

Contribution from the Institut für Anorganische Chemie, Universität Fribourg, Perolles, CH-1700 Fribourg, Switzerland, Dipartimento di Chimica "G. Ciamician", Università di Bologna, via Selmi 2, 40126 Bologna, Italy, and Istituto FRAE-CNR, via de' Castagnoli 1, 40126 Bologna, Italy

## Synthesis and Characterization of a New Family of Luminescent *cis*-(4,4'-X<sub>2</sub>-5,5'-Y<sub>2</sub>-2,2'-bipyridine)<sub>2</sub>Os(CO)Cl(PF<sub>6</sub>) Complexes (X = NEt<sub>2</sub>, OMe, Me, H, Cl, Y = H; X = H, Y = Me; X = Y = Me): Control of Excited-State Properties by Bipyridyl Substituents

Leopoldo Della Ciana,<sup>\*,†,‡</sup> Walter J. Dressick,<sup>\*,†,§</sup> Diana Sandrini,<sup>||</sup> Mauro Maestri,<sup>||</sup> and Mauro Ciano<sup>⊥</sup>

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The synthesis and characterization of a new family of luminescent *cis*-(4,4'-X<sub>2</sub>-5,5'-Y<sub>2</sub>-2,2'-bipyridine)<sub>2</sub>Os(CO)Cl(PF<sub>6</sub>) complexes (X = NEt<sub>2</sub>, OMe, Me, H, Cl, Y = H; X = H, Y = Me; X = Y = Me) are described. Conventional <sup>1</sup>H NMR, spin-decoupling, and nuclear Overhauser effect (NOE) experiments are utilized for structure determinations of the complexes and complete assignment of proton resonances for the complexes and free ligands in CD<sub>3</sub>CN solution (supplementary material). Nonradiative deactivation of the luminescent metal-to-ligand charge-transfer (MLCT) excited states is dominant for all complexes and is governed by the energy gap law. Linear correlations of electrochemical, IR (CO stretching frequency), and absorption/emission properties of the complexes with Hammett  $\sigma$  constants of the bipyridyl substituent groups are established and provide a convenient method for the prediction and control of ground- and excited-state properties within the family.

### Introduction

The chemistry of  $\alpha$ -diimine complexes of Os(II) has enjoyed rapid growth in recent years in connection with fundamental studies of electron-transfer reactions<sup>1-5</sup> and the search for new catalytic redox reagents.<sup>6-9</sup> Of particular interest to us has been the development of luminescent Os(II) complexes as surrogates for the well-studied Ru(bpy)<sub>3</sub><sup>2+</sup> (bpy is 2,2'-bipyridine) complex and its derivatives in solar energy conversion schemes.<sup>1,3,10-12</sup> In this regard, a variety of new Os(II) complexes exhibiting metal-to-ligand charge-transfer (MLCT) luminescence and based on the (bpy)Os<sup>II</sup> and *cis*-(bpy)<sub>2</sub>Os<sup>II</sup> moieties have recently been described.<sup>13-17</sup> For such complexes, quantitative control of ground- and excited-state properties has been convincingly demonstrated via adjustment of the  $\pi$ -acceptor strength of the remaining non-bpy ligands.<sup>15,18-20</sup> Quantitative control of excited-state properties through systematic variation of substituents on an  $\alpha$ -diimine ligand such as bpy has not yet been demonstrated for Os(II).<sup>21</sup> Despite this shortcoming, the ability to tune excited-state properties using nonchromophoric ligands greatly increases the usefulness of such complexes as photocatalysts.<sup>22</sup>

One complex of special interest as a photocatalyst in solar energy conversion schemes is *cis*-(phen)<sub>2</sub>Os(CO)Cl(PF<sub>6</sub>), where phen is 1,10-phenanthroline. In one example involving a Hg-based scheme, this complex has shown a remarkable ability to inhibit energy-degrading back-electron-transfer reactions in micellar solutions.<sup>23</sup> Although this complex is readily synthesized in a one-step reaction from the well-known *cis*-(phen)<sub>2</sub>OsCl<sub>2</sub> complex,<sup>24</sup> further work in which phen has been replaced by other  $\alpha$ -diimine ligands has been limited.<sup>16</sup> In order to extend further the range of this Os(II) chromophore, we describe here the synthesis of a new family of *cis*-L<sub>2</sub>Os(CO)Cl(PF<sub>6</sub>) complexes (L = 4,4'-X<sub>2</sub>-5,5'-Y<sub>2</sub>-2,2'-bipyridine; X = NEt<sub>2</sub>, OMe, Me, H, Cl, Y = H; X = H, Y = Me; X = Y = Me). All complexes are characterized by elemental analysis, <sup>1</sup>H NMR and IR (CO stretching frequency) spectroscopy, cyclic voltammetry, MLCT excited-state lifetime, and absorption/fluorescence spectroscopy techniques in MeCN solutions. Our results for the *cis*-L<sub>2</sub>Os(CO)Cl<sup>+</sup> complexes are compared with and interpreted by using information available for related Os(II) systems.<sup>16,17</sup> Correlations of specific ground- and excited-state properties with Hammett  $\sigma$  constants for the L substituents are discussed as a convenient tool for the prediction

and control of these properties by the  $\alpha$ -diimine ligand within the family.

### Experimental Section

**Materials.** Chemicals and solvents obtained from Fluka AG were "purum" grade unless otherwise noted. All substances received from Merck were "pro analysi" grade. Materials were used as received except where noted.

Toluene, methanol, acetone, diethyl ether (anhydrous), formic acid (98-100%), sulfuric acid, sodium dithionite, and LiCl were all received

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<sup>†</sup> Universität Fribourg.

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<sup>§</sup> Current address: Geo-Centers, Inc., 10903 Indian Head Highway, Fort Washington, MD 20744.

<sup>||</sup> Università di Bologna.

<sup>⊥</sup> Istituto FRAE-CNR.

from Merck. Triphenylphosphine, 1,2-bis(diphenylphosphino)ethane (diphos),  $(\text{NH}_4)_2\text{OsCl}_6$ , 10% Pd/C, KOH (pellets), NaOH, and glycerine and ethylene glycol (both water-free) were all "puriss" grade from Fluka AG. Anhydrous  $\text{CaCl}_2$ , Raney nickel alloy, butyronitrile, tetraethylammonium perchlorate (TEAP),  $\text{NH}_4\text{PF}_6$ , 3-picoline, and 3,4-lutidine were also purchased from Fluka AG. Butyronitrile<sup>25</sup> and TEAP<sup>26</sup> were purified according to established procedures prior to use. 3-Picoline and 3,4-lutidine were dried over KOH for 24 h and vacuum-distilled from KOH immediately prior to use. The 3-picoline fraction boiling at 155–156 °C (10 mmHg) and the 3,4-lutidine fraction boiling at 189–190 °C (10 mmHg) were collected.  $\text{NH}_4\text{PF}_6$  was dissolved in water in sufficient quantity to obtain a saturated solution. The filtered solution was diluted with an equal volume of distilled water and used for the isolation of metal complexes (vide infra).

Acetonitrile was far-UV HPLC grade from Romil Chemicals Ltd. (Shephed Leics LE12 9BS, England).  $\text{CD}_3\text{CN}$  for the  $^1\text{H}$  NMR studies was used as received from ICN Biomedicals, Inc. Alumina for chromatography (neutral, activity II/III) was obtained from Merck (Aluminiumoxid 90). Argon gas (99.9%) was used as received from Carbagas AG. Carbon monoxide was generated by the dehydration of  $\text{HCOOH}$  with concentrated  $\text{H}_2\text{SO}_4$  as described in the literature.<sup>27</sup> The gas was dried by passage through two Deuschel bottles containing concentrated  $\text{H}_2\text{SO}_4$ . Traces of  $\text{CO}_2$  and  $\text{SO}_2$  were removed from the CO prior to use by passing the gas through a Deuschel bottle containing KOH pellets.

The ligands 2,2'-bipyridine (bpy, **2a**) and 4,4'-dimethyl-2,2'-bipyridine ( $4^2\text{-Me}_2\text{bpy}$ , **4a**) were Fluka AG "puriss" grade and were used without further purification. The ligands 5,5'-dimethyl-2,2'-bipyridine ( $5^2\text{-Me}_2\text{bpy}$ , **3a**) and 4,4',5,5'-tetramethyl-2,2'-bipyridine ( $\text{Me}_4\text{bpy}$ , **5a**) were prepared by Raney nickel coupling of 3-picoline and 10% Pd/C coupling of 3,4-lutidine, respectively.<sup>28</sup> The preparations of 4,4'-dichloro-2,2'-bipyridine ( $\text{Cl}_2\text{bpy}$ , **1a**),<sup>29</sup> 4,4'-bis(*N,N*-diethylamino)-2,2'-bipyridine ( $(\text{NEt}_2)_2\text{bpy}$ , **7a**),<sup>30</sup> and 4,4'-dimethoxy-2,2'-bipyridine ( $(\text{OMe})_2\text{bpy}$ , **6a**)<sup>30</sup> also followed literature procedures.

**Syntheses. General Comments.** All work was conducted in an efficient fume hood. Syntheses were conducted under an argon atmosphere with argon bubble degassing of the reactants for 15 min prior to reaction unless noted otherwise. Yields are reported from the appropriate  $\text{cis-L}_2\text{OsCl}_2 \cdot x\text{H}_2\text{O}$  complex unless otherwise specified. Reactions were usually carried out at the 150-mg scale based on the necessary Os starting material. Cationic complexes were isolated as  $\text{PF}_6^-$  salts and purified by neutral alumina chromatography (Activity II/III, 1:2 v/v MeCN/toluene eluant) as described previously for the  $\text{cis}(\text{bpy})_2\text{Os}(\text{CO})\text{Cl}(\text{PF}_6)$  parent complex.<sup>17</sup> The desired complex was in the leading band on the column and separated completely from trailing impurity bands unless otherwise specified.

**$\text{cis-L}_2\text{OsCl}_2 \cdot x\text{H}_2\text{O}$  Complexes.** These complexes were prepared following the guidelines in the literature procedure described for  $\text{L} = \text{bpy}$ .<sup>17</sup> The complexes were obtained in >80% yield from  $(\text{NH}_4)_2\text{OsCl}_6$  and contained one to three waters of hydration (elemental analysis, Table S-I, supplementary material). In the case of  $\text{L} = (\text{NEt}_2)_2\text{bpy}$ , however, the product was best formulated as  $\text{cis}((\text{NEt}_2)_2\text{bpy})_2\text{Os}^{\text{III}}\text{Cl}_2(\text{Cl}) \cdot 5\text{H}_2\text{O}$  on the basis of elemental analysis results and reactivity (vide infra). Because this complex was somewhat water soluble, minimal washing with ice-cold water was employed during workup. In all cases, however, the complexes were used without additional purification in subsequent reactions.

**$\text{cis-L}_2\text{Os}(\text{CO})\text{Cl}(\text{PF}_6)$  Complexes.** These compounds were prepared, with the exception of  $\text{L} = (\text{NEt}_2)_2\text{bpy}$ , by bubbling CO gas into a suspension of the appropriate  $\text{cis-L}_2\text{OsCl}_2 \cdot x\text{H}_2\text{O}$  complex in refluxing ethylene glycol for 2 h, as described for  $\text{L} = \text{bpy}$ .<sup>16</sup> The title compounds were obtained after chromatography in the following yields:  $\text{L} = \text{bpy}$ , 65%;  $\text{L} = 5^2\text{-Me}_2\text{bpy}$ , 79%;  $\text{L} = 4^2\text{-Me}_2\text{bpy}$ , 65%;  $\text{L} = (\text{OMe})_2\text{bpy}$ , 33%. The  $\text{L} = \text{Me}_4\text{bpy}$  complex required only a 1-h reflux time and was prepared in 64% yield. The synthesis of the  $\text{L} = \text{Cl}_2\text{bpy}$  complex required a 2-h reflux in glycerine and provided the compound in 44% yield.

**$\text{cis}((\text{NEt}_2)_2\text{bpy})_2\text{Os}(\text{CO})\text{Cl}(\text{PF}_6)$ .** This complex was prepared in a two-step procedure involving an intermediate  $\eta^1$ -diphos complex. Into a 25-mL round-bottom flask was added 224 mg (0.228 mmol) of  $\text{cis}((\text{NEt}_2)_2\text{bpy})_2\text{Os}^{\text{III}}\text{Cl}_2(\text{Cl}) \cdot 5\text{H}_2\text{O}$ , 140 mg (0.351 mmol) of diphos, 30 mL of 1:1 v/v ethanol/water, and a Teflon stirbar. The suspension was

refluxed for 3 h. The product was isolated as a  $\text{PF}_6^-$  salt. Chromatography followed by direct evaporation of solvent with a rotary evaporator yielded a dull orange solid. This material (proposed  $\text{cis}((\text{NEt}_2)_2\text{bpy})_2\text{Os}(\eta^1\text{-diphos})\text{Cl}(\text{PF}_6)$ ) was not characterized further but was immediately suspended in a 100-mL round-bottom flask containing 10 mL of glycerine and refluxed with stirring for 2 h to yield a bright red-orange solution. The product was isolated as the  $\text{PF}_6^-$  salt and chromatographed to give 134 mg (60%) of  $\text{cis}((\text{NEt}_2)_2\text{bpy})_2\text{Os}(\text{CO})\text{Cl}(\text{PF}_6)$ .

**$\text{cis}(\text{Me}_4\text{bpy})_2\text{Os}(\text{PPh}_3)\text{Cl}(\text{PF}_6)$ .** This olive green complex was prepared in 74% yield by reflux of  $\text{cis}(\text{Me}_4\text{bpy})_2\text{OsCl}_2 \cdot 2\text{H}_2\text{O}$  with  $\text{PPh}_3$  in 1:1 v/v ethanol/water using the conditions described in the literature preparation for  $\text{L} = \text{bpy}$ .<sup>17</sup>

**$\text{cis}-(4^2\text{-Me}_2\text{bpy})_2\text{Os}(\text{diphos})(\text{PF}_6)_2$ .** This orange complex was prepared in 42% yield by the reaction of  $\text{cis}-(4^2\text{-Me}_2\text{bpy})_2\text{OsCl}_2 \cdot \text{H}_2\text{O}$  with diphos in ethylene glycol following the literature procedure described for  $\text{cis}(\text{bpy})_2\text{Os}(\text{diphos})(\text{PF}_6)_2$ .<sup>17</sup>

**Measurements.** Electrochemical measurements were carried out at room temperature in MeCN solution containing 0.1 M TEAP as supporting electrolyte. Cyclic voltammograms were recorded in argon-bubble-degassed solutions by using a PAR 273 apparatus with 100 mV/s sweep rates. The classical three-electrode setup comprising a saturated calomel reference electrode (SCE), Pt-wire auxiliary electrode, and either a Pt-bead (oxidations) or a hanging-Hg-drop (reductions) working electrode was employed for all measurements.

Absorption spectra in MeCN solution were recorded with a Kontron Uvikon 860 spectrophotometer. Uncorrected emission spectra were obtained in MeCN solution at room temperature and butyronitrile glass at 77 K by using a Perkin-Elmer LS 5 spectrofluorimeter equipped with a Hamamatsu R928 phototube. Emission spectra were corrected by hand in 5-nm intervals for variations in monochromator-photomultiplier response with wavelength.

Emission lifetimes were measured by using either the same spectrofluorimeter working in the phosphorescence mode or an Edinburgh 199 DS single-photon-counting apparatus. Where necessary, the solutions were deaerated by repeated freeze-pump-thaw cycles. In all cases, single exponential decays were observed. The error in lifetime values so obtained was estimated to be <10%. Emission quantum yields were estimated with the optically diluted method<sup>31</sup> using  $\text{Ru}(\text{bpy})_3^{2+}$  in aerated aqueous solution as a standard ( $\Phi_{\text{em}} = 0.028$ ).<sup>32</sup>

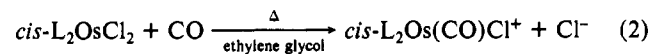
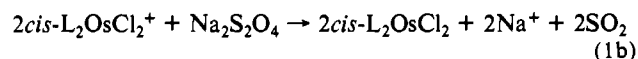
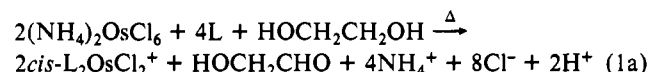
Infrared spectra were obtained for the complexes in KBr (Fluka IR spectroscopy grade) pellets in the region 4000–450  $\text{cm}^{-1}$  by using a Perkin-Elmer 683 infrared spectrophotometer. In addition, IR spectra for solutions of the  $\text{cis-L}_2\text{Os}(\text{CO})\text{Cl}(\text{PF}_6)$  complexes in dry MeCN (NaCl cell, 1-mm path) in the CO stretching region (2000–1800  $\text{cm}^{-1}$ ) were also recorded.

Proton NMR spectra of the  $\text{cis-L}_2\text{Os}(\text{CO})\text{Cl}(\text{PF}_6)$  complexes and the L ligands were obtained in  $\text{CD}_3\text{CN}$  solution. Sample concentrations were typically 14–18 mg/mL. For the  $\text{Me}_4\text{bpy}$  ligand and its complex, saturated solutions were employed. Proton NMR, spin-decoupling, and nuclear Overhauser effect (NOE) experiments were all conducted on a Bruker 360 spectrometer at 360 MHz. The proton resonance at  $\delta = 1.93$  ppm due to trace  $\text{CH}_3\text{CN}$  in the  $\text{CD}_3\text{CN}$  was used as an internal standard for calibration of the spectra.

Microanalyses were carried out by CIBA-Geigy, KA-Forschungszentrum, Marly 170/004, Switzerland.

## Results and Discussion

**Syntheses.** The syntheses of the  $\text{cis-L}_2\text{Os}(\text{CO})\text{Cl}^+$  and  $\text{cis-L}_2\text{OsCl}_2$  complexes are accomplished by straightforward adaptation of the literature methods<sup>16,17</sup> for all L except  $\text{L} = (\text{NEt}_2)_2\text{bpy}$  (vide infra). The appropriate reactions are shown in eq 1 and 2.<sup>33</sup> All complexes are obtained in reasonable yields



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(33) Generation of  $\text{cis-L}_2\text{Os}(\text{CO})\text{Cl}^+$  complexes in pure form using  $\text{HCOOH}$ <sup>16,17</sup> as an in situ CO source fails here. Although the  $\text{cis-L}_2\text{Os}(\text{CO})\text{Cl}^+$  complexes do form in significant amounts, contamination with unidentified, inseparable side products is unavoidable.

**Table I.** CO Stretch Frequency and Electrochemical Properties of *cis*-L<sub>2</sub>Os(CO)Cl(PF<sub>6</sub>) Complexes<sup>a</sup>

complex	code <sup>b</sup>	$\sigma^c$	IR $\nu(\text{CO})^d$	electrochemical parameters <sup>f</sup>			
				$E_o$	$E_{r,i}^g$	$E_o^*$	$E_r^*$
(Cl <sub>2</sub> bpy) <sub>2</sub> Os(CO)Cl(PF <sub>6</sub> )	1	0.23	1960 (1956, 1923 <sup>e</sup> )	1.25	-1.05 -1.23 -1.75 <sup>h</sup>	-0.60	0.80
(bpy) <sub>2</sub> Os(CO)Cl(PF <sub>6</sub> )	2	0.00	1952 (1941)	1.18	-1.29 -1.50	-0.75	0.64
(5 <sup>2</sup> -Me <sub>2</sub> bpy) <sub>2</sub> Os(CO)Cl(PF <sub>6</sub> )	3	-0.07	1948 (1940)	1.13	-1.44 -1.64	-0.90	0.59
(4 <sup>2</sup> -Me <sub>2</sub> bpy) <sub>2</sub> Os(CO)Cl(PF <sub>6</sub> )	4	-0.17	1944 (1940, <sup>e</sup> 1931)	1.09	-1.38 -1.59	-0.89	0.60
(Me <sub>4</sub> bpy) <sub>2</sub> Os(CO)Cl(PF <sub>6</sub> )	5	-0.24	1940 (1912, 1935 <sup>e</sup> )	1.04	-1.53 -1.72 -1.96 <sup>h</sup>	-1.02	0.53
((OMe) <sub>2</sub> bpy) <sub>2</sub> Os(CO)Cl(PF <sub>6</sub> )	6	-0.27	1936 (1938, 1925 <sup>e</sup> )	0.98	-1.43 -1.62	-0.89	0.44
((NEt <sub>2</sub> ) <sub>2</sub> bpy) <sub>2</sub> Os(CO)Cl(PF <sub>6</sub> )	7	-0.83	1910 (1896)	0.60	-1.78 -1.96	-1.31	0.13

<sup>a</sup> Values in MeCN solution except where noted. <sup>b</sup> Numerical identification codes for complexes discussed in the text. <sup>c</sup> Hammett  $\sigma$  constants from ref 38. Values shown are sums of contributions from the 4,4'-positions ( $\sigma_p$ ) and 5,5'-positions ( $\sigma_m$ ) of L. <sup>d</sup> Values for CO stretch frequency in cm<sup>-1</sup> in MeCN solution. Values in parentheses are for samples in KBr pellets. <sup>e</sup> Shoulder. <sup>f</sup> Values in V vs SCE at 298 K in 0.1 M TEAP/MeCN solution, as defined in the text. <sup>g</sup> Value for the *i*th reduction (*i* = 1, 2, 3). <sup>h</sup> Irreversible process. Potential of peak cathodic current reported.

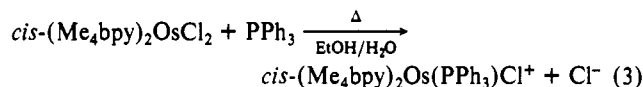
(note Experimental Section) and exhibit satisfactory elemental analysis. Proton NMR spectra of all the *cis*-L<sub>2</sub>Os(CO)Cl(PF<sub>6</sub>) complexes indicate complete magnetic inequivalence of the ring protons of the coordinated L. This observation suffices to firmly establish the *cis* configuration of the *cis*-L<sub>2</sub>Os(CO)Cl(PF<sub>6</sub>) complexes studied here. Elemental analysis results and the details and discussion of the <sup>1</sup>H NMR spectra of the free L and *cis*-L<sub>2</sub>Os(CO)Cl(PF<sub>6</sub>) complexes are provided in the supplementary material (Tables S-I-S-III and Figures S-1).

Attempts to prepare Os(II) complexes containing the L = (NEt<sub>2</sub>)<sub>2</sub>bpy ligand using the methods of eqs 1 and 2 are unsuccessful. In the case of eq 1, for example, the product isolated for L = (NEt<sub>2</sub>)<sub>2</sub>bpy has been identified as the chloride salt of *cis*-((NEt<sub>2</sub>)<sub>2</sub>bpy)<sub>2</sub>Os<sup>III</sup>Cl<sub>2</sub><sup>+</sup> on the basis of elemental analysis and reactivity (vide infra).

Attempts to treat *cis*-((NEt<sub>2</sub>)<sub>2</sub>bpy)<sub>2</sub>Os<sup>III</sup>Cl<sub>2</sub>(Cl) with CO according to eq 2 also fail and yield only the PF<sub>6</sub><sup>-</sup> salt of the starting material. Apparently, ethylene glycol is an insufficiently strong reductant to effect reduction to the reactive Os(II) form of the complex. The absence of reaction is in this instance consistent with the substitution inertness of related Os(III) complexes.<sup>35</sup>

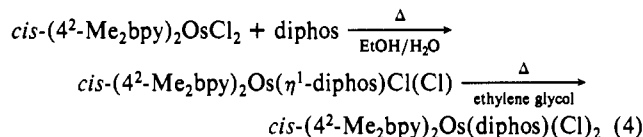
The preparation of *cis*-((NEt<sub>2</sub>)<sub>2</sub>bpy)<sub>2</sub>Os(CO)Cl(PF<sub>6</sub>) can be accomplished via a two-step reaction sequence initiated by reaction of *cis*-((NEt<sub>2</sub>)<sub>2</sub>bpy)<sub>2</sub>Os<sup>III</sup>Cl<sub>2</sub>(Cl) with excess diphos in refluxing ethanol/water. The general reaction of *cis*-L<sub>2</sub>OsCl<sub>2</sub> with excess

phosphine ligand results in substitution of one Cl<sup>-</sup> by the phosphine,<sup>17</sup> as shown for L = Me<sub>4</sub>bpy with PPh<sub>3</sub> in eq 3. Use of

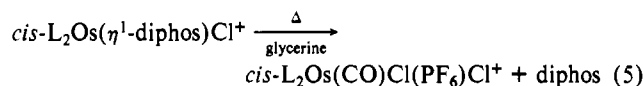


potentially chelating ligands such as diphos yields the corresponding  $\eta^1$ -diphos systems. For *cis*-((NEt<sub>2</sub>)<sub>2</sub>bpy)<sub>2</sub>Os<sup>III</sup>Cl<sub>2</sub>(Cl), diphos is a sufficiently strong reductant to effect reduction to the Os(II) form prior to substitution and isolation of the proposed *cis*-((NEt<sub>2</sub>)<sub>2</sub>bpy)<sub>2</sub>Os( $\eta^1$ -diphos)Cl<sup>+</sup> species.

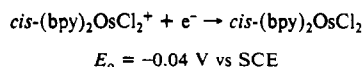
Closure of  $\eta^1$ -diphos intermediates can be accomplished in moderate yield by reflux, as shown in eq 4 for the L = 4<sup>2</sup>-Me<sub>2</sub>bpy



system. Reflux in glycerine, however, can lead to replacement of the coordinated phosphine ligand by CO, as shown in eq 5. For



(34) (a) The inability to isolate an Os(II) complex in this case cannot be explained with certainty pending the results of a detailed investigation of the chemistry of the *cis*-L<sub>2</sub>OsCl<sub>2</sub> complexes. We note, however, that the observed behavior is qualitatively consistent with the properties of (NEt<sub>2</sub>)<sub>2</sub>bpy vs bpy as ligands. For example, the known oxidation of *cis*-(bpy)<sub>2</sub>OsCl<sub>2</sub> in MeCN<sup>34b</sup>



is facile. (NEt<sub>2</sub>)<sub>2</sub>bpy is a much stronger electron donor than bpy (vide infra). For the *cis*-L<sub>2</sub>Os(CO)Cl<sup>+</sup> complexes (note Table I), replacement of bpy by (NEt<sub>2</sub>)<sub>2</sub>bpy results in a cathodic shift of 580 mV in  $E_o$ . A shift of similar magnitude in the analogous *cis*-L<sub>2</sub>OsCl<sub>2</sub> system gives an estimate of  $E_o = -0.62$  V vs SCE for L = (NEt<sub>2</sub>)<sub>2</sub>bpy. This value is sufficiently cathodic to permit oxidation of Os(II) to Os(III) by O<sub>2</sub> ( $E_r$  for O<sub>2</sub>/O<sub>2</sub><sup>-</sup> is ca. -0.5 V vs SCE)<sup>34c</sup> in MeCN. Extension of these arguments to aqueous solution is complicated by a lack of  $E_o$  data for the Os complexes and the pH dependence of the O<sub>2</sub> reduction. If valid, however, similar arguments in aqueous solution provide one possible explanation for the isolation of the *cis*-((NEt<sub>2</sub>)<sub>2</sub>bpy)<sub>2</sub>Os<sup>III</sup>Cl<sub>2</sub><sup>+</sup> species in our experiments. (b) Kober, E. M. Ph.D. Thesis, University of North Carolina, Chapel Hill, NC, 1982. (c) Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Nonaqueous Systems*; Marcel Dekker, Inc.: New York, 1970.

(35) Griffith, W. P. *The Chemistry of the Rarer Platinum Metals*; Interscience: New York, 1967.

L = 4<sup>2</sup>-Me<sub>2</sub>bpy and Me<sub>4</sub>bpy, the *cis*-L<sub>2</sub>Os(CO)Cl(PF<sub>6</sub>) yields are 3% and 11%, respectively, and eq 5 represents a relatively minor pathway. In the case of L = (NEt<sub>2</sub>)<sub>2</sub>bpy, the *cis*-((NEt<sub>2</sub>)<sub>2</sub>bpy)<sub>2</sub>Os(CO)Cl(PF<sub>6</sub>) complex is produced in 60% yield and eq 5 is the predominant pathway for reaction.

The yields of the *cis*-L<sub>2</sub>Os(CO)Cl<sup>+</sup> complexes obtained via eq 5 parallel ligand basicity as measured by Hammett  $\sigma$  constants of the L substituents (Table I). Our preliminary results suggest that increased basicity at the Os(II) center facilitates the reaction pathway illustrated in eq 5. In support of this statement, reaction of *cis*-(Me<sub>4</sub>bpy)<sub>2</sub>Os(PPh<sub>3</sub>)Cl(PF<sub>6</sub>) in glycerine yields *cis*-(Me<sub>4</sub>bpy)<sub>2</sub>Os(CO)Cl(PF<sub>6</sub>) in only 4% yield vs 11% yield obtained (vide supra) from the reaction of *cis*-(Me<sub>4</sub>bpy)<sub>2</sub>Os( $\eta^1$ -diphos)Cl(PF<sub>6</sub>). Such an observation is consistent with expectations based on the relative basicity of PPh<sub>3</sub> (pK = 3.3) vs diphos (pK = 4.7).<sup>36</sup>

**Properties and Correlations.** Tables I and II summarize our findings in room temperature MeCN solution concerning the ground- and excited-state properties of the *cis*-L<sub>2</sub>Os(CO)Cl(PF<sub>6</sub>) complexes. Our characterization of this family of complexes

(36) Raham, M. M.; Liu, H.-Y.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* 1989, 8, 1.

Table II. Absorption and Emission Properties of *cis*-L<sub>2</sub>Os(CO)Cl(PF<sub>6</sub>) Complexes<sup>a</sup>

complex <sup>b</sup>	absorption λ, nm (ε) <sup>d</sup>	emission					
		λ(298 K), <sup>e</sup> nm	τ, ns	λ(77 K), <sup>f</sup> nm	τ, ns	Φ <sub>em</sub>	k <sub>nr</sub> , <sup>g</sup> s <sup>-1</sup>
1	503 (3300)	765	14	670	620	<1 × 10 <sup>-3</sup>	>6 × 10 <sup>7</sup>
	360 (7700)						
	286 (34 150)						
	217 (46 400)						
2	480 (2800)	695	82	635	1520	8.7 × 10 <sup>-3</sup>	1.2 × 10 <sup>7</sup>
	351 (6000)						
	287 (30 000)						
3	469 (2500)	690	249	605	1810	2.2 × 10 <sup>-2</sup>	3.9 × 10 <sup>6</sup>
	348 <sup>h</sup> (5700)						
	295 (28 600)						
	266 (28 800)						
4	476 (3000)	695	76	625	920	6.3 × 10 <sup>-3</sup>	1.3 × 10 <sup>7</sup>
	349 (6800)						
	283 (33 150)						
	210 (42 500)						
	210 (48 000)						
5	464 (3000)	690	268	600	1900	4.9 × 10 <sup>-2</sup>	3.5 × 10 <sup>6</sup>
	342 <sup>h</sup> (6800)						
	289 (35 300)						
	271 (36 300)						
6	471 (2900)	700	25	660	900	2.0 × 10 <sup>-3</sup>	4.0 × 10 <sup>7</sup>
	355 (7550)						
	264 (41 300)						
	223 (56 500)						
7	470 (4200)	700	42	650	1100	4.3 × 10 <sup>-3</sup>	2.4 × 10 <sup>7</sup>
	372 (14 900)						
	267 (77 150)						
	205 (42 250)						

<sup>a</sup> MeCN solution and 298 K except where noted. <sup>b</sup> Numerical code as in Table I. <sup>c</sup> Wavelength of the absorption maxima. <sup>d</sup> Extinction coefficient in M<sup>-1</sup> cm<sup>-1</sup>. <sup>e</sup> Wavelength of the corrected emission maxima. <sup>f</sup> Highest energy feature of the corrected emission maxima in butyronitrile glass at 77 K. <sup>g</sup> k<sub>nr</sub> = τ<sup>-1</sup>(1 - Φ<sub>em</sub>). This equation is valid for unit values of intersystem crossing efficiencies in the complexes. Intersystem crossing efficiencies have been shown to be unity for related luminescent Os(II) complexes (Caspar, J. V. Ph.D. Thesis, University of North Carolina, Chapel Hill, NC, 1982). <sup>h</sup> Shoulder.

includes data for CO IR absorptions, UV-visible absorptions, MLCT emissions and lifetimes, and electrochemical redox potentials for each complex. We now turn our attention to the discussion of each of these properties.

IR spectra of the complexes in the carbonyl stretch region are a function of both sample environment and the nature of the L substituent. As shown in Table I, spectra taken in KBr pellets consist of broad, often split bands. Such behavior is consistent with strong environmental interactions usually observed for lower symmetry species.<sup>37</sup> Spectra obtained in fluid MeCN solution exhibit the single absorption expected for the *cis*-L<sub>2</sub>Os(CO)Cl<sup>+</sup> complexes. These data indicate that ν<sub>CO</sub> also varies with the nature of the L substituent as measured by Hammett values. A linear plot of ν<sub>CO</sub> vs Hammett σ constant<sup>38</sup> is obtained in Figure 1. A Hammett relationship<sup>39-41</sup> defined by eq 6 is obtained where ν<sub>CO</sub><sup>o</sup>

$$\nu_{\text{CO}} = \nu_{\text{CO}}^{\circ} - (477.3 \text{ cm}^{-1})\rho_{\text{CO}}\sigma \quad (6)$$

represents the carbonyl absorption in cm<sup>-1</sup> for the reference (L = bpy) complex, 477.3 is the constant for the expression of the Hammett equation in cm<sup>-1</sup> units at 25 °C, and ρ<sub>CO</sub> is the sensitivity parameter (vide infra) for the system. The Hammett σ is defined for this work as the sum of σ<sub>p</sub> and σ<sub>m</sub> and represents the total electronic effects of the L substituents. σ<sub>p</sub> and σ<sub>m</sub> refer to substituents at the 4,4'- and 5,5'-positions on L, respectively.

For the ν<sub>CO</sub> vs σ plot of Figure 1 and eq 6, a value of ρ<sub>CO</sub> = -0.101 is calculated. The negative value is indicative of generation

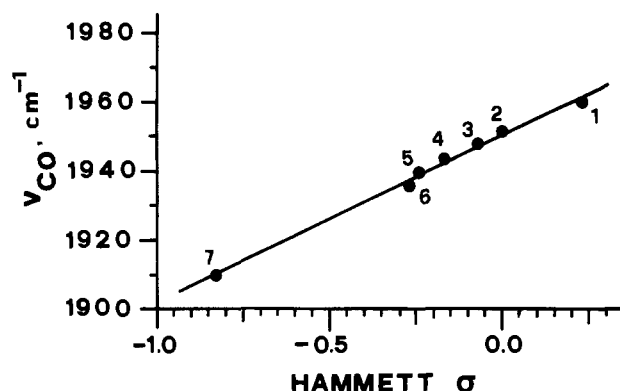
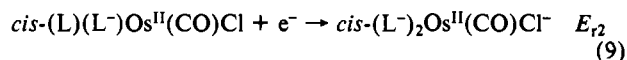
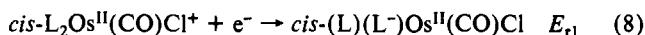
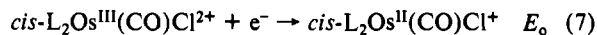


Figure 1. IR correlation with Hammett σ constants of the L substituents. Correlation of ν<sub>CO</sub> (cm<sup>-1</sup>) with σ in MeCN solution is shown. Slope = 48.4 cm<sup>-1</sup>; intercept = 1951 cm<sup>-1</sup>; correlation coefficient = r = 0.99.

of positive charge as the negatively polarized O atom moves away from the C center in CO during absorption. The small absolute value of ρ<sub>CO</sub> is expected, given the large separation of the CO from the L substituents. These observations are also consistent with changes in L-Os-CO π-back-bonding within the *cis*-L<sub>2</sub>Os(CO)Cl<sup>+</sup> family and the behavior of related complexes containing the *cis*-(bpy)<sub>2</sub>Os(CO)- unit.<sup>16</sup>

Electrochemical redox potentials defined by eqs 7-9 are also listed in Table I for each complex. In each case a reversible



one-electron oxidation of the Os(II) center to Os(III) is noted. Two reversible one-electron reductions are also observed corre-

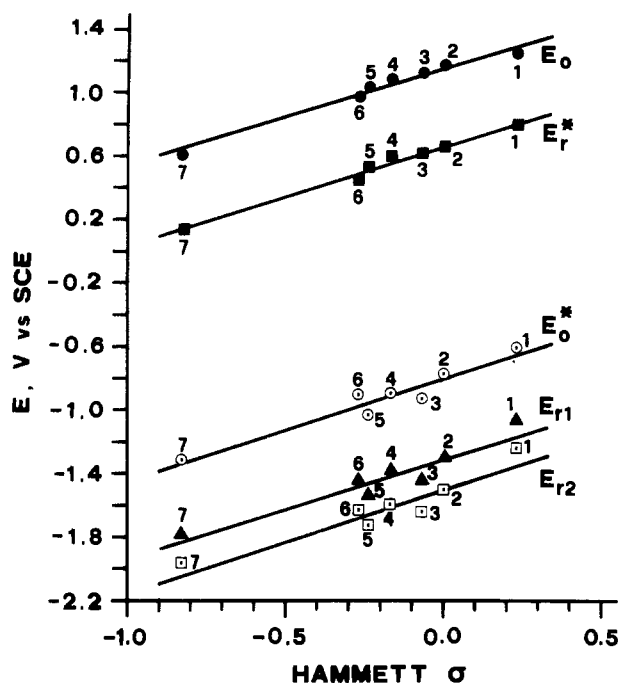
(37) Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1963.

(38) Ritchie, C. D.; Sager, W. F. *Prog. Org. Chem.* **1967**, *2*, 323.

(39) Exner, O. In *Advances in Linear Free Energy Relationships*; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1972.

(40) Chapman, N. B., Shorter, J., Eds. *Correlation Analysis in Chemistry, Recent Advances*; Plenum Press: New York, 1978.

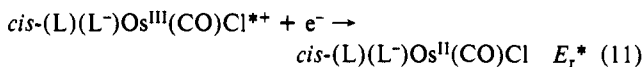
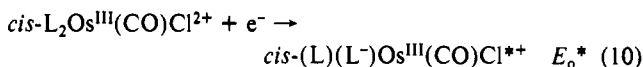
(41) Exner, O. *Correlation Analysis of Chemical Data*; Plenum Press: New York, 1988.



**Figure 2.** Correlation of electrochemical properties with Hammett  $\sigma$  constants:  $E_0$  (●), slope = 0.64 V, intercept = 1.16 V,  $r = 0.98$ ;  $E_r^*$  (■), slope = 0.64 V, intercept = 0.66 V,  $r = 0.99$ ;  $E_0^*$  (○), slope = 0.65 V, intercept = 0.79 V,  $r = 0.95$ ;  $E_{r1}$  (▲), slope = 0.64 V, intercept = -1.29 V,  $r = 0.92$ ;  $E_{r2}$  (□), slope = 0.63 V, intercept = -1.49 V,  $r = 0.91$ .

responding to sequential one-electron reduction of the coordinated L.<sup>17</sup> The  $E_0$  values span a range of 650 mV, and both  $E_{r1}$  and  $E_{r2}$  span a 630-mV range within the family of complexes.<sup>42</sup>

Redox potentials for the MLCT excited states as defined in eqs 10–13 can also be estimated.  $E_{em}^\circ$  is the potential (in volts)



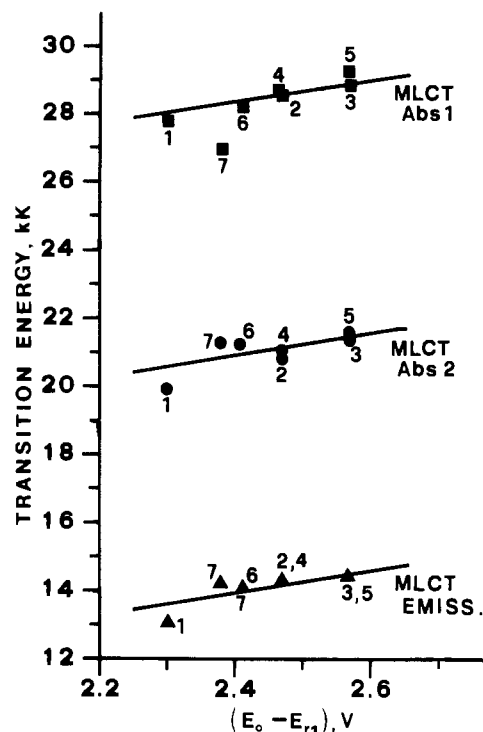
$$E_0^* = E_0 - E_{em}^\circ \quad (12)$$

$$E_r^* = E_{r1} + E_{em}^\circ \quad (13)$$

corresponding to the energy of the corrected emission maximum.<sup>43</sup> Results shown in Table I indicate that the excited states of the  $cis-L_2Os(CO)Cl^+$  complexes are moderate to good reductants but poor to moderate oxidants in solution at room temperature.

Monotonic variations of both ground- and excited-state redox potentials of the complexes with changing L substituent are also noted in Table I. Similar variations have been observed previously for redox potentials of the analogous  $RuL_3^{2+}$  complexes.<sup>44,45</sup>

(42) (a) Additional reductions are observed at -1.96 and ca. -1.75 V for 5 and 1, respectively. We assign these processes to direct reduction of the Os(II) center in  $cis-(L)_2Os^{II}(CO)Cl^+$  to Os(I) by comparison with analogous *fac*-(L)<sub>3</sub>Re(CO)<sub>3</sub>Cl complexes.<sup>42b</sup> For 1, this process is irreversible and leads to decomposition of the complex. (b) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1983**, 536. (43) (a)  $E_0^*$  values are usually obtained from a detailed vibrational analysis of the emission spectrum via radiationless decay theory.<sup>43b</sup> In the absence of such an analysis, corrected low-temperature  $E_{em}$  values provide a reasonable estimate for  $E_0^*$ . We use corrected  $E_{em}$  values at 77 K in butyronitrile glass (note Figure 3 caption) for the calculation of  $E_0^*$  and  $E_r^*$  in Table I. Substitution of MeCN by butyronitrile is not expected to introduce significant error in this case, since  $E_{em}$  appears unaffected under similar conditions in related MLCT systems.<sup>43c</sup> (b) Caspar, J. V. Ph.D. Thesis, University of North Carolina, Chapel Hill, NC, 1982. (c) Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5583. (44) Neveux, P. E., Jr. Ph.D. Thesis, University of North Carolina, Chapel Hill, NC, 1987.



**Figure 3.** Spectral transitions vs  $(E_0 - E_{r1})$  for  $cis-L_2Os(CO)Cl^+$  complexes in MeCN solution. Transition energies of the two lowest energy absorption bands and the emission from Table II are plotted vs  $(E_0 - E_{r1})$ : absorption band 1 (■), slope =  $4.6 \times 10^3 \text{ cm}^{-1} \text{ V}^{-1}$ , intercept =  $17.2 \times 10^3 \text{ cm}^{-1}$ ,  $r = 0.90$ ; absorption band 2 (●), slope =  $4.1 \times 10^3 \text{ cm}^{-1} \text{ V}^{-1}$ , intercept =  $10.9 \times 10^3 \text{ cm}^{-1}$ ,  $r = 0.61$ ; emission band (▲), slope =  $4.04 \times 10^3 \text{ cm}^{-1} \text{ V}^{-1}$ , intercept =  $4.3 \times 10^3 \text{ cm}^{-1}$ ,  $r = 0.69$ . Regression analysis of absorption band 1 does not include complex 7. (kK =  $10^3 \text{ cm}^{-1}$ .)

Redox potentials of the  $RuL_3^{2+}$  complexes have been successfully correlated with values of the L substituents by using the Hammett equation<sup>45</sup>

$$E = E' + 0.0591 \rho_E \sigma \quad (14)$$

$E$  (V) is the potential for a complex containing any L with substituent characterized by the Hammett constant  $\sigma$ .  $E'$  (V) is the corresponding potential for the reference L = bpy complex. The sensitivity parameter for the process is  $\rho_E$ , and the constant 0.0591 (V) is appropriate for the expression of the Hammett equation in units of V at 25 °C.

The application of eq 14 in the  $cis-L_2Os(CO)Cl^+$  systems is illustrated in Figure 2. The redox potentials  $E_0$ ,  $E_{r1}$ ,  $E_{r2}$ ,  $E_0^*$ , and  $E_r^*$  defined by eqs 7–13 are each plotted vs  $\sigma$ , and linear relationships are obtained in all cases. The sensitivity parameter  $\rho_E$  is large and positive (ca. 11 in all cases), clearly reflecting the fact that the redox phenomena occur much closer to the L substituents than carbonyl IR absorption and are therefore more strongly affected. In all cases, one full electron is added to the system and the resulting strong reduction of positive charge is indicated by  $\rho_E \gg 0$ .

We note also that the observed  $\rho_E$  in Figure 2 is insensitive to changes in the oxidation state of the complexes within the  $cis-L_2Os(CO)Cl^+$  family. Addition of an electron to a complex does not affect the sensitivity of that system to further reduction for the range of oxidation states examined here. Consequently, Figure 2 provides a basis for the estimation of ground- and excited-state properties of any  $cis-L_2Os(CO)Cl^+$  family member from the readily accessible Hammett  $\sigma$  for the L substituent. Similar correlations utilizing  $E_0$  in place of the Hammett  $\sigma$  have been observed for related Os(II) systems in which non-L auxiliary ligands control these properties.<sup>18</sup> Our results verify the appli-

(45) Skarda, V.; Cook, M. J.; Lewis, A. P.; McAuliffe, G. S. G.; Thomson, A. J.; Robbins, D. J. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1309.

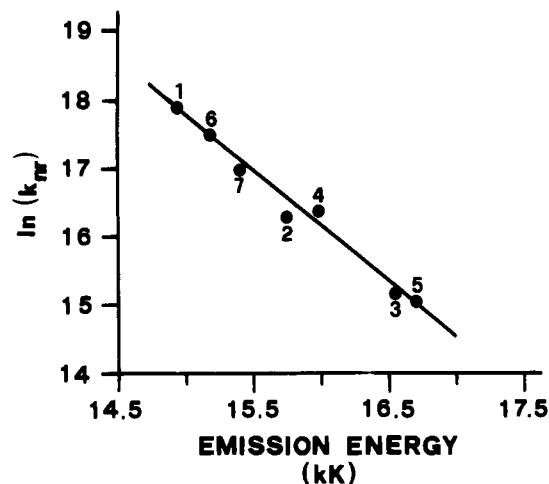


Figure 4. Energy gap law correlation for *cis*-L<sub>2</sub>Os(CO)Cl<sup>+</sup> complexes. Slope =  $-1.60 \times 10^3 \text{ cm}^{-1}$ ; intercept = 41.8;  $r = 0.99$ .

cability of similar procedures to systems in which these properties are governed by the nature of the substituents on the ligand L.

**Absorption and Emission Spectra.** All the *cis*-L<sub>2</sub>Os(CO)Cl<sup>+</sup> complexes studied are stable in room-temperature MeCN solution. Absorption spectra (Table II) are similar to those reported earlier for complexes containing the *cis*-(bpy)<sub>2</sub>Os(CO)- unit.<sup>16,17</sup> The lowest energy band, with  $\epsilon_2 = 3000\text{--}4000 \text{ M}^{-1} \text{ cm}^{-1}$ , occurs for each complex below 400 nm. A second band with  $\epsilon_1 = 6000\text{--}8000 \text{ M}^{-1} \text{ cm}^{-1}$  is observed in the 350–400-nm region, occasionally as a shoulder on the higher energy UV bands. The correlation of absorption maxima for these bands with differences between the oxidation potential and first reduction potential ( $E_o - E_{r1}$ ) for the complexes in Figure 3 provides a basis for their assignment as  $d\pi(\text{Os}) \rightarrow \pi^*(L)_i$  ( $i = 1, 2$ ) MLCT transitions. Ligand L<sub>1</sub> is *cis* to Cl and L<sub>2</sub> is *cis* to CO in our notation for the complexes (Figure S-1, supplementary material). The lowest energy MLCT state (Figure 5) corresponds to a transition involving L<sub>2</sub>, in agreement with analogous assignments for related compounds.<sup>14</sup>

The unorthodox behavior observed in Figure 3 for complexes containing good electron donors such as the NEt<sub>2</sub> group may have its origins in the presence of an additional excited state for these species.<sup>46</sup> For each complex the transitions occurring above 300 nm can be assigned as L-localized  $\pi \rightarrow \pi^*$  transitions, consistent with assignments in related complexes.<sup>16,17</sup>

A weak emission, strongly quenched by O<sub>2</sub>, is observed for all the *cis*-L<sub>2</sub>Os(CO)Cl<sup>+</sup> complexes in room-temperature MeCN solution. This emission is assigned as a  $d\pi(\text{Os}) \leftarrow \pi^*(L)$  MLCT on the basis of its correlation with  $E_o - E_{r1}$  (Figure 3). Corresponding MLCT excited-state lifetimes,  $\tau$ , vary over the range 14–268 ns and are comparable in magnitude to values observed for OsL<sub>2</sub><sup>2+</sup> complexes.<sup>34b</sup> At 77 K, substantial increases in lifetimes and sharpening of the emission spectra occur. This behavior is consistent with predictions of the current model of MLCT excited-state deactivation in which decay of the MLCT state to the ground state is dominated by radiationless processes in fluid solution.<sup>43b,c</sup> In the absence of accessible dd excited states, the natural logarithm of the deactivation rate via nonradiative processes,  $k_{nr}$ , is linearly related to the energy difference between the lowest vibrational levels of the ground and MLCT states,  $E^{00}$ .

(46) One possibility is the presence of a ligand-to-metal charge-transfer (LMCT) state involving the NEt<sub>2</sub> group. Since oxidation of the NEt<sub>2</sub> group to NEt<sub>2</sub><sup>+</sup> occur at ca. 1.3–1.4 V vs SCE, using this value and  $E_{r1}$  for 7 gives an estimate of  $E_{abs} = 1.4 - (-1.78) = 3.18 \text{ V}$  (~390 nm) for the LMCT transition. A second possibility, suggested by a reviewer, is the presence of a ligand-localized  $n\pi^*$  transition:



We are unable to distinguish between these possibilities from the available data. In either case, however, the transition could mask the true position of the higher energy MLCT band, introducing the deviation noted in Figure 3.

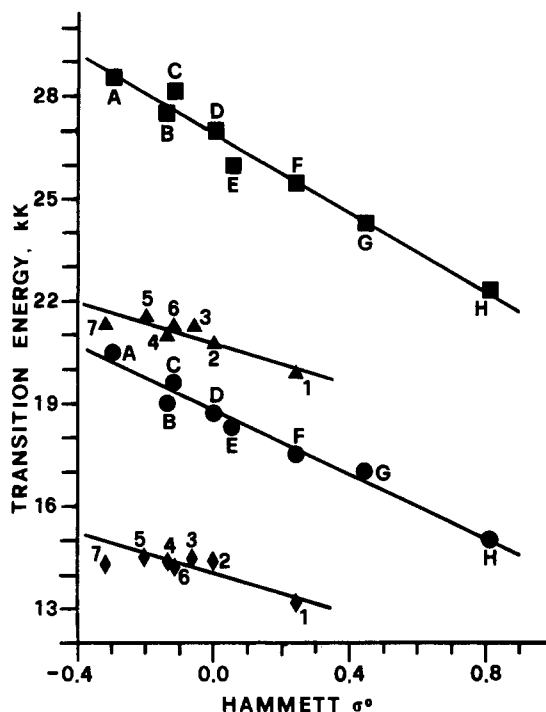


Figure 5. Spectral property correlations with Hammett  $\sigma^o$  constants:<sup>51</sup> Os absorption ( $\blacktriangle$ ), slope =  $-2.78 \times 10^3 \text{ cm}^{-1}$ , intercept =  $20.8 \times 10^3 \text{ cm}^{-1}$ ,  $r = 0.87$ ; Os emission ( $\blacklozenge$ ), slope =  $-1.98 \times 10^3 \text{ cm}^{-1}$ , intercept =  $14.0 \times 10^3 \text{ cm}^{-1}$ ,  $r = 0.62$ ; Re absorption ( $\blacksquare$ ), slope =  $-5.76 \times 10^3 \text{ cm}^{-1}$ , intercept =  $26.9 \times 10^3 \text{ cm}^{-1}$ ,  $r = 0.99$ ; Re emission ( $\bullet$ ), slope =  $-4.65 \times 10^3 \text{ cm}^{-1}$ , intercept =  $18.8 \times 10^3 \text{ cm}^{-1}$ ,  $r = 0.98$ . Data are shown for *cis*-L<sub>2</sub>Os(CO)Cl<sup>+</sup> and *fac*-(L)Re(CO)<sub>3</sub>Cl complexes<sup>53</sup> in MeCN solution at 25 °C. Re data (X,  $E_{abs}$  (V),  $E_{em}$  (V),  $\sigma^o$ ; Y = H for all complexes): (A) NH<sub>2</sub>, 28.6, 20.5, -0.30; (B) OCH<sub>3</sub>, 28.1, 19.6, -0.12; (C) CH<sub>3</sub>, 27.5, 19.0, -0.14; (D) H, 27.0, 18.7, 0.00; (E) Ph, 26.0, 18.3, 0.05; (F) Cl, 25.5, 17.5, 0.24; (G) CO<sub>2</sub>Et, 24.3, 17.0, 0.44; (H) NO<sub>2</sub>, 22.3, 15.0, 0.81. The  $\sigma^o$  values for the substituents *p*-NEt<sub>2</sub>, (*m*+*p*)-Me, and *m*-Me in the *cis*-L<sub>2</sub>Os(CO)Cl<sup>+</sup> series are -0.32, -0.20, and -0.06, respectively.

Nonradiative deactivation rates can be obtained by measurements of luminescence quantum yield.

A plot of  $\ln k_{nr}$  vs  $E_{cm}$  for the *cis*-L<sub>2</sub>Os(CO)Cl<sup>+</sup> complexes is shown in Figure 4. A linear correlation is observed with slope =  $-12.9 \text{ eV}^{-1}$  and intercept = 41.8. Values of the slope and intercept in plots such as Figure 4 provide valuable insight into the nature of the nonradiative deactivation mechanisms operating in our systems. Two general types of behavior have been noted previously.<sup>34b,47–50</sup> For complexes such as *cis*-L<sub>2</sub>RuX<sub>2</sub>, LOsX<sub>4</sub>, and *cis*-L<sub>2</sub>OsX<sub>2</sub> ( $X \neq \text{CO}$ ) containing no coordinated CO ligands, nonradiative decay is dominated by L-based C–C vibrational stretch modes (ca. 1350  $\text{cm}^{-1}$ ) and slopes of ca.  $-7.5 \text{ eV}^{-1}$  and intercepts of 28–30 are observed. Complexes containing units such as *fac*-(L)Re(CO)<sub>3</sub>- or *cis*-(bpy)<sub>2</sub>Os(CO)-, in which coordinated CO ligands are present,<sup>50</sup> exhibit slopes of  $< -12 \text{ eV}^{-1}$  and intercepts of  $> 30$ . These differences have been attributed to replacement of the C–C stretch modes by CO vibrational stretch modes (ca. 2000  $\text{cm}^{-1}$ ) as the dominant acceptor vibrations for nonradiative decay for the CO-containing complexes. The *cis*-L<sub>2</sub>Os(CO)Cl<sup>+</sup> complexes studied here clearly exhibit behavior that is well within the range expected for CO-containing species.

Correlations of spectral data with Hammett  $\sigma^o$  (a modified set of substituent constants obtained<sup>51</sup> by averaging their values over many reactions)<sup>52</sup> can also be attempted for the *cis*-L<sub>2</sub>Os(CO)Cl<sup>+</sup>

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complexes, as shown in Figure 5. A similar plot spanning a larger range of  $\sigma^\circ$  values for a series of *fac*-(L)Re(CO)<sub>3</sub>Cl complexes<sup>53</sup> is included for comparison. It is clear from Figure 5 that, while excellent linear correlations with  $\sigma^\circ$  Hammett constants are exhibited by the absorption and emission energies of the *fac*-(L)-Re(CO)<sub>3</sub>Cl complexes, considerable scatter occurs for the data relative to the *cis*-L<sub>2</sub>Os(CO)Cl<sup>+</sup> complexes. Such scatter perhaps reflects inherent uncertainties in the band positions and the limited range of L for which complexes are synthetically accessible in the Os series.

A comparison of the *cis*-L<sub>2</sub>Os(CO)Cl<sup>+</sup> and *fac*-(L)Re(CO)<sub>3</sub>Cl complexes in Figure 5 yields  $\rho_{Os}(\text{abs}) = 5.83$ ,  $\rho_{Os}(\text{em}) = 4.15$  and  $\rho_{Re}(\text{abs}) = 12.07$ ,  $\rho_{Re}(\text{em}) = 9.75$ , respectively, for these two series. These values are obtained from eq 15, where  $\nu$  and  $\nu^\circ$  represent

$$\nu = \nu^\circ - (477 \text{ cm}^{-1})\rho_M\sigma^\circ \quad (15)$$

the transition energies in cm<sup>-1</sup> for the unknown and reference (L = bpy) complexes, respectively.  $\rho_M$  is the sensitivity parameter for complexes of metal M, and the remaining terms are defined at 25 °C analogous to eq 6 or 14. The large positive  $\rho_M$  value in each case is consistent with charge generation processes occurring near the L substituents, as expected for these transitions. The factor of ca. 2 difference between  $\rho_{Re}$  and  $\rho_{Os}$  can be accounted for by symmetry differences between the two families of complexes.<sup>41</sup> Comparable values of  $\rho_M$  are obtained after application of the necessary correction consistent with the proposed identical natures of the transitions (i.e., MLCT) for each family of complexes.

- (52) (a) The two sets are rather similar, showing significant differences only for powerful +M groups such as NR<sub>2</sub> and OR. Such variations reflect the fact that resonance contributions to  $\sigma$  values are dependent on the electronic demands of a reaction.<sup>52b</sup> Thus, while the original Hammett  $\sigma$  constants, obtained by designating the ionization, in water at 25 °C, of meta- and para-substituted benzoic acids (i.e. a weak acceptor system) as the standard reference reaction, tend to emphasize the mesomeric effects of the donor groups, the unbiased values  $\sigma^\circ$  provide a better fit for systems with nonconjugated reaction centers. Since it is not always possible to determine a priori the electronic demands of a reaction ( $\sigma^+$  and  $\sigma^-$  scales have also been proposed for strong acceptor and strong donor systems, respectively), the best approach remains to choose whichever scale produces the best fit. (b) Reynolds, W. F.; Dais, P.; Taft, R. W.; Topson, R. D. *Tetrahedron Lett.* **1981**, 22, 1795.
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## Conclusions

We summarize our findings concerning the family of *cis*-L<sub>2</sub>Os(CO)Cl<sup>+</sup> complexes as follows:

(1) *cis*-L<sub>2</sub>Os(CO)Cl(PF<sub>6</sub>) complexes can be synthesized from the reaction of *cis*-L<sub>2</sub>OsCl<sub>2</sub> (L ≠ (NEt<sub>2</sub>)<sub>2</sub>bpy) with CO in ethylene glycol in a straightforward extension of literature methods.<sup>16</sup> For L = (NEt<sub>2</sub>)<sub>2</sub>bpy, *cis*-((NEt<sub>2</sub>)<sub>2</sub>bpy)<sub>2</sub>Os(CO)Cl<sup>+</sup> can be produced by reflux of a *cis*-((NEt<sub>2</sub>)<sub>2</sub>bpy)<sub>2</sub>Os( $\eta^1$ -phosphine)Cl(PF<sub>6</sub>) intermediate in glycerol. Preliminary experiments indicate that the importance of this new pathway to the *cis*-L<sub>2</sub>Os(CO)Cl<sup>+</sup> species is a strong function of the basicity of the Os(II) center.

(2) The *cis*-L<sub>2</sub>Os(CO)Cl(PF<sub>6</sub>) complexes are assigned the *cis* configuration on the basis of results of <sup>1</sup>H NMR experiments. Using spin-decoupling and NOE experiments, it is possible to completely assign (note supplementary material) the proton resonances of the complexes. This represents the first application of the NOE technique to our knowledge in the study of luminescent ( $\alpha$ -diimine)Os<sup>II</sup> complexes. The configuration of the L about the Os(II) center can be assigned unambiguously by using chemically intuitive arguments based on the NMR results.

(3) Ground- and excited-state properties of the *cis*-L<sub>2</sub>Os(CO)Cl(PF<sub>6</sub>) complexes are similar to those observed for related complexes.<sup>16,17</sup> MLCT excited-state deactivation is dominated by nonradiative processes via CO stretch acceptor vibrations. Correlations of IR, electrochemical, and spectral properties of the complexes with Hammett substituent constants are observed. Control of these properties by the L substituent in this family of complexes permits their estimation for any new member through knowledge of its Hammett constant.

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**Supplementary Material Available:** Discussion of structure assignment and <sup>1</sup>H NMR analysis, tables of data for elemental and <sup>1</sup>H NMR analysis, and a structure of the *cis*-L<sub>2</sub>Os(CO)Cl(PF<sub>6</sub>) complexes (12 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,  
Purdue University, West Lafayette, Indiana 47907-3699

## Photophysical Studies of Copper Phenanthrolines Bound to DNA

Ramasamy Tamilarasan and David R. McMillin\*

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Electronic absorption and emission studies have been carried out for Cu(phen)<sub>2</sub><sup>+</sup>, Cu(dmp)<sub>2</sub><sup>+</sup>, and Cu(bcp)<sub>2</sub><sup>+</sup> interacting with a range of DNA duplexes, where phen denotes 1,10-phenanthroline, dmp denotes 2,9-dimethyl-1,10-phenanthroline, and bcp denotes 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline. Hypochromism is observed in the visible absorption bands of all three copper(I) complexes, but the bcp complex is unique in that binding to DNA causes the appearance of a measurable luminescence signal at room temperature. At low DNA-P/Cu ratios Cu(bcp)<sub>2</sub><sup>+</sup> appears to bind to DNA polymers in an aggregated form, but at high DNA-P/Cu ratios the complex binds as a monomer. The adduct of the bcp complex with DNA must be relatively rigid in the vicinity of the copper center because solvent-induced, exciplex quenching of the excited state is strongly inhibited. This suggests that the complex binds by intercalation, and emission polarization data support this model. The limiting emission intensity varies with the type of DNA used and is greater with poly(dA-dT)-poly(dA-dT) than with poly(dG-dC)-poly(dG-dC), possibly because propeller twisting facilitates intercalation. Interaction probably occurs within the major groove since T4 DNA, which is glycosylated in the major groove, does not induce monomer emission. None of the duplexes studied induced emission from Cu(dmp)<sub>2</sub><sup>+</sup>, presumably because the dmp complex binds by another mechanism. Yeast tRNA was also effective at inducing emission from Cu(bcp)<sub>2</sub><sup>+</sup>; hence the complex is also capable of intercalating into an A-form duplex.

### Introduction

Metal complexes containing polypyridine and/or 1,10-phenanthroline (phen) ligands have been shown to be useful probes of DNA polymers because of binding interactions that occur in aqueous media.<sup>1-3</sup> Various chemical and physical methods can

be used to characterize these systems. For example, photophysical techniques are being used to obtain information about DNA

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