</sub>]Cl<sub>2</sub>, 73396-21-1; [Ru(2-Me(phen))<sub>3</sub>]Cl<sub>2</sub>, 73396-20-0; [Ru(2,9-Me<sub>2</sub>phen)<sub>3</sub>]Cl<sub>2</sub>, 73396-19-7; [Os(6-Me(bpy))<sub>3</sub>]Cl<sub>2</sub>, 73396-18-6; [Os(6,6'-Me<sub>2</sub>bpy)<sub>3</sub>]Cl<sub>2</sub>, 73396-17-5; [Os(2-Me(phen))<sub>3</sub>]Cl<sub>2</sub>, 73396-16-4; [Os(2,9-Me<sub>2</sub>phen)<sub>3</sub>]Cl<sub>2</sub>, 73396-15-3; Ru(bpy)<sub>3</sub>Cl<sub>2</sub>, 14323-06-9; Ru(phen)<sub>3</sub>Cl<sub>2</sub>, 23570-43-6; Os(bpy)<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub>, 15928-87-7; Os(phen)<sub>3</sub>Cl<sub>2</sub>, 73466-62-3; 2,2-bipyridine, 366-18-7; 2-methylpyridine, 109-06-8; K<sub>2</sub>OsCl<sub>6</sub>, 16871-60-6.

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## Unsymmetrical Bis-Phosphorus Ligands. 12. Synthesis and Nuclear Magnetic Resonance Studies of Some Derivatives of Bis(diphenylphosphino)methane<sup>1,2</sup>

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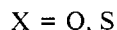
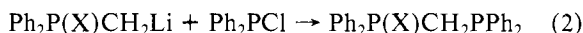
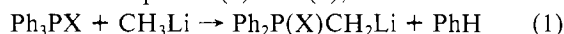
The complete series of 15 compounds of the type (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P(X)CH<sub>2</sub>P(Y)(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, where X and Y (X = Y and X ≠ Y) are an electron pair, O, S, Se, or CH<sub>3</sub><sup>+</sup>, have been synthesized. In addition, several coordination compounds of the monoselenide ligand, viz., [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P(Se)CH<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]M(CO)<sub>4</sub>, where M = Cr, Mo, or W, and [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P(Se)CH<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]HgX<sub>2</sub>, where X = Cl, Br, or I, have been prepared. Where appropriate these compounds have been characterized by proton, carbon-13, and phosphorus-31 NMR spectrometry. From a correlation between the chemical shifts of the methylene protons and the charge on phosphorus in the (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P(X)CH<sub>2</sub>P(Y)(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> derivatives, it is found that the effective positive charge on phosphorus increases in the order (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P- < (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P(O)- < (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P(S)- < (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P(Se)- < (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PCH<sub>3</sub><sup>+</sup>. Coupling constants of phosphorus with selenium-77, carbon-13, and phosphorus are given as are selenium-phosphorus stretching frequencies as measured by Raman spectroscopy.

Bis(diphenylphosphino)methane (dppm) has been extensively used as a ligand,<sup>3</sup> and the chemistry of its dioxide (dppmO<sub>2</sub>) its disulfide (dppmS<sub>2</sub>), and to a lesser extent its diselenide (dppmSe<sub>2</sub>) is also well-known.<sup>4-7</sup> However, only very recently the monoxide (dppmO)<sup>8</sup> and monosulfide (dppmS)<sup>9</sup> have been examined as ligands, and it was found that they have a preference for bonding in chelated fashion via the chalcogen and phosphine to form a five-membered chelate ring. It was therefore of interest to extend these studies to include the monoselenide derivative (dppmSe) (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P(Se)CH<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> of dppm. The selenium compounds offer the additional advantage of having another nuclear magnetic resonance (NMR) active nucleus, viz., selenium-77, of 7.58% natural abundance and a nuclear spin of one-half. From the correlations observed in the <sup>1</sup>H NMR spectra of the earlier dppm derivatives, it seemed profitable to extend the synthetic aspects of this study to include all 15 of the compounds (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P(X)CH<sub>2</sub>P(Y)(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, where X and Y (X = Y and X ≠ Y) are an electron pair, oxygen, sulfur, selenium, or the methyl cation. Eight of these compounds had been synthesized

and characterized previously.<sup>10-17</sup>

### Results and Discussion

We found the most efficient synthesis of dppmSe to be the direct stoichiometric reaction of dppm and red elemental selenium in equimolar amounts in refluxing toluene or benzene. The progress of the reaction can be followed visually by the disappearance of the red selenium. The standard procedure for the synthesis of (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PSe from (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P and KSeCN in acetonitrile<sup>18</sup> works also for dppmSe although significant amounts (perhaps 20%) of dppmSe<sub>2</sub> are also produced. This impurity necessitates considerable purification procedures in order to isolate dppmSe from the mixture. It was also found that the reaction sequence (1) and (2),<sup>8,9,15-17</sup> which is con-



venient for the synthesis of dppmO and dppmS, does not work well for the selenide, in which case very little dppmSe is produced, but unidentified side products of selenium with horrible odors are produced. Because of the well-known

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