Possible Reduction Mechanisms. The low solubility and high oxygen sensitivity of the reduced complexes $[Rh(bpy)_2]^0$ and $[Rh(bpy)_2]^-$ in acetonitrile and other organic solvents makes further mechanistic experiments very difficult. We can, by analogy to the known stoichiometric chemistry of rhodium and iridium phosphines with CO_2, propose reasonable mechanistic possibilities for the catalytic chemistry.

The electrochemical results show that the initial CO_2 reduction chemistry originates in the two-electron-reduction product $[Rh(bpy)_2]^-$ and that the proton requirement in the reduction products is derived from the supporting electrolyte. Since $[Rh(bpy)_2]^+$ *must* be reduced by 2e before catalysis occurs, and the reduction takes place at the bpy ligands, the bpy(π^*) levels act as "electron reservoirs" for the net two-electron reduction of CO_2. An interaction between CO_2 and the reduced complex is required to explain the appearance of H_2 as a product and the use of the quaternary ammonium electrolyte as a proton source, whether for the production of formate or of H_2. An appealing set of reactions that may play a role are shown in eq 7 and 8. The first

$$[Rh(bpy)_2]^- + CO_2 \rightarrow [Rh(bpy)_2CO_2]^- \quad (7)$$

$$[Rh(bpy)_2CO_2]^- + N(n\text{-}Bu)_4^+ \rightarrow [Rh(bpy)_2CO_2H] + H_3CCH_2CH{=}CH_2 + N(n\text{-}Bu)_3 \quad (8)$$

step involves binding to the highly reduced, electron-rich, anionic complex. Although the nature of the presumed complex between $[Rh(bpy)_2]^-$ and CO_2 and the mode of CO_2 binding are not known, it is tempting to speculate that CO_2 is carbon-bound. With such binding and extensive electronic donation from the electron-rich metal to CO_2 the oxygen atoms could become sufficiently basic to attack the tetraalkylammonium atoms of the supporting electrolyte. Precedents for oxygen basicity in metal–CO_2 complexes is provided by the examples of $Rh(das)_2(\eta^1\text{-}CO_2)Cl$[19] and $[Co(salen)(CO_2)K(THF)]_n$.[20] Following protonation, a bound formate anion in $[Rh(bpy)_2CO_2H]$ should behave chemically in a fashion analogous to that of bound Cl^- in $[Rh(bpy)_2Cl]$, i.e., rapid dissociation to give $[Rh(bpy)_2]^+$ for reentry into the reduction cycle via eq 9.

$$[Rh(bpy)_2CO_2H] \xrightarrow{CH_3CN} [Rh^{I}(bpy)_2]^+ + H{-}\overset{\overset{O}{\|}}{C}{-}O^- \quad (9)$$

Although such reaction sequences may play a role, especially early in the catalysis, it is clear that the underlying chemistry is far more complex as shown by (1) the appearance of H_2 as a competitive product, (2) the change in the HCO_2^-/H_2 ratio with electrolysis time, (3) the appearance of the black solid during the electrolysis period, and (4) the loss of the well-defined bpy(π^*)-based electrochemistry as the electrolysis proceeds. Nonetheless, when the tetra-*n*-butylammonium ion is used as the source of protons, the catalysts are able to achieve initial formate production rates of ca. 0.2 turnover/min at −1.55 V at a carbon-cloth electrode with a current efficiency of up to 80%.

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Registry No. *cis*-$[Rh(bpy)_2(TFMS)_2](TFMS)$, 116971-15-4; *cis*-$[Rh(bpy)_2Cl_2]Cl{\cdot}2H_2O$, 22710-42-5; *cis*-$[Rh(bpy)_2Cl(TFMS)](TFMS)$, 116971-17-6; *cis*-$[Rh(4,4'\text{-}(t\text{-}Bu)_2bpy)_2Cl_2]Cl$, 116996-77-1; *cis*-$[Rh(4,4'\text{-}(t\text{-}Bu)_2bpy)_2Cl_2](PF_6)$, 116996-79-3; *cis*-$[Ir(bpy)_2Cl_2][TFMS]$, 116971-18-7; *cis*-$[Ir(bpy)_2Cl_2]Cl$, 22710-60-7; *cis*-$[Ir(bpy)_2(TFMS)_2]$-$[TFMS]$, 91030-49-8; $[Ir(bpy)_3][PF_6]_3$, 91042-30-7; *cis*-$[Ir(bpy)_2H_2]$-$[PF_6]$, 91172-41-7; *cis*-$[Ir(bpy)_2(PPh_3)H][PF_6]_2$, 91042-32-9; *cis*-$[Rh(bpy)_2Cl_2][ClO_4]$, 49727-33-5; CO_2, 124-38-9.

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Contribution from the Department of Chemistry,
The University of North Carolina, Chapel Hill, North Carolina 27514

Synthetic Routes to New Polypyridyl Complexes of Osmium(II)

Edward M. Kober, Jonathan V. Caspar, B. Patrick Sullivan,* and Thomas J. Meyer*

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New luminescent complexes of Os(II) that contain either 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen) as the chromophoric acceptor ligand have been prepared by a combination of established and new synthetic methods. Extensive use of Os(IV) and Os(III) precursors, e.g., $Os^{IV}(bpy)Cl_4$ and *mer*-$Os^{III}(PMe_2Ph)_3Cl_3$, has led to the preparation of materials with ancillary ligands such as tertiary phosphines as preparative intermediates, including $Os^{III}(bpy)(PMe_2Ph)Cl_3$ and *cis*-$Os^{II}(phen)(diphosphine)Cl_2$. Further substitution of chloro ligands into complexes such as these results in the formation of emissive complexes of Os(II). Another new synthetic route utilizes the versatile Os(II) precursor $Os(bpy)_2CO_3$, which allows the facile preparation of dicationic, disubstituted species such as $[Os(bpy)_2(norbornadiene)]^{2+}$. Another general procedure, based on the control of solvent and temperature in the substitution chemistry of *cis*-$Os(bpy)_2Cl_2$, has been further developed to produce a variety of new complexes of the types *cis*-$[Os(bpy)_2(L)Cl]^+$ and *cis*-$[Os(bpy)_2(L)_2]^{2+}$, where L is a phosphine, arsine, nitrogen, or olefin donor ligand. In a few cases, phosphine entering groups cause the cis geometry to be unfavorable and new *trans*-$[Os(bpy)_2(L)_2]^{2+}$ complexes have also been isolated. The resultant complexes comprise the largest family of transition-metal-based excited-state reagents with "tunable" photophysical and redox properties available. When possible, the new complexes have been characterized by UV–visible spectroscopy, emission spectroscopy, cyclic voltammetry, and ^{31}P and/or ^1H NMR spectroscopy.

Introduction

Since the discovery of $[Ru(bpy)_3]^{2+}$ as an efficient photosensitizer, an enormous effort has been expended on the synthesis and chemistry of related polypyridine complexes of Ru, particularly those with the ligands 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen). Such complexes have proven to be of value in the development of redox catalysts[1] and in the study of ground- and excited-state electron-transfer processes.[2] The excited states of $[Ru(bpy)_3]^{2+}$ and similar complexes have been utilized in energy

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conversion schemes based on electron-transfer quenching.[3] Other ground-state applications of ruthenium polypyridine complexes have come in the stoichiometric or catalytic redox transformations of organic molecules[4] or small inorganic molecules or ions such as H_2O, Cl^-, NO_2^-, or CO_2.[1,5] Additionally, the possibilities of extending the homogeneous solution chemistry to polymer- or surface-bound complexes or to metal complexes in micelles have been explored, often with encouraging results.[6]

An obvious extension of the ruthenium polypyridine chemistry is to that of the analogous complexes of Os, where similarities in chemical properties have been observed.[7] Because of the lanthanide contraction, metal–ligand both lengths for analogous complexes are very similar, thereby minimizing differences in steric effects and solvation.

In principle, comparisons between the two in reactivity and thermodynamic properties can be rather cleanly associated with electronic factors. Differences in electronic structure exist. They include the following: (1) a larger value of $10Dq$ for Os, which leads to higher energies for d–d excited states; (2) a lower third ionization energy for Os, which leads to a lower redox potential for complexes of M(II) and consequent stabilization of higher oxidation states; (3) greater extension of the metal d orbitals for Os, which can enhance metal–ligand back-bonding; (4) a larger value of λ, the spin–orbit coupling constant, for Os, which causes extensive mixing of excited states of different spin multiplicities.

A limited number of polypyridyl complexes of Os(II) have been reported, and these mainly involve coligands that are "classical", σ-donating in character, rather than the strong-field ligands with well-developed π-acceptor properties that are commonly found in organometallic chemistry.[8-10] The results obtained in earlier work have led to a general assignment of some of the electronic absorption bands,[10] and in several studies the electrochemistry of selected complexes has also been investigated.[11-13] However, given the clear value of polypyridyl complexes of Os(II) in explaining the photochemistry and photophysics of metal to ligand charge-transfer (MLCT) excited states, the underlying synthetic chemsistry has received only scant attention.[14,15]

In this paper the synthesis and characterization of a variety of complexes of the type $[Os^{II}(N\text{-}N)_2(L)(L')]^{n+}$ (N-N = bpy, phen) are reported, particularly where L and L′ are π-acid ligands. For most of the complexes the coordination geometry at the metal is cis with respect to the N-N chelating ligands although for Ru some trans complexes[16] have also been isolated. The synthesis of a series of complexes of the type $[Os^{II}(N\text{-}N)(L)_4]^{n+}$, where the ligands L are not necessarily equivalent, is also reported, and the spectral, electrochemical, and chemical properties of the Os(II) complexes are presented and compared to those of analogous complexes of Ru. Earlier, the syntheses of polypyridyl complexes of Os containing oxo,[17] NO,[18] hydrido and carbonyl,[19] or alkyl/alkene/alkyne[20] ligands based on methods similar to those presented here were reported.

The synthetic chemistry presented here has enabled us to produce an extended series of related complexes having tunable redox properties and, more importantly, having MLCT excited-state properties that can be varied systematically by changing the nonchromophoric ligands.[21,22] An extensive set of previous results is available from attempts to enhance the excited-state properties of $[Ru(bpy)_3]^{2+}$ by replacing the bpy ligand with various other nitrogen heterocycles and diimine ligands.[23] However, the series

Table I. Elemental Analysis Data for Mono(polypyridyl) Complexes

complex	% calcd			% found		
	C	H	N	C	H	N
$Os(bpy)Cl_4$	24.60	1.64	5.74	24.73	1.75	5.60
$Os(phen)Cl_4$	28.14	1.57	5.47	28.30	1.27	5.4
$Os(bpy)(PPhMe_2)Cl_3$	36.58	3.22	4.74	36.30	3.17	4.68
$Os(bpy)(PPh_3)Cl_3$	47.03	3.22	3.92	46.19	3.19	3.59
cis-$Os(bpy)(dppm)Cl_2$	52.43	3.75	3.50	51.28	3.91	2.99
cis-$Os(phen)(dppb)Cl_2$	56.82	3.61	3.16	56.22	3.61	3.04
cis-$Os(phen)(dppy)Cl_2$	54.48	3.58	3.35	54.05	3.42	3.65
$Os(phen)(dppb)(CO_3)^a$	57.33	3.78	3.11	57.52	3.89	3.08
mer-$[Os(bpy)(PEt_3)_3Cl](PF_6)$	38.16	6.06	3.18	37.90	6.02	3.19
mer-$[Os(bpy)(PMe_3)_3Cl](PF_6)$	30.24	4.67	3.71	30.29	5.05	3.50
mer-$[Os(bpy)(PPhMe_2)_3Cl](PF_6)$	43.39	4.39	2.98	43.27	4.46	3.04
mer-$[Os(bpy)(PPh_2Me)_3Cl](PF_6)$	52.20	4.20	2.48	52.06	4.33	2.61
mer-$[Os(bpy)(PPhMe_2)_3NO_2](PF_6)^a$	42.11	4.47	4.33	42.29	4.03	4.25
$[Os(bpy)(diars)_2](PF_6)_2$	29.80	3.31	2.32	30.01	3.62	2.17
$[Os(phen)(diars)_2](PF_6)_2$	31.18	3.27	2.27	31.19	3.03	2.24
$[Os(bpy)(dppm)_2](PF_6)_2$	51.28	3.70	1.99	50.84	3.70	1.91
$[Os(bpy)(dppy)_2](PF_6)_2$	52.10	3.68	1.96	52.06	3.65	1.98
$[Os(phen)(dppy)_2](PF_6)_2{}^b$	55.19	3.91	1.81	55.06	3.81	1.64

[a] H_2O of crystallization. [b] Toluene of crystallization.

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of complexes presented here represents the most extensive series of photochemically and thermally stable photosensitizers known to date and should find application in a variety of energy conversion studies.

Experimental Section

Measurements. Electrochemical data were obtained by cyclic voltammetry with a Princeton Applied Research 173 potentiostat and a "home-built" triangular waveform generator[24] along with a Hewlett-Packard 7015B XY recorder. A platinum-bead working electrode, platinum-wire auxiliary electrode, and saturated sodium chloride calomel electrode (SSCE) were used in a single-compartment-cell configuration. Solution volumes of ca. 3 mL were used that were ca. 10^{-3} M in complex. Spectrograde acetonitrile from Burdick and Jackson was stored over 4-Å molecular sieves but otherwise was used as received. The supporting electrolyte was either tetraethylammonium perchlorate (TEAP) or tetra-*n*-butylammonium hexafluorophosphate (TBAH), which was present in 0.1 M concentration. Solutions were deaerated by nitrogen bubbling for ca. 10 min and were maintained under a nitrogen stream at ambient temperatures (23 ± 2 °C). Calculation of $E_{1/2}$ values was by averaging the potential values for the highest current response on the anodic and cathodic sweeps, which were generally carried out at a scan rate of 200 mV/s. For coulometric experiments, a similar setup was employed except that a three-compartment cell and platinum-gauze working electrodes were used. The current passed was measured by digital coulometer.

Visible and UV spectra were measured by using either Cary 17 or Bausch and Lomb 210 UV recording spectrophotometers. Quantitative measurements were made by using matched quartz 1 cm path length cells with acetonitrile or methylene chloride (Spectrograde from Burdick and Jackson) as solvent. Qualitative measurements to test reaction conditions were made by using quartz 1-cm cells with the solvent typically being a water/acetone mixture.

Infrared spectral measurements were obtained with a Beckman IR 4250 recording spectrophotometer by using KBr pellets.

Proton and ^{31}P (proton decoupled) NMR spectral data were acquired with a Bruker Cryospec WM250 NMR spectrometer at 250 and 100 MHz, respectively. For proton NMR spectra all shift data were reported versus TMS as internal standard. For ^{31}P spectral data 0.1 M phosphoric acid was used as an external standard.

Emission spectral data were obtained for CH_3CN solutions at room temperature on a SLM Model 8000 single-photon-counting spectrofluorimeter. The values of the emission spectral maxima data are corrected for photomultiplier wavelength response with programs supplied by the manufacturer.

Elemental analyses (C, H, N) were provided by Integral Microanalytic Laboratories, Inc., Raleigh, NC 27514. The results are given in Tables I and II.

Abbreviations. The following abbreviations for ligands are used: bpy = 2,2′-bipyridine; phen = 1,10-phenanthroline; N-N = bpy or phen; py = pyridine; pz = pyrazine; 4,4′-bpy = 4,4′-bipyridine; norb = norbornadiene; DMSO = dimethyl sulfoxide; DMF = dimethylformamide; S = weakly coordinated solvent molecule (EtOH, H_2O); P = monodentate tertiary phosphine or arsine ligand; P-P = bidentate phosphine or arsine ligand; das = *cis*-1,2-bis(dimethylarsino)benzene; dppb = *cis*-1,2-bis(diphenylphosphino)benzene; dppe = 1,2-bis(diphenylphosphino)ethane; dppm = bis(diphenylphosphino)methane; dppy = *cis*-1,2-bis(diphenylphosphino)ethylene; dpae = 1,2-bis(diphenylarsino)ethane. Note that the cis designation for the complexes refers to the disposition of the bpy or phen ligands.

Materials. $(NH_4)_2OsCl_6$ was purchased from Englehard. $Os(bpy)_2(CN)_2$ was prepared as previously described.[10] The polypyridyl ligands were purchased from Aldrich Chemical Co. and were used as received. Acetonitrile for preparations or chromatography was of spetroscopic grade, purchased from Fisher Chemical Co. All other materials were of reagent grade, obtained from commercial sources and used without further purification. Acetonitrile/toluene mixtures for chromatographic purposes were redistilled for recycling. A 4/1:1 (v/v) azeotrope of acetonitrile/toluene occurs at 81.1 °C (a fraction distilling between 79 and 82 °C was collected), followed by pure toluene at 110 °C (the fraction distilling above 105 °C was collected). These fractions were then dried by passing them through a column of anhydrous $MgSO_4$.

General Syntheses of $(N-N)_2$ Complexes. Complexes of the type $[Os(N-N)_2(L)Cl]^+$ and $[Os(N-N)_2(L)_2]^{2+}$ were prepared and isolated as PF_6^- salts by one of the following three methods: (A) $Os(N-N)_2Cl_2$ and L were heated at reflux in a ca. 1:1 $EtOH/H_2O$ solution. Larger proportions of EtOH were used when required to dissolve the reacting ligand. Upon completion of the reaction (4–8 h), excess NH_4PF_6 was added, EtOH was removed by rotary evaporation, and the salt was isolated by filtration. (B) $Os(N-N)_2Cl_2$ and L were heated at reflux in ethylene glycol. Upon completion of the reaction (4–8 h), the mixture was allowed to cool, and then water and excess NH_4PF_6 were added. The precipitated complex was isolated by filtration and dried. (C) Slightly greater than 2 equiv of HPF_6 or *p*-toluenesulfonic acid was added to a suspension of $Os(N-N)_2CO_3$ in either dimethylformamide or 1-butanol. The solution was stirred for several minutes until it appeared that all of the solid had dissolved to give a dark brown solution. The ligand L was added and the solution heated at reflux. When the reaction was complete (8–12 h), the cooled solution was added slowly to a 10-fold excess of ether, causing the complex to precipitate or separate as an oil. The product was isolated by filtration or decantation and dissolved in a water/acetone mixture. An excess of solid NH_4PF_6 was added, the acetone removed by rotary evaporation, and the precipitated complex isolated by filtration.

The syntheses were typically monitored for the extent of reaction by using UV–visible spectroscopy after dilution of an aliquot of the reaction mixture with water/acetone. Syntheses using methods B and C were routinely conducted under a nitrogen blanket although an inert atmosphere was only required if the added, free ligand was susceptible to oxidation. To ensure complete metathesis to the PF_6^- salt, a second

Table II. Elemental Analysis Data for Bis(polypyridyl) Complexes

complex	% calcd			% found		
	C	H	N	C	H	N
$Os(bpy)_2CO_3$[a]	42.39	3.22	9.51	42.78	2.60	9.41
$[Os(bpy)_2(py)Cl](PF_6)$	39.40	2.78	9.19	39.31	2.55	9.00
$[Os(bpy)_2(4,4'\text{-bpy})Cl](PF_6)$[a]	42.05	3.03	9.80	42.01	2.85	9.83
$[Os(bpy)_2(CH_3CN)Cl](PF_6)$	36.50	2.64	9.67	36.13	2.38	9.54
$[Os(bpy)_2(pz)Cl](PF_6)$[b]	39.46	3.17	10.23	39.26	2.96	10.14
$[Os(bpy)_2)(AsPh_3)Cl](PF_6)$	46.15	3.14	5.67	46.74	3.05	5.76
$[Os(bpy)_2(PPh_3)Cl](PF_6)$	48.29	3.30	5.93	47.96	2.98	5.91
$[Os(bpy)_2(py)_2](PF_6)_2$	37.90	2.76	8.84	37.73	2.53	8.75
$[Os(bpy)_2(4,4'\text{-bpy})_2](PF_6)_2$[c]	38.51	2.82	8.99	38.39	2.28	8.91
$[Os(bpy)_2(py)(pz)](PF_6)_2$[c]	34.69	3.49	9.77	34.76	3.01	9.55
$[Os(phen)_2(CH_3CN)_2](PF_6)_2$	36.45	2.40	9.11	36.15	2.12	8.57
$[Os(bpy)_2(PPh_2Me)NO_2](PF_6)$	44.35	3.27	7.84	44.45	3.42	7.96
$[Os(bpy)_2(CH_3CN)_2](PF_6)_2$	32.96	2.52	9.61	32.79	2.25	9.50
$[Os(bpy)_2(pz)_2](PF_6)_2$[a]	34.64	2.68	11.54	34.56	2.13	11.51
$[Os(bpy)_2(PPh_3)NO_2](PF_6)$	47.75	3.28	7.33	47.76	3.38	7.09
trans-$[Os(phen)_2(PPhMe_2)_2](PF_6)_2$	43.02	3.43	5.02	42.96	3.19	4.98
trans-$[Os(bpy)_2(PPh_2Me)_2](PF_6)_2$	46.31	3.56	4.70	46.62	3.63	4.75
$[Os(bpy)_2(diars)](PF_6)_2$	33.41	2.99	5.19	33.17	2.53	5.06
$[Os(phen)_2(diars)](PF_6)_2$	36.25	2.86	4.97	36.92	2.44	4.83
$[Os(phen)_2(CO)Cl](PF_6)$[d]	38.21	2.14	6.99	38.07	1.73	7.20
$[Os(bpy)_2(CO)Cl](PF_6)$	35.47	1.96	7.88	35.35	1.96	7.79
cis-$[Os(bpy)_2(PPh_2Me)_2](PF_6)_2$[d]	45.21	3.51	4.54	44.99	3.41	4.49
$[Os(bpy)_2(dppm)](PF_6)_2$	45.93	3.25	4.76	46.09	3.47	4.65
$[Os(phen)_2(dpae)](PF_6)_2$	47.97	3.22	4.48	47.81	3.02	4.61
$[Os(bpy)_2(dppe)](PF_6)_2$[a]	45.70	3.48	4.64	45.31	3.48	4.60
$[Os(phen)_2(dppe)](PF_6)_2$[a]	47.86	3.37	4.46	47.94	3.03	4.20
$[Os(phen)_2(dppm)](PF_6)_2$	48.05	3.13	4.57	48.06	2.88	4.22
$[Os(bpy)_2(dppb)](PF_6)_2$	48.47	3.27	4.52	48.38	3.27	4.28
$[Os(bpy)_2(dppy)](PF_6)_2$	46.47	3.22	4.71	46.41	3.10	4.57
$[Os(phen)_2(dppy)](PF_6)_2$[a]	47.78	3.21	4.46	47.73	2.70	4.35
$[Os(bpy)_2(CNMe)_2](PF_6)_2$	32.95	2.52	9.61	32.72	2.88	9.52
$[Os(bpy)_2(CNCH_2Ph)_2](PF_6)_2$	42.11	2.92	8.19	41.45	2.80	7.89
$[Os(bpy)_2(CO)(NO_2)](PF_6)$	34.96	2.24	9.71	35.12	2.08	9.61
$[Os(bpy)_2(norb)](PF_6)_2$	36.65	2.71	6.33	37.19	2.67	6.41
$[Os(bpy)_2(DMSO)_2](PF_6)_2$	30.38	2.97	5.91	30.35	2.70	5.79

[a] H_2O of crystallization. [b] Acetone of crystallization. [c] $2H_2O$ of crystallization. [d] $1/2CH_2Cl_2$ of crystallization.

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precipitation from NH_4PF_6/water/acetone was often performed.

The crude reaction products isolated by any of the above methods were purified by column chromatography by using neutral alumina as the column support and acetonitrile/toluene mixtures as the eluent. The separations were typically monitored by visible absorption spectra and by their intense luminescence (with the use of a hand-held UV light source) during chromatography. The monocationic products could be eluted with 1:1 acetonitrile/toluene mixture, while the dications required at least a 2:1 mixture. A small percentage (0.5–2%) of methanol was sometimes added to increase the rate of elution. The solvent was removed by rotary evaporation, the complex dissolved in a small volume of acetonitrile or acetone, and the acetonitrile solution added dropwise to a large excess of stirred ether. The precipitated complex was collected by filtration and washed several times with fresh ether (ca. 30 mL).

Complexes of the type $[Os(N\text{-}N)_2(L)Cl](PF_6)$ were typically the first products eluted from the column and could be isolated in 70–90% yields. Occasionally, a small amount of unidentified yellow material preceded the chloro complexes on the column, but it was easily separated and discarded. The disubstituted products, which were collected at long elution times, were sometimes contaminated with monosubstituted products that eluted first. In these cases a second chromatographic separation was performed. The requirement for a second purification cycle decreased the 70–90% yields to 30–70% yields.

Complexes synthesized by the methods described above are shown in Tables I and II. The synthetic procedures used for other complexes are described below.

***cis*-Os(N-N)$_2$Cl$_2$.** The *cis*-dichloro complex was prepared by the method of Buckingham et al.,[8] except that $(NH_4)_2OsCl_6$ was used as the osmium percursor since NH_4Cl remains in solution. An alternate synthesis involved the reaction between $(NH_4)OsCl_6$ and 2 equiv of bpy or phen in ethylene glycol heated at reflux. In a typical preparation $(NH_4)_2OsCl_6$ (1.0 g) and bpy (0.72 g) in 50 mL of ethylene glycol were heated at reflux for 45 min under N_2. Since the crude reaction mixture contained both *cis*-$Os(bpy)_2Cl_2$ and *cis*-$[Os(bpy)_2Cl_2]^+$, an equal volume of saturated aqueous sodium dithionite was added to the cooled reaction mixture in order to reduce excess Os(III) to Os(II). The purple-black precipitate that had formed was isolated by filtration, washed with water to remove $[Os(bpy)_3]^{2+}$ and other ionic products, and washed with large volumes of ether. Yields in excess of 85% were routinely obtained.

Os(N-N)$_2$CO$_3$. To a suspension of 500 mg of *cis*-$Os(N\text{-}N)_2Cl_2$ in dearated water was added 2 g of Na_2CO_3. The resulting mixture was heated at reflux under an atmosphere of N_2. After 2 h the solution was cooled to room temperature, another 2 g of Na_2CO_3 was added, and the solution was heated to reflux again. This procedure was repeated once more, at which time the black microcrystalline product was isolated from the cooled reaction mixture by filtration. The product was washed several times with 20 mL of basic water (pH >9) until the washings appeared pale brown. The complex then was washed twice with 20 mL of ether and dried in a vacuum oven at 70 °C for 8 h. The yield was 0.36 g (70%). IR: ν(C=O) 1660 cm^{-1}.

***cis*-[Os(N-N)$_2$(CH$_3$CN)$_2$](PF$_6$)$_2$.** A 0.1-g amount of $Os(N\text{-}N)_2CO_3$ was suspended in 30 mL of CH_3CN, and 5 drops of HPF_6 (65%) were added. After the solution was heated at reflux for 1 h, the complex was isolated as the PF_6^- salt and purified by chromatography. IR: ν(C≡N) 2263 cm^{-1}.

***cis*-[Os(bpy)$_2$(CNCH$_3$)$_2$](PF$_6$)$_2$.** A 0.06-g amount of *cis*-$Os(bpy)_2(CN)_2$, 1.0 mL of iodomethane, and 0.1 g of KPF_6 were added to 30 mL of CH_3CN, and the solution was heated at reflux for 4 h. The complex was isolated as the PF_6^- salt and purified by chromatography. IR: ν(C≡N) 2150, 2190 cm^{-1}.

***cis*-[Os(bpy)$_2$(CNCH$_2$Ph)$_2$](PF$_6$).** The analogous benzyl isocyanide complex was prepared as described above except that 1.0 mL of benzyl bromide was used in place of iodomethane. IR: ν(C≡N) 2130, 2170 cm^{-1}.

***cis*-[Os(bpy)$_2$(py)(pz)](PF$_6$).** A 0.05-g amount of $Os(bpy)_2CO_3$ was suspended in 30 mL of dimethylformamide, and 4 drops of HPF_6 (65%) were added while a slow stream of N_2 was blown through the solution. The solution was kept under N_2 and heated at reflux for 15 min to ensure complete formation of the $(DMF)_2$ complex. After cooling of the solution to room temperature, 180 mg of pyrazine was added and the solution heated at reflux for another 1 h. After the solution was cooled a second time, 4 mL of pyridine was added and the solution heated at reflux for an additional 1 h. The complex was isolaed as the PF_6^- salt as described above and purified by chromatography. The minor products *cis*-$[Os(bpy)_2(py)_2](PF_6)_2$ and *cis*-$[Os(bpy)_2(pz)_2](PF_6)_2$ could also be isolated from the reaction mixture. The former preceded and the latter followed the desired product as it eluted from the column.

***cis*- and *trans*-[Os(bpy)$_2$(PPh$_2$Me)$_2$](PF$_6$)$_2$.** Both bis(phosphine) salts were obtained in roughly equal amounts from the same reaction. *cis*-$Os(bpy)_2Cl_2$ (150 mg, 1 equiv) and PPh_2Me (240 mg, 5 equiv) were heated at reflux in ethylene glycol for 12 h followed by chromatography with 2:1 toluene/CH_3CN. The trans isomer is dark red and was eluted first, followed by the red-orange cis isomer. NMR data (recorded in CH_3CN) are as follows. cis complex: $^{31}P\{^1H\}$ δ −24.5 (s); ^1H δ 1.9 (d, $^2J_{P\text{-}H}$ = 8 Hz, 6 H, PPh_2Me). trans complex: $^{31}P\{^1H\}$ δ −15.5 (s); ^1H δ 1.2 (t, $J_{P\text{-}H}$ = 3 Hz, 6 H, PPh_2Me).

***trans*-[Os(bpy)$_2$(PMe$_2$Ph)$_2$](PF$_6$)$_2$.** This salt was prepared as above except that PMe_2Ph was used as the ligand. For dimethylphenylphosphine as the ligand the cis isomer was not completely characterized due to difficulty in purification.

***cis*-[Os(bpy)$_2$(L)(NO$_2$)](PF$_6$) (L = CO, PPh$_3$, PPh$_2$Me).** Salts containing the nitro group were prepared by allowing ca. 150 mg of *cis*-$[Os(bpy)_2(L)Cl](PF_6)$ to react with a large excess of $NaNO_2$ (1.0 g) in 50 mL of 1:1 ethylene glycol/water heated at reflux. The reaction times were 26 h for L = CO, 3 h for L = PPh_3, and 6 h for L = PPh_2Me. The complexes were isolated as PF_6^- salts and purified by chromatography by using 2:1 toluene/CH_3CN as the eluent. Yields were 70–90%. ν(CO) = 1965 cm^{-1}.

***cis*-[Os(bpy)$_2$(PPh$_2$Me)(CH$_3$CN)](PF$_6$)$_2$.** The mixed nitrile–phosphine complex was prepared by dissolving *cis*-$[Os(bpy)_2(PPh_2Me)(NO_2)](PF_6)$ in a minimal amount of CH_3CN and adding several drops of concentrated HPF_6. The initial red solution became colorless, indicating the formation of *cis*-$[Os(bpy)_2(PPh_2Me)(NO)](PF_6)_3$. The solution was added dropwise to a large excess of ether to precipitate this pale yellow intermediate. It was collected and redissolved in CH_3CN, and 1 equiv of $AsPh_4N_3$ was added to the solution. The reaction mixture was allowed to stir for 4 h, and then the complex was precipitated by addition to ether. After purification by chromatography by using 2:1 toluene/CH_3CN as eluent, the desired salt was isolated in 20% yield.

Os(N-N)Cl$_4$. These two compounds were prepared by slight modifications of the procedure of Buckingham et al.[9b] In a typical reaction $(NH_4)_2OsCl_6$ (1.0 g, 1.0 equiv) was dissolved in 50 mL of 3 N HCl at 70 °C. To the mixture was slowly added a solution of N-N (0.42 g, 1.02 equiv) dissolved in a minimum volume of 3 N HCl, and the salt $[OsCl_6](phenH)(NH_4)$ or $[OsCl_6](bpyH_2)$ precipitated from solution. After the mixture was cooled for 2 h at 0 °C, the product was filtered out, washed successively with cold 3 N HCl, cold water, and ether, and then dried at 70 °C under vacuum for 48 h. The well-dried salts were pyrolyzed in the solid state at 290 °C (molten salt bath, i.e., a mixture of Na and K nitrates) under argon to give the desired products. Reaction times depended upon the scale with a minimum reaction time of ca. 5 h. The progress of the reaction was monitored by periodically withdrawing an aliquot of the reaction mixture and analyzing the contents by using cyclic voltammetry in DMF with 0.1 M TEAP as supporting electrolyte. At intermediate reaction times for the bpy complex, a wave at −0.31 V appeared, which might be attributable to a "dangling bpy" complex. The reaction was continued until the intermediate had disappeared. The brown to yellow-brown products were extremely insoluble in most solvents. The only purification required was to stir the product for 12 h in 3 N HCl and then for 4 h in nitromethane, followed by filtration and washing with ether.

Os(bpy)(PMe$_2$Ph)Cl$_3$ and [Os(bpy)(PMe$_2$Ph)$_3$Cl](PF$_6$). To 20 mL of deoxygenated 2-methoxyethanol were added 150 mg of $Os(bpy)Cl_4$ and 2.0 g of PMe_2Ph in an inert-atmosphere box. Upon addition of the phosphine, the solution began to turn red-purple over a period of ca. 1–2 min. The mixture was heated at reflux for 1 h and then allowed to cool to room temperature, at which time the crystalline, deep red complex was filtered out and air-dried. Recrystallization from 1:1 methylene chloride/ethanol by using the solvent gradient method gave 84 mg (46%) of pure trichloro product.

An aqueous NH_4PF_6 solution was added to the filtrate of the original reaction solution and the majority of the liquid decanted from a greasy precipitate. The precipitate was filtered out and washed with H_2O followed by ether. It was subsequently dissolved in 2:1 toluene/acetonitrile solution and chromatographed with the same mixture. Two predominant fractions were separated, yielding 30 mg of the trichloro complex as the first band and 45 mg of $[Os(bpy)(PMe_2Ph)_3Cl](PF_6)$ as the second band. The yield of the latter complex based on Os was 16%.

***mer*-[Os(bpy)(P)$_3$Cl](PF$_6$) (P = PPh$_2$Me, PPhMe$_2$, PMe$_3$, PEt$_3$).** In a typical reaction, $Os(bpy)Cl_4$ (100 mg, 1.0 equiv) was allowed to react with $PPhMe_2$ (140 mg, 5.0 equiv) in ethylene glycol heated at reflux for 3 h. The ionic products were isolated as PF_6^- salts and purified as described above. Typical yields were 80–90%. $[Os(bpy)(PMe_2Ph)_3Cl](PF_6)$ could also be prepared in high yield by the reaction between *mer*-$Os(PMe_2Ph)_3Cl_3$[25] and bpy in ethylene glycol heated at reflux for 2 h. NMR (proton data obtained in CD_3CN; phosphorus data in CH_3CN) spectra are as follows. PPh_2Me complex: ^1H δ 1.4 (t, $J_{P\text{-}H}$

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= 4 Hz, 6 H), 2.4 (d, J_{P-H} = 8 Hz, 3 H); $^{31}P\{^1H\}$ δ −35.0 (t, $^2J_{P-P}$ = 18 Hz), −36.6 (d, $^2J_{P-P}$ = 17 Hz). $PPhMe_2$ complex: ^1H δ 1.1 (t, J_{P-H} = 4 Hz, 6 H), 1.2 (t, J_{P-H} = 4 Hz, 6 H), 2.0 (d, J_{P-H} = 6 Hz, 6 H); $^{31}P\{^1H\}$ δ −33.9 (t, $^2J_{P-P}$ = 19 Hz), −44.5 (d, $^2J_{P-P}$ = 19 Hz). PMe_3 complex: ^1H δ 0.9 (t, J_{P-H} = 4 Hz, 18 H), 1.7 (d, J_{P-H} = 8 Hz, 9 H); $^{31}P\{^1H\}$ δ −49.7 (t, $^2J_{P-P}$ = 21 Hz), −41.3 (d, $^2J_{P-P}$ = 20 Hz). PEt_3 complex: $^{31}P\{^1H\}$ δ −34.9 (t, $^2J_{P-P}$ = 18 Hz), −36.4 (d, $^2J_{P-P}$ = 17 Hz).

$Os(bpy)(PPh_3)Cl_3$. The trichloro complex was prepared as described above except that 150 mg of $Os(bpy)Cl_4$ and 250 mg of PPh_3 were used. The mixture was heated at reflux for 5 h and cooled to room temperature, and the solid was recrystallized from 1:1 CH_2Cl_2/EtOH, giving 144 mg (67%) of pure product.

$[Os(N-N)(dppm)_2](PF_6)_2$. To a suspension of 150 mg of dppm in 15 mL of glycerol was added 50 mg of $Os(N-N)Cl_4$. The mixture was heated at reflux for 15 min accompaned by vigorous stirring. After cooling of the mixture to room temperature, 10 mL of H_2O and 10 mL of saturated aqueous NH_4PF_6 were added while vigorous stirring was maintained. The resulting yellowish brown solid was collected by filtration and washed copiously with H_2O, ether, and toluene. The precipitate was dissolved in ca. 60 mL of 1:1 CH_3CN/toluene and the CH_3CN slowly removed by rotary evaporation. The resulting bright yellow, microcrystalline product was isolated by filtration, washed with ether, and air-dried. The yield was 74 mg (54%). The complex was found to be peculiarly unstable to the chromatographic conditions used for purifying the majority of the complexes in this study.

$[Os(N-N)(P-P)_2](PF_6)_2$ (P-P = dppy, das). These salts were all prepared in a manner similar to that described for the dppm complex above. In a typical reaction, $Os(phen)Cl_4$ (150 mg, 1.0 equiv), and dppy (406 mg, 3.5 equiv) were heated at reflux in 40 mL of ethylene glycol for 4 h. The complex was isolated as the PF_6^- salt, which was purified by chromatography. Typical yields were 70–80%.

***cis*-$Os(N-N)(P-P)Cl_2$ (P-P = dppm, dppy, dppb).** In a typical reaction, 200 mg of $Os(bpy)Cl_4$ and 400 mg of dppm (2.5 equiv) were added to 25 mL of diglyme, and the reaction mixture was heated at reflux for 4 h. The mixture was cooled and 75 mL of ether was added, resulting in the precipitation of a greenish brown solid. The solid was collected by filtration and dissolved in CH_2Cl_2, and the solution was slowly dripped into a large excess of ether. Filtration of the suspension yielded a dark green solid, which was washed with absolute EtOH and ether and then air-dried. The yield was 203 mg (63%).

$Os(N-N)(P-P)CO_3$ (P-P = dppb, dppm). In a typical reaction, 200 mg of the corresponding *cis*-dichloro complex was suspended in 25 mL of H_2O and 1 g of Na_2CO_3 was added. The mixture was heated at reflux while vigorous stirring was maintained for 5 h. After the reaction mixture had cooled to room temperature, the solid was isolated by filtration and washed copiously with water and then ether. The solid was dissolved in CH_2Cl_2 (5–25 mL) and the solution added dropwise to ca. 200 mL of stirring ether. The reprecipitated solid was isolated by filtration (65–75% yield).

***mer*-$[Os(bpy)(PMe_2Ph)_3(NO_2)](PF_6)$.** To 150 mg of *mer*-$[Os(bpy)(PMe_2Ph)Cl](PF_6)$ suspended in 50 mL of 1:1 ethylene glycol/water was added 500 mg of $NaNO_2$. The mixture was heated at reflux under a N_2 atmosphere for 3 h, after which time 75 mL of aqueous NH_4PF_6 was added to precipitate the complex. The crude product was washed with H_2O and ether and then air-dried. Chromatography with 2:1 toluene/CH_3CN yielded 91 mg of the red-brown product.

$[Os(N-N)(py)_4](PF_6)_2$. To 100 mg of $Os(N-N)Cl_4$ suspended in 40 mL of 1:1 ethylene glycol/water was added 10 mL of pyridine. The mixture was heated at reflux under a N_2 atmosphere for 6 h, after which time the solution had changed from the red-brown color of $[Os(N-N)(py)_3Cl]^+$ to the green color of $[Os(N-N)(py)_4]^{2+}$. The solution was cooled to room temperature, and the complex was precipitated by the addition of aqueous NH_4PF_6. The green salt was purified by chromatography and isolated in 60% yield.

Results and Discussion

Synthesis of (N-N) Derivatives. The synthetic methods for generating complexes containing a single polypyridyl ligand based on the high-valent precursors $Os(N-N)Cl_4$[9b] and *mer*-$Os(P)_3Cl_3$[25] are summarized in Scheme I. Although complexes of the type $Os(N-N)Cl_4$ have been known for some years, a detailed investigation of their substitution chemistry has not appeared. A more convenient pyrolytic preparation of the $Os(N-N)Cl_4$ complexes is given in the Experimental Section along with appropriate conditions for substitution of up to three chloro ligands by tertiary phosphines. As an example of the substitution chemistry, the reaction of $Os(N-N)Cl_4$ in 2-methoxyethanol heated at reflux in the presence of either PPh_3 or PMe_2Ph results in a red to red-purple solution from which the red Os(III) complex $Os(N-N)(P)Cl_3$ can be isolated in moderate yield. As a side product in the filtrate, the complex *mer*-$[Os(N-N)(PMe_2Ph)_3Cl](PF_6)$ can be isolated in low yield (see below). No effort was made to assign the stereochemistry of the trichloro products.

Under the more vigorous conditions of ethylene glycol heated at reflux, several phosphines (PMe_2Ph, PPh_2Me, PEt_3) react with $Os(bpy)Cl_4$ to give the corresponding *mer*-$[Os(bpy)(P)_3Cl]^+$ complexes (see Scheme I). In all cases the $^{31}P\{^1H\}$ NMR spectra display a doublet and a triplet, which is consistent with either a fac or mer structure. However, the equivalent trans phosphines are found to be "virtually" coupled to the methyl protons (or methylene protons for PEt_3), an observation that is sufficient to establish the mer stereochemistry.[26]

Further substitution of $[Os(bpy)(P)_3Cl]^+$ with excess phosphine was not observed to a significant degree. Only for PMe_2Ph were small amounts of a product with the properties expected for $[Os(bpy)(P)_4]^{2+}$ observed during chromatography. The inability to obtain tetrasubstitution appears to be mostly due to steric congestion since $[Os(N-N)(py)_4]^{2+}$ can be readily synthesized from $Os(N-N)Cl_4$ by heating with a large excess of pyridine in a refluxing ethylene glycol/water solution. However, relatively facile chloro substitution was found for the reaction between $[Os(bpy)(P)_3Cl]^+$ and nitrite ion in polar, high-boiling reaction media (eq 1). The product is presumed to have retained the mer

$$mer\text{-}[Os(bpy)(P)_3Cl]^+ + NO_2^- \xrightarrow{HO\frown OH} mer\text{-}[Os(bpy)(P)_3(NO_2)]^+ + Cl^- \quad (1)$$

stereochemistry since the same high-temperature reaction conditions were used in the synthesis of the parent chloro complex.

The reaction between $Os(N-N)Cl_4$ and bidentate phosphine ligands (such as dppm, dppb, and dppy) in diglyme heated at reflux gives the dark green or red-brown complexes *cis*-$Os(N-N)(P-P)Cl_2$ directly from the reaction mixture. The assignment of the cis stereochemistry is based solely on their reactivity. The presumed *cis*-dichloro complexes undergo reactions under mild conditions with neutral ligands (such as CO or PMe_2Ph) to give the known monosubstituted complexs that have the cis stereochemistry (eq 2).[19] In a similar manner, treatment of several of the dichloro

$$cis\text{-}Os(N\text{—}N)(P\text{—}P)Cl_2 + L \xrightarrow{HO\frown OMe} cis\text{-}[Os(N\text{—}N)(P\text{—}P)(L)Cl]^+ + Cl^- \quad (2)$$

complexes in hot aqueous ethanol with a large excess of Na_2CO_3 yields a carbonato complex with the required cis stereochemstry of the P-P and N-N ligands (eq 3). The use of carbonato com-

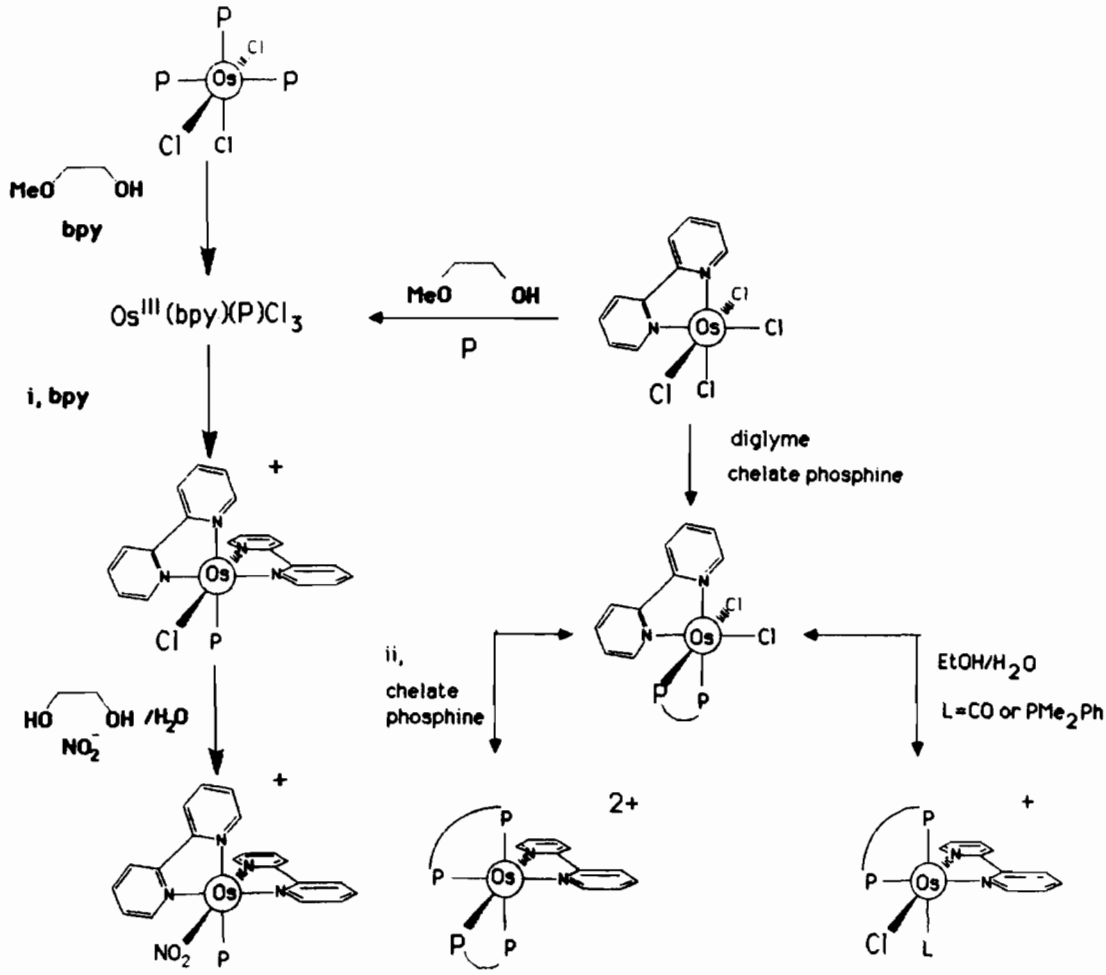
$$Os(N-N)(P-P)Cl_2 + CO_3^{2-} \xrightarrow{EtOH/H_2O} Os(N-N)(P-P)(CO_3) + 2Cl^- \quad (3)$$

plexes as synthetic reagents will be discussed in a later section. As indicated above, the use of thermal conditions in the reaction between bidentate phosphine or arsine ligands and $Os(N-N)Cl_4$ results in good to excellent yields of the bright yellow complexes $[Os(N-N)(P-P)_2]^{2+}$ (P-P = dppy, dppm, das). Interestingly, while dppy and das form complexes effectively in ethylene glycol heated at reflux, dppm requires the use of the higher boiling solvent glycerol. The necessity for more vigorous conditions may arise because of the unfavorable bite angle of the dppm ligand at the osmium center.

Reactions of the precursor *mer*-$Os(P)_3Cl_3$ (P = PMe_2Ph, PEt_3) with bpy can also be used as an alternate route to complexes of Os(II). While reaction in toluene between *mer*-$Os(PMe_2Ph)_3Cl_3$ and a stoichiometric quantity of bpy results in very little change after ca. 2 h, the same reaction in 2-methoxyethanol produces a mixture of products that includes principally $Os(bpy)(PMe_2Ph)Cl_3$, *mer*-$[Os(bpy)(PMe_2Ph)_3Cl]^+$, and *cis*-$[Os(bpy)_2(PMe_2Ph)Cl]^+$. A small amount of material identified by elemental analysis as $Os(bpy)(PMe_2Ph)_2Cl_2$ was also isolated, but no attempt was made

(26) Jenkins, J. M.; Shaw, B. L. *J. Chem. Soc. A* **1966**, 770.

Scheme I[a]



[a] Conditions: (i) the preparation of $[Os(chelate)_2(phosphine)Cl]^+$ was by the direct reaction between the chelate and *mer*-$Os(phosphine)_3Cl_3$ under forcing conditions; (ii) the preparation of $[Os(chelate)(diphos)_2]^{2+}$ was by the direct reaction between $Os(chelate)Cl_4$ and the diphosphine under forcing conditions (see text).

to maximize its formation. The reaction at the same stoichiometry but in ethylene glycol heated at reflux for 2 h leads to a moderate yield (ca. 50%) of *mer*-$[Os(bpy)(PMe_2Ph)_3Cl]^+$. If *mer*-$Os(PMe_2Ph)_3Cl_3$ is heated with a 20-fold excess of phen in ethylene glycol at reflux, the complex *cis*-$[Os(phen)_2(PMe_2Ph)Cl]^+$ is formed in high yield.

Synthesis of $(N\text{-}N)_2$ Complexes from *cis*-Dichloro Precursors. The use of the complexes *cis*-$Os(N\text{-}N)_2Cl_2$ as precursors to complexes of the type *cis*-$[Os(N\text{-}N)_2(L)Cl]^+$ and *cis*-$[Os(N\text{-}N)_2L_2]^{2+}$ is an extension of earlier synthetic routes described by Buckingham et al.[8-11] Although the preparations of the *cis*-$Os(N\text{-}N)_2Cl_2$ complexes are adequately described in the earlier work, we have developed a somewhat easier "one-pot" procedure from which large quantities of the dichloride can be isolated.[27] The one-pot procedure should have wide applicability in the preparation of ring-substituted bpy and phen derivatives and in the preparation of complexes containing similar diimine ligands.

The procedure involves heating stoichiometric quantities of the N-N chelating ligand and $(NH_4)_2OsCl_6$ in ethylene glycol for 45 min (1–3 mM scale; see Experimental Section) followed by cooling of the reaction mixture, addition of aqueous sodium dithionite to reduce Os(III) to Os(II), and collection by filtration, followed by washing of the purple-brown solid product. The selection of mono- vs disubstitution products in the reactions between *cis*-$Os(N\text{-}N)_2Cl_2$ and excess ligand (L) depends principally upon the temperature used, as will be indicated below. The synthetic methods used for the preparation of the new $(N\text{-}N)_2$ complexes are summarized in Scheme II.

When *cis*-$Os(bpy)_2Cl_2$ is heated at reflux in $EtOH/H_2O$ solution, the sparingly soluble purple-brown starting complex slowly dissolves to give a brown solution. The visible spectrum of the solution, with λ_{max} at 525, 437, and 365 nm and weaker bands at 770 and 700 nm, is consistent with that expected for the solvated species *cis*-$[Os(bpy)_2(S)Cl]^+$ (S = H_2O, EtOH). The dissociation of halide and the accompanying spectral shifts are consistent with those found for the Ru analogues, where solvation is well established.[28]

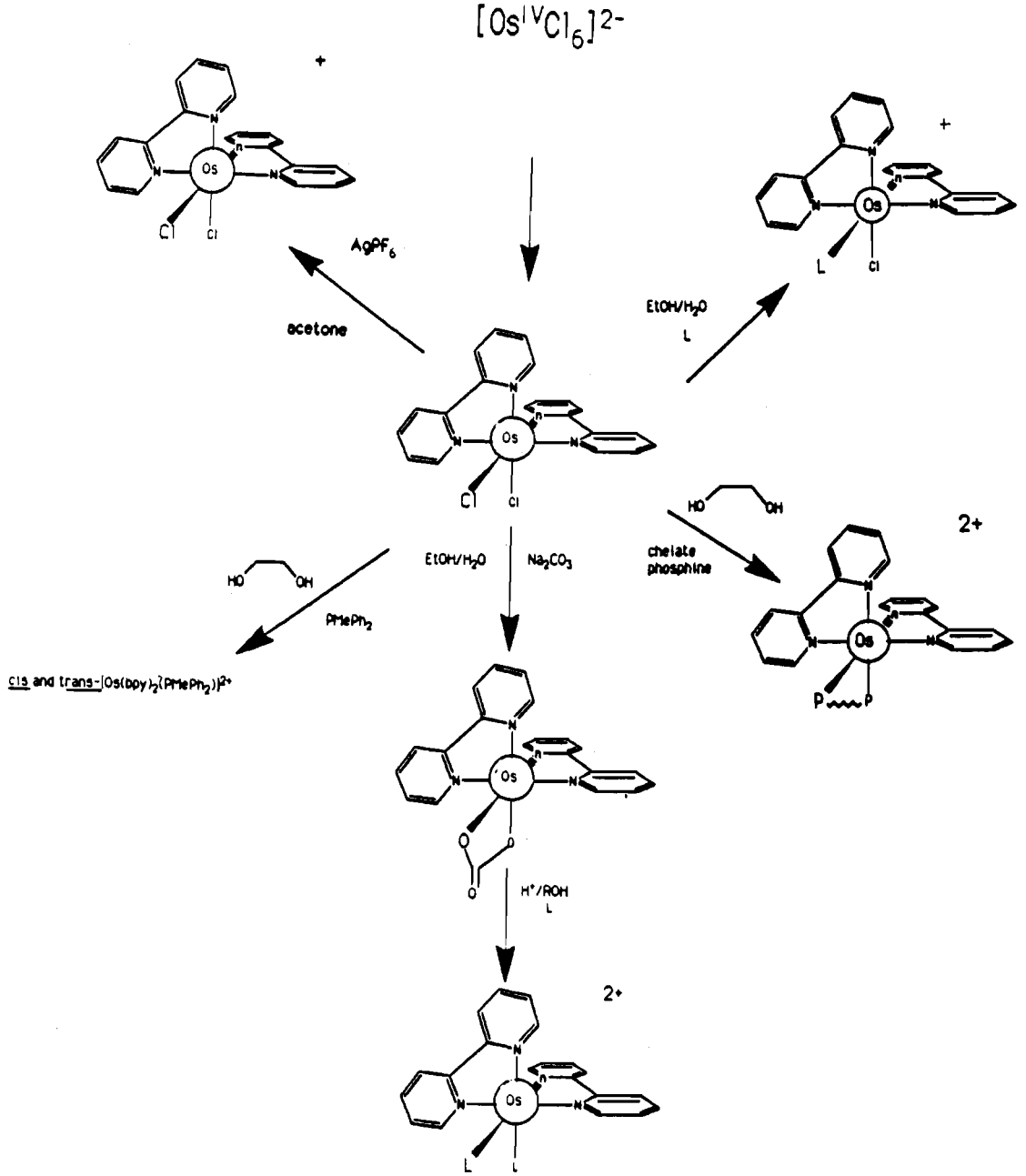
The reactions between *cis*-$Os(N\text{-}N)_2Cl_2$ and excess ligand L (such as phosphines, amines, or unsaturated hydrocarbons) in $EtOH/H_2O$ at reflux proceed through the solvated complexes as intermediates to give the monosubstituted products *cis*-$[Os(N\text{-}N)_2(L)Cl]^+$ in ca. 3–12 h, depending on L. The conditions outlined in Table III and the general procedures given in the Experimental Section are meant to be used together as a guide to the preparation of specific complexes. Prolonged heating in the presence of excess L results in the slow but efficient production of complexes of the type *cis*-$[Os(N\text{-}N)_2(L)_2]^{2+}$; typically, several days were required for completion of such reactions. Because of the sluggishness of the reactions with bidentate ligands (such as dppm), the reactions can be readily halted at the unidentate stage (to give, for example, *cis*-$[Os(N\text{-}N)_2(\eta^1\text{-dppm})Cl]^+$, a reaction that can be exploited in the synthesis of ligand-bridged complexes.[29]

(27) An alternate "one-pot" synthesis has also been reported: Geno, M. J. K.; Dawson, J. H. *Inorg. Chem. Acta* **1985**, *97*, L41.

(28) (a) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334. (b) Bosnich, B.; Dwyer, F. P. *Aust. J. Chem.* **1966**, *19*, 2235. (c) Maspero, F.; Ontaggi, G. *Justus Liebigs Ann. Chem.* **1974**, *64*, 115.

(29) Kober, E. M.; Goldsby, K. A.; Narayana, D. N. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 4303.

Scheme II



The synthesis of complexes of the type *cis*-$[Os(N\text{-}N)_2(L)_2]^{2+}$ can be accomplished more rapidly by the prolonged heating of *cis*-$Os(N\text{-}N)_2Cl_2$ with excess L in ethylene glycol, method B in Table III. This method is especially convenient for ligands of high thermal stability and low volatility.

A very useful synthetic technique for the preparation of analogous complexes of Ru is the use of Ag^+ to remove chloride ligands to form labile solvated complex intermediates.[28a,30] The use of Ag^+ does not succeed for the analogous complexes of Os. Even in methyl ethyl ketone solution heated at reflux under a N_2 atmosphere, the reaction with $AgPF_6$ was unsuccessful; either no spectroscopic change occurred or the conditions resulted in oxidation to Os(III). However, Cl^- is readily displaced by NO_2^- in hot ethylene glycol/water solution, for example, to give *cis*-$[Os(bpy)_2(L)(NO_2)]^+$ (L = CO, PPh_3, PPh_2Me). The nitro complexes are useful intermediates, since the bound NO_2^- ligand can be readily converted into bound NO^+ by the addition of acid.[18] The NO^+ ligand is then susceptible to attack by N_3^-, which results in the elimination of N_2 and N_2O to give the corresponding solvated complex $[Os(bpy)_2(L)(S)]^{2+}$.[31] The nitro/nitrosyl route was used for preparation of complexes with L = PPh_2Me and S = CH_3CN, although in rather low yield, and this chemistry was not pursued extensively.

An attempt was made to develop an alternate route to the synthesis of mixed-ligand complexes based on sequential ligand addition. Unfortunately, the attempt to prepare *cis*-$[Os(bpy)_2(py)(pz)]^{2+}$ by the reaction between *cis*-$[Os(bpy)_2(pz)Cl](PF_6)$ and excess pyridine in $EtOH/H_2O$ heated at reflux resulted only in the production of *cis*-$[Os(bpy)_2(py)Cl]^+$ and *cis*-$[Os(bpy)_2(py)_2]^{2+}$.

Synthesis of $(N\text{-}N)_2$ Complexes from $Os(N\text{-}N)_2CO_3$. The carbonato complex $Os(bpy)_2CO_3$ provides an efficient route for the synthesis of complexes of the type $[Os(N\text{-}N)_2(L)_2]^{2+}$ that are not readily prepared by the ethylene glycol route described above (Scheme II). The addition of acid to a suspension of sparingly soluble $Os(bpy)_2CO_3$ in DMF results in the formation of a brown solution with intense absorption bands at λ_{max} = 513, 428, and

(30) (a) Connor, J. A.; Meyer, T. J.; Sullivan, B. P. *J. Am. Chem. Soc.* **1979**, *18*, 1388. (b) Sullivan, B. P.; Baumann, J. A.; Meyer, T. J.; Salmon, D. J.; Lehmann, H.; Ludi, A. *J. Am. Chem. Soc.* **1977**, *99*, 7368.

(31) (a) Callahan, R. W.; Meyer, T. J. *Inorg. Chem.* **1977**, *16*, 574. (b) Adeyemi, S. A.; Miller, F. J.; Meyer, T. J. *Ibid.* **1972**, *11*, 994.

Table III. Preparative Conditions for Complexes of the Type *cis*-$[Os(N\text{-}N)_2(L)(L')]^{n+}$ with *cis*-$Os(bpy)_2Cl_2$ as the Precursor

final ligands L and L'	method[a]	molar excess of L	reaction time
(py)(Cl)	A	500×	6 h
(4,4′-bpy)(Cl)	A	20×	12 h
(pz)(Cl)	A	20×	4 h
(CH_3CN)(Cl)	A	500×	12 h
(PPh_3)(Cl)	A	20×	10 h
(PPh_2Me)(Cl)	A	20×	10 h
($AsPh_3$)(Cl)	A	20×	12 h
(CO)(Cl)	B	*b*	1 h
N-N	A	4×	3 h
$(py)_2$	B	50×	2 h
$(4,4'\text{-bpy})_2$	A	100×	7 days
das	B	5×	6 h
dppb	B	3×	3 h
dppy	B	3×	3 h
dppe	B	5×	10 h
dppm	B	3×	3 h
dpae	B	5×	10 h
$(DMSO)_2$	C	*c*	3 h
$(pz)_2$	A	100×	7 days
norb	C	20×	3 h
$(CH_3CN)_2$	C	*c*	4 h

[a] The reactions were carried out in 30–50 mL of solvent with 100–300 mg of starting complex. The synthetic methods are described in the Experimental Section. [b] Gas slowly bubbled through solution. [c] Used as the reaction solvent.

354 nm and a weak band at 740 nm while addition of a base (e.g. triethylamine) gives a purple solution from which $Os(bpy)_2CO_3$ precipitates. Similar behavior was noted in acetone, methyl ethyl ketone, and nitromethane, but in alcohols or CH_3CN the acid–base behavior was not reversible. In CH_3CN the initial color of the reaction mixture containing $Os(bpy)_2CO_3$ and acid is brown-green; only after 1 h of reflux did the solution change to the green color of *cis*-$[Os(N\text{-}N)_2(CH_3CN)_2]^{2+}$, suggesting that $[Os(N\text{-}N)_2(CO_3H)]^+$ is stable in weakly coordinating solvents, with stronger ligands being required to induce the loss of CO_2. We presume that the brown-green intermediate in CH_3CN is *cis*-$[Os(N\text{-}N)_2(CH_3CN)(H_2O)]^{2+}$ or a protonated form of a carbonato complex.

The reaction between $Os(bpy)_2(CO_3)$, acid, and an added ligand such as PPh_3 in refluxing acetone, methyl ethyl ketone, or nitromethane results in very slow spectral changes after the initial protonation step, the nature of which are not understood. In alcoholic solvents or in DMF, however, spectral changes occur over a time scale of hours when the solutions were heated at reflux in the presence of a variety of ligands. After short periods of heating (ca. 1 h), the electronic spectra of the solutions were consistent with *cis*-$[Os(bpy)_2(L)(S)]^{2+}$ (S = solvent) as the predominant species. For the case of L = py and L′ = py, addition of a large excess of the second ligand L′ to a boiling solution of *cis*-$[Os(bpy)_2(L)(S)]^{2+}$ gave *cis*-$[Os(bpy)_2(L)(L')]^{2+}$ as the major product, in contrast to the reaction between $[Os(bpy)_2(pz)Cl]^+$ and py in refluxing $EtOH/H_2O$, which gave *cis*-$[Os(bpy)_2(py)Cl]^+$ and *cis*-$[Os(bpy)_2(py)_2]^{2+}$ as products.

Synthesis of Complexes of the Type *cis*-$[Os(bpy)_2(CNR)_2]^{2+}$. The dicyano complex *cis*-$Os(bpy)_2(CN)_2$ can be readily prepared by exchange of Cl^- by CN^- in a polar solvent as has been described previously.[10] From *cis*-$Os(bpy)_2(CN)_2$, osmium(II) isocyanide complexes were prepared by reactions with mild alklating agents (such as MeI or $PhCH_2Br$) as shown in eq 4. In a photochemical

$$cis\text{-}Os(bpy)_2(CN)_2 + 2MeI \rightarrow cis\text{-}[Os(bpy)_2(CNMe)_2]^{2+} + 2I^- \quad (4)$$

sense the isocyanide complexes are of particular interest because the strong electron-withdrawing nature of the isocyanide ligand results in excited states of high energy.

Isolation of Trans Complexes. Complexes of the types $[Os(N\text{-}N)_2(L)_2]^{2+}$ or $[Os(N\text{-}N)_2(L)(L')]^{2+}$ can have either the cis or trans stereochemistry around the metal. Previous synthetic routes for complexes of either Ru(II) or Os(II) typically favor the cis geometry although, recently, general routes to complexes of the type *trans*-$[Ru(bpy)_2(L)_2]^{n+}$ have been reported.[16] The two isomers are readily identified by NMR spectroscopic techniques. The trans isomers have approximately D_{2h} or C_{2v} symmetry and are expected to show two doublets and two triplets (to first order) in the bpy region (δ 6–9). The cis complexes have either C_2 or C_1 symmetry and are expected to exhibit more complex first-order spectra in the bpy region (four doublets and four triplets for the C_2 complexes). On the basis of these criteria, the majority of complexes here were shown to have the cis stereochemistry. The only exceptions were found for complexes containing bulky phosphine ligands, and for one case, $[Os(bpy)_2(PMePh_2)_2]^{2+}$, both isomers could be obtained.

For metal complexes containing two or more alkylphosphine ligands, proton NMR spectroscopy provides an additional basis for the assignment of stereochemistry. The phenomenon of "virtual coupling" leads to unusual $^{31}P\text{–}^1H$ coupling constants in transition-metal complexes containing trans phosphines.[26] As a consequence, alkyl protons adjacent to trans ^{31}P (spin $^1/_2$) nuclei appear as triplets instead of as doublets. Thus, the methyl proton signal in *trans*-$[Os(bpy)_2(PPh_2Me)_2]^{2+}$ is observed as a triplet, while the methyl resonance in the cis isomer appears as a simple doublet. As expected, both complexes showed only a single phosphine peak in the $^{31}P\{^1H\}$ spectrum. The use of the resonance pattern for the alkyl protons is particularly appropriate for these complexes since resonances from the aryl protons of the phosphine ligands occur in the same region as the bpy protons. Another criterion for distinguishing between cis and trans isomers is via their visible spectra because of differences in both band shapes and absorption energies (see below).

Electrochemical Properties. Electrochemical data for the various complexes as obtained by cyclic voltammetry are summarized in Tables IV and V. The observed couples were all "reversible" (except as noted), where reversibility as used here implies that the separation between the anodic and cathodic peak potentials was less than 80 mV and no degradation products were observed on the following scan. Coulometric measurements for many of the couples established that they correspond to one-electron processes. The general behavior is quite similar to that of the Ru analogues, and assignments of the various couples follow directly from previous work.[11–13,28a,30,32] Figure 1 shows a typical cyclic voltammogram.

The data for the $(N\text{-}N)_1$ complexes are summarized in Table IV. For the first two entries, two oxidative processes are observed, which are assigned to the Os(IV/III) and Os(III/II) couples. The second process is irreversible and probably involves loss of a Cl^- ligand. No oxidative processes were observed to the solvent limit at ca. +2.0 V. For the second two entries, both an oxidative and a reductive process are observed. Both processes are reversible, and the former can be assigned to the Os(IV/III) couple, and the latter, to the Os(III/II) couple. The remaining complexes all exhibit a reversible oxidation, which can be assigned to the Os(III/II) couple. A second oxidative process is sometimes observed at a potential ca. 1 V more positive than that of the first couple. This is apparently an oxidation of Os(III) to Os(IV) and is frequently irreversible (see Figure 1). A single reductive process assigned to an N-N reduction, which is usually reversible, is also observed for these complexes. Its potential is relatively insensitive to the ligand environment at the metal.

The data for the complexes of the type $(N\text{-}N)_2$ are summarized in Table V. The first oxidative process, which is typically reversible, corresponds to a Os(III/II) couple with a second, frequently irreversible Os(III) → Os(IV) oxidation occurring at potentials 1.0–1.5 V more positive. Typically, two bpy-centered reduction processes are observed, while, for the phen complexes, one reversible reduction is observed, the second being complicated by an apparent adsorption process.

Irreversible reductions are often observed for complexes that contain a halide ligand. The irreversibility is usually caused by

(32) Johnson, E. C.; Sullivan, B. P.; Salmon, D. J.; Adeyemi, S. A.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 2211.

Table IV. Electrochemical and Spectroscopic Data for Complexes of the Type $[Os(N\text{-}N)(L)_4]^{n+}$ in CH_3CN

	complex[a]	$E_{1/2}^{ox}$, V[b]	$E_{1/2}^{red}$, V[b]	color or absorption maximum λ_{max}, cm^{-1} (ϵ, M^{-1} cm^{-1})	emission λ_{max}, cm^{-1} (fwhm, cm^{-1})
1	$Os(bpy)Cl_4$		+0.42, −0.88[c]	brown	
2	$Os(phen)Cl_4$		+0.44, −0.86[c]	tan-brown	
3	$Os(bpy)(PPhMe_2)Cl_3$	0.88	−0.56	red	
4	$Os(bpy)(PPh_3)Cl_3$	0.96	−0.46	red	
5	*cis*-$Os(bpy)(dppm)Cl_2$[d]	0.32, 1.66[c]	−1.66[c]	16 260 (1680), 23 360 (4890)	
6	*cis*-$Os(phen)(dppb)Cl_2$[d]	0.37	−1.65[c]	17 390 (2570), 19 800 (2790), 23 150 (6290)	
7	*cis*-$Os(phen)(dppy)Cl_2$[e]	0.43, 1.68[c]		17 540 (2010), 19 920 (2160), 23 420 (4110)	
8	$Os(phen)(dppb)(CO_3)$	0.49, 1.48		dark red-brown	
9	*mer*-$[Os(bpy)(PEt_3)_3Cl]^+$	0.52	−1.51	red	
10	*mer*-$[Os(bpy)(PMe_3)_3Cl]^+$	0.60	−1.52	red	
11	*mer*-$[Os(bpy)(PPhMe_2)_3Cl]^+$	0.65	−1.52	17 360 (830), 20 620 (1170), 25 640 (3190), 26 740 (3180)	
12	$Os(phen)(py)_4^{2+}$	0.72	−1.32	green	12 890 (1640)
13	*mer*-$[Os(bpy)(PPh_2Me)_3Cl]^+$	0.75	−1.47	17 760 (810), 21 050 (1110), 25 580 (2930), 26 950 (2940)	
14	*mer*-$[Os(bpy)(PPhMe_2)_3(NO_2)]^+$	1.05	−1.45	red-brown	14 370
15	$[Os(bpy)(das)_2]^{2+}$	1.46	−1.27	yellow	16 890 (3190)
16	$[Os(phen)(das)_2]^{2+}$	1.47	−1.25	27 630 (4590)	17 370 (3005)
17	$[Os(bpy)(dppm)_2]^{2+}$	1.72	−1.49	yellow	
18	$[Os(bpy)(dppy)_2]^{2+}$	1.81	−1.21	yellow	18 620 (3440)
19	$[Os(phen)(dppy)_2]^{2+}$	1.84	−1.25	34 600 (2820), 37 450 (3680)	19 250 (3260)

[a] Cationic complexes have PF_6^- counterions. [b] Potentials versus the SSCE, with a Pt-button or Pt-disk working electrode and a sweep rate of 200 mV/s. Recorded in CH_3CN solution with 0.1 M TEAH as supporting electrolyte, except as noted. [c] Irreversible couple; E_p reported. [d] Recorded in CH_2Cl_2 with 0.1 M TBAH as supporting electrolyte. [e] Recorded in 1:1 CH_3CN/CH_2Cl_2 with 0.1 M TBAH as supporting electrolyte.

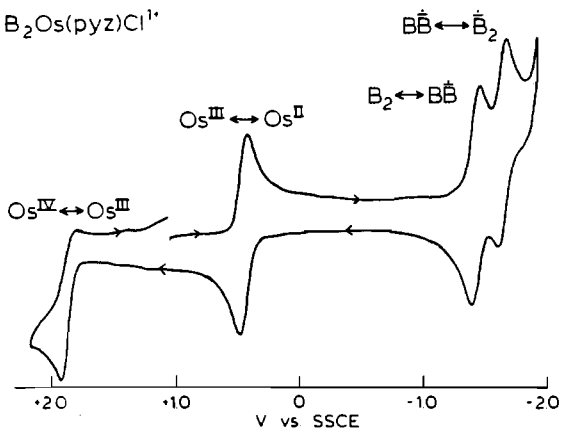


Figure 1. Cyclic voltammogram for *cis*-$[Os(bpy)_2(pyz)Cl](PF_6)$ in 0.1 M TBAH/CH_3CN at a scan rate of 100 mV/s by using a Pt-button working electrode. Note the irreversible behavior of the Os(IV/III) couple.

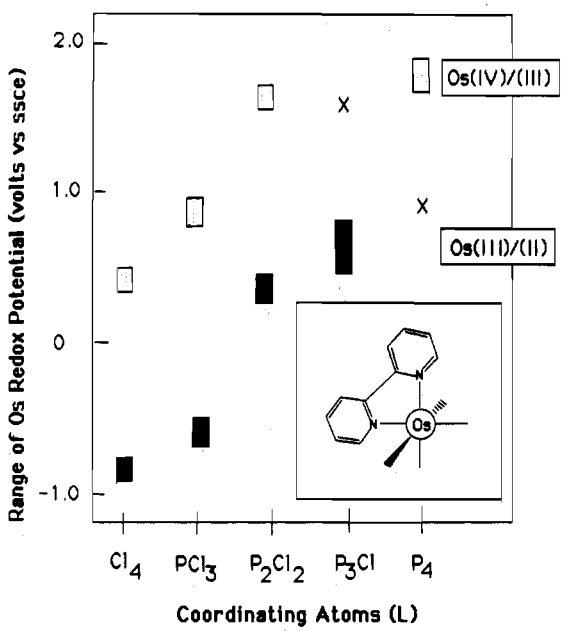


Figure 2. Diagram illustrating the range in redox potentials (by the bars) for both the Os(IV/III) and Os(III/II) couples for complexes of the type $Os(chelate)(P)_nCl_{4-n}$ (where n, the number of coordinating phosphine atoms, varies from 0 to 4). Data are not available in the regions marked with ×.

a rapid halide loss and replacement by the solvent (CH_3CN). For *cis*-$Os(bpy)_2Cl_2$, both free Cl^- (E_p = +0.96 V) and *cis*-$[Os(bpy)_2(CH_3CN)Cl]^+$ ($E_{1/2}$ = +0.41) are observed upon cycling through the bpy reductions. Similar behavior has been observed for the analogous Ru complexes,[28a] although the halide loss appears to occur at a slower rate for the Os complexes and typically does not occur on the cyclic voltammetry time scale until the second ligand-based reduction is reached. Rapid ligand-exchange processes induced by ligand-localized reduction are potentially of importance in reductive electrocatalytic schemes based on these complexes, as discussed in more detail elsewhere.[33]

Comparison of cyclic voltammograms for the cis–trans isomeric pairs reveals two noteworthy differences. First, the trans isomer is easier to oxidize by ca. 100 mV than is the cis isomer, as has been found for other octahedral complexes of Ru(II) and Os(II).[20,34] Second, the two ligand-centered reductions are separated by only 100 mV for the trans complexes, while the separation is 150–200 mV for the cis isomers. The decrease for the trans isomers is presumably due to smaller electrostatic repulsion between the reduced ligands because of a larger separation distance.

An important point that emerges from the electrochemical data is that the reduction potentials of the Os(II) complexes can be tuned quite readily over a large range by simple ligand modifications. As can be seen from Tables IV and V, the Os(III/II) potential varies from −0.04 V for *cis*-$[Os(N\text{-}N)_2Cl_2]^{+/0}$ to +1.84 V for $[Os(N\text{-}N)(dppy)_2]^{3+/2+}$. In general when Cl^- ligands are replaced by pyridyl groups or ligands containing P-donor atoms, a significant positive shift in the reduction potential is observed, with the P-donor atom ligands having the greater effect. These data are graphically illustrated in Figure 2. As has been discussed by others,[35,36] the effect of the ligand in determining redox potentials can be thought of in terms of the resulting effect on the electron density at the metal center. Ligands that are strong σ or π donors increase the ease of metal oxidation, while strong

(33) Sullivan, B. P.; Conrad, D.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 3640.
(34) (a) Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 1037. (b) Sullivan, B. P.; Calvert, J. M.; Meyer, T. J. *Ibid.* **1980**, *19*, 1404.
(35) Taube, H. *Pure Appl. Chem.* **1979**, *51*, 901.
(36) (a) Sarupa, A. C.; Fenske, R. F. *Inorg. Chem.* **1975**, *14*, 247. (b) Treichel, P. M.; Mueh, H. J.; Bursten, B. E. *Isr. J. Chem.* **1977**, *15*, 253. (c) Treichel, P. M.; Mueh, H. J.; Bursten, B. E. *J. Organomet. Chem.* **1976**, *110*, C49.

Table V. Electrochemical and Spectroscopic Data for Complexes of the Type $[Os(N\text{-}N)_2(L)(L')]^{n+}$ at Room Temperature in CH_3CN

	complex[a]	$E_{1/2}^{ox}$, V[b]	$E_{1/2}^{red}$, V[b]	color or absorption maximum λ_{max}, cm^{-1} (ϵ, M^{-1} cm^{-1})	emission λ_{max}, cm^{-1} (fwhm, cm^{-1})
20	$Os(bpy)_2Cl_2$	−0.04, 1.39	−1.61, −1.87[c]	12 200 (2900), 17 800 (10 500), 21 400 (9500), 26 200 (10 500)[d]	
21	$Os(phen)_2Cl_2$	−0.04	−1.60	purple	
22	$Os(bpy)_2CO_3$			12 200 (3000), 17 200 (10 000), 21 000 (9800), 25 700 (10 500)[d]	
23	$[Os(bpy)_2(py)Cl]^+$	0.35, 1.81[e]	−1.46, −1.73[c]	13 600 (2900), 20 000 (10 500), 23 400 (15 200), 28 000 (11 600)	
24	$[Os(bpy)_2(4,4'\text{-bpy})Cl]^+$	0.318, 1.83[e]	−1.43, −1.64[c]	15 200 (2950), 19 400 (15 200), 24 400 (15 200)	
25	$[Os(bpy)_2(CH_3CN)Cl]^+$	0.41, 1.87[e]	−1.45, −1.72[c]	14 500 (2800), 20 200 (8700), 24 300 (8200), 28 600 (8300)	
26	$[Os(bpy)_2(pz)Cl]^+$	0.43, 1.88[e]	−1.40, −1.66[c]	15 400 (2800), 20 000 (11 000), 24 600 (11 400)	
27	$[Os(bpy)_2(AsPh_3)Cl]^+$	0.51, 1.83[e]	−1.47, −1.76[c]	15 500 (2700), 21 200 (8700), 24 700 (8000), 28 600 (8500)	
28	$[Os(bpy)_2(PPh_3)Cl]^+$	0.56, 1.85[e]	−1.43, −1.71[c]	16 000 (2600), 21 900 (8100), 29 200 (7800)	
29	$[Os(phen)_2(py)_2]^{2+}$	0.74	−1.30	green	13 400 (2000)
30	$[Os(bpy)_2(py)_2]^{2+}$	0.75, 2.39[e]	−1.31, −1.53	16 300 (2600), 22 700 (12 000), 25 600 (10 000), 28 800 (17 000)	13 000
31	$[Os(bpy)_2(4,4'\text{-bpy})_2]^{2+}$	0.81	−1.30, −1.53	17 000 (2800), 21 000 (19 000), 26 000 (24 000)	
32	$[Os(bpy)_2(py)(pz)]^{2+}$	0.84	−1.31, −1.45	17 200 (3100), 21 800 (13 000), 23 100 (13 000), 26 600 (15 000)	13 700 (2210)
33	$[Os(phen)_2(CH_3CN)_2]^{2+}$	0.87	−1.36	22 860 (12 600), 24 770 (12 400)	14 530 (2380)
34	$[Os(bpy)_2(PPh_2Me)(NO_2)]^+$	0.89	−1.41, −1.65	brown	13 600
35	$[Os(bpy)_2(CH_3CN)_2]^{2+}$	0.91, 2.46[e]	−1.31, −1.53	18 000 (2700), 22 400 (9700), 27 600 (7600), 29 300 (7900)	14 120 (2320)
36	$[Os(bpy)_2(pz)_2]^{2+}$	0.97	−1.24, −1.38	18 200 (2700), 22 400 (9700), 27 600 (7600), 29 300 (7900)	13 930 (2290)
37	$[Os(bpy)_2(PPh_3)(NO_2)]^+$	0.97	−1.42, −1.65	green-brown	13 890
38	$[Os(bpy)_2(PPh_2Me)(CH_3CN)]^{2+}$	1.05	−1.36, −1.55	orange-red	14 660 (2740)
39	*trans*-$[Os(phen)_2(PPhMe_2)_2]^{2+}$	1.09	−1.28	16 780 (1280), 17 640 (1350), 22 240 (11 600)	14 880 (2340)
40	*trans*-$[Os(bpy)_2(PPh_2Me)_2]^{2+}$	1.10	−1.23, −1.44	16 780 (1620), 17 540 (1700), 22 350 (10 000)	14 920 (2280)
41	$[Os(bpy)_2(das)]^{2+}$	1.11	−1.27, −1.50	19 300 (2000), 24 000 (7100), 25 900 (7300)	14 660 (2860)
42	$[Os(phen)_2(das)]^{2+}$	1.11	−1.26	24 040 (9040), 25 970 (10 300)	15 040 (2740)
43	$[Os(phen)_2(CO)Cl]^+$	1.14	−1.24	21 880 (3990), 26 600 (5160)	14 290
44	$[Os(bpy)_2(CO)Cl]^+$	1.18	−1.25, −1.49	20 800 (3100), 28 300 (6400)	14 660 (3120)
45	*cis*-$[Os(bpy)_2(PPh_2Me)_2]^{2+}$	1.21	−1.22, −1.49	20 600 (1610), 24 690 (6300), 26 320 (6680)	15 110 (2880)
46	$[Os(bpy)_2(dppm)]^{2+}$	1.27	−1.26, −1.47	20 800 (1900), 26 400 (7200)	15 530 (3110)
47	$[Os(phen)_2(dpae)]^{2+}$	1.28	−1.25	26 520 (6470)	16 080 (3010)
48	$[Os(bpy)_2(dpp)]^{2+}$	1.30	−1.27, −1.50	21 400 (2100), 26 600 (7300)	15 630 (3050)
49	$[Os(phen)_2(dppe)]^{2+}$	1.30	−1.23	26 560 (6470)	16 130 (2830)
50	$[Os(phen)_2(dppm)]^{2+}$	1.32	−1.24	26 560 (10 700)	16 020 (3000)
51	$[Os(bpy)_2(dppb)]^{2+}$	1.34	−1.27, −1.50	21 300 (2100), 26 900 (7600)	15 720 (3140)
52	$[Os(bpy)_2(dppy)]^{2+}$	1.34	−1.27, −1.50	21 800 (2100), 27 000 (7000)	16 820 (3150)
53	$[Os(phen)_2(dppy)]^{2+}$	1.36	−1.23	27 050 (8180)	16 420 (2980)
54	$[Os(bpy)_2(CNMe)_2]^{2+}$	1.44	−1.27, −1.43	22 200 (sh), 26 800 (6000)	16 890 (3140)
55	$[Os(bpy)_2(CNCH_2Ph)_2]^{2+}$	1.50	−1.23, −1.38	22 200 (sh), 26 300 (sh), 27 600 (7200)	17 240 (3130)
56	$[Os(bpy)_2(CO)(NO_2)]^+$	1.54	−1.24, −1.44	orange	16 230
57	$[Os(bpy)_2(norb)]^{2+}$	1.64[e]	−1.14, −1.35[c]	22 100 (4000), 28 600 (sh)	
58	$[Os(bpy)_2(DMSO)_2]^{2+}$	1.79[e]	−1.20, −1.40	22 600 (sh), 28 200 (5700)	17 390 (3290)

[a] Cationic complexes have PF_6^- counterions. Stereochemistry is cis unless otherwise stated. [b] Potentials versus the SSCE with a Pt-button or Pt-disk working electrode and a sweep rate of 200 mV/s. Recorded in CH_3CN solution with 0.1 M TEAH as supporting electrolyte, except as noted. [c] Cl^- loss observed. [d] CH_2Cl_2 solution. [e] Irreversible couple; E_p reported.

π-acid ligands increase the difficulty of metal oxidation. Based upon the Os(III/II) potential, the relative order of increasing electron-withdrawing ability of the various ligands is as follows: $Cl^- < py \sim P(alkyl)_3 < RCN < P(aryl)_3 < CNR < olefin < R_2SO$ (S-bound) $< CO < NO^+$. The ordering is in line with estimates made by other means.[37]

A comparison between M(III/II) potentials for structurally analogous Os and Ru complexes of 2,2′-bipyridine is illustrated in Figure 3. Linear correlations exist for couples having similar charge types. In equivalent complexes, Os is easier to oxidize than Ru by ca. 0.3–0.5 V.[38] A similar ease of oxidation of Os compared to Ru has also been found for pentaammine and tetraammine complexes,[35] and the general trend is consistent with the inherent stability of third-row vs second-row transition metals in higher oxidation states. The slopes of the correlations in Figure 3 show that the Ru(III/II) couple is more susceptible to ligand variations than is the Os couple by a factor of 1.1, which is consistent with Os being slightly "softer" and less responsive to ligand perturbations. The separate correlations with charge type are an expected result of the differences in solvation energies. A significant difference between Ru and Os does occur for the M(IV/III) couple. The Os(IV/III) couple can be readily observed for several of the complexes reported here at potentials 1.0–1.5 V more positive than potentials for the Os(III/II) couple. The separation between the Ru(IV/III) and Ru(III/II) couples is considerably

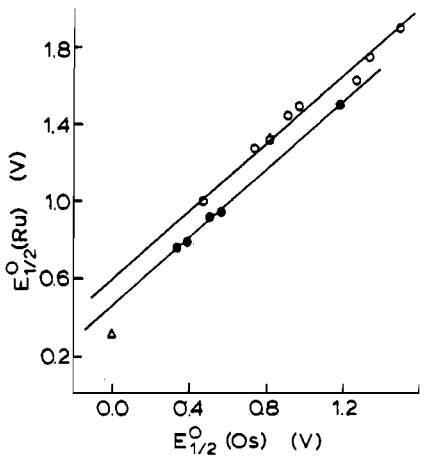


Figure 3. Comparisons of M(III/II) potentials for analogous Os and Ru complexes. The horizontal axis indicates the $E_{1/2}$ values for the Os(II/III) complexes, and the vertical axis indicates the $E_{1/2}$ values for the Ru(II/III) analogues. For Ru data, see ref 28, 30, 32, and 33. Complexes are identified as follows: ○ = $M^{II}(bpy)_2(L)_2^{2+}$; ● = $M^{II}(bpy)_2(L)Cl^+$; △ = $M^{II}(bpy)_2Cl_2$. L is a neutral phosphine or N donor atom ligand.

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(38) See, for example: Warren, L. F.; Bennet, M. S. *Inorg. Chem.* **1976**, *15*, 3126.

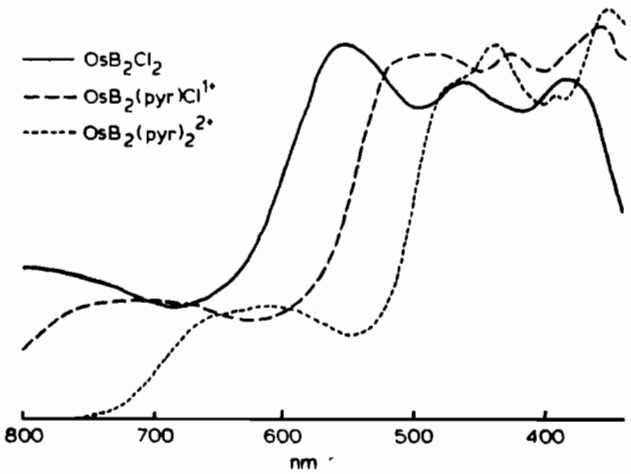

Figure 4. Electronic spectra in the visible region for a series of complexes of different charge types that illustrate the complexity of the MLCT spectral manifolds. Note that the entire manifold shifts to higher energies as the chloro ligand is replaced by pyrazine (pyr). The spectral data were recorded for CH_3CN solutions of the complexes.

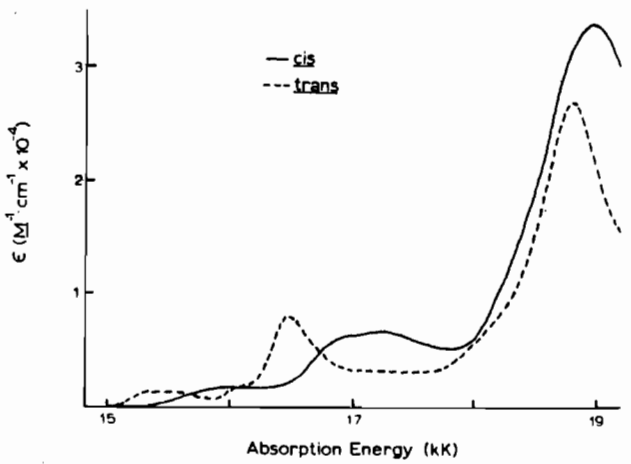

Figure 5. Visible absorption spectra for *cis*- and *trans*-$[Os(bpy)_2(PPh_2Me)_2](PF_6)_2$ in CH_3CN. 1 kK = 1000 cm^{-1}.

larger, and the Ru(IV/III) couple is rarely observed for analogous complexes of Ru because the potentials are at or near the solvent limit.[39]

Potentials for the N-N-based reductions do show a slight dependence upon the potential of the M(III/II) couple in that as it becomes easier to oxidize the metal, it becomes more difficult to reduce the N-N ligand. Electronic connection between the two lies in back-bonding. The metal becomes easier to oxidize because its d orbitals are destabilized by the increase in charge at the metal center or, from a molecular orbital point of view, by enhanced metal–ligand mixing. In response, N-N π^* orbitals become destabilized because of their overlap and bonding interactions with the $d\pi$ orbitals and, hence, it becomes more difficult to add an electron to these orbitals. From the result that the N-N reduction potential shifts by ca. 10% as much as the metal-based oxidation potential for a given ligand change, it can be inferred that the extent of mixing between the metal $d\pi$ and N-N π^* orbitals is ca. 10%. A detailed model for the interaction has been presented elsewhere.[40]

Electronic Spectra. The typical visible absorption spectra of the complexes are quite complicated, with numerous peaks and shoulders (see Figure 4). Spectra of several of the $(N\text{-}N)_2$ complexes that illustrate this point have been reported previously.[8-11,14,19,21,22]

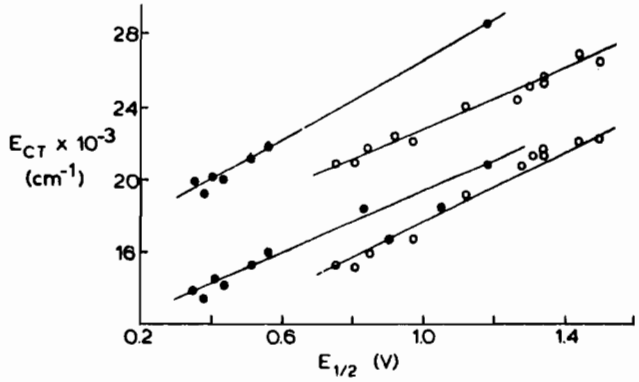

Figure 6. Charge-transfer-band energies for the two lowest energy MLCT transitions as a function of $E_{1/2}$ for the Os(III/II) couple. Filled circles are for $[Os(bpy)_2(L)Cl]^+$ and open circles are for $[Os(bpy)_2(L)_2]^{2+}$ complexes. Data are taken from Tables IV and V.

Of note are the considerable differences between the spectra of the cis–trans pairs. The trans isomers exhibit more structure, but greater simplicity, since the individual absorption bands tend to be significantly narrower (see Figure 5). These differences provide a qualitative basis for distinguishing between isomers.

For the $(N\text{-}N)_1$ complexes little structure is seen because of their spectral simplicity (see Table IV). This lack of structure is the result of the relatively high energy of the absorption bands and an accompanying increase in bandwidth, a phenomenom that has been documented quantitatively in emission spectral studies.[22,41] Polypyridyl-containing complexes of Os(III) having low-energy absorption bands typically show much more structure than complexes having high-energy bands.

The visible absorption spectra of $(N\text{-}N)_2$ complexes have two main features (for examples, see Figure 4). Several intense bands ($\epsilon \sim 10000$ M^{-1} cm^{-1}) appear at higher energy, with weaker components of approximately one-third the intensity occurring at ca. 5000 cm^{-1} lower energy. A summary of the positions of the main bands is given in Tables IV and V for several of the complexes. Both sets of bands can be assigned to Os ($d\pi$) → bpy, phen (π^*) MLCT transitions, which is confirmed here by the fact that both sets of bands move linearly to higher energy as the Os(III/II) couple is shifted to higher potentials. A correlation between the Os(III/II) potential and the energy of the first strong absorption band is shown in Figure 6. The slope is seen to have the expected value of ca. 1.0. It has been previously demonstrated that the more intense transitions are to excited states predominantly singlet in character, while the lower energy transitions are to states predominantly triplet in character.[41,43] The fact that the intensities are comparable emphasizes that there is considerable mixing between the spin states. Charge-transfer transitions to the π^* orbitals of other nitrogen heterocycles (and possibly to the $d\pi$ orbitals of the phosphine ligands) are also present in the spectra. The complexes also show two strong bands (with several shoulders) in the UV region ($\lambda_{max} \sim 295$ nm ($\epsilon \sim 30000$ M^{-1} cm^{-1}) and $\lambda_{max} \sim 250$ nm ($\epsilon \sim 20000$ M^{-1} cm^{-1})) that are assigned as the $\pi \rightarrow \pi^*$ transitions of the bpy or phen ligands.[10]

Photophysical and Photochemical Properties. Many of the complexes luminesce noticeably at room temperature in solution, and the emission is broad (fwhm = 4000 cm^{-1}) and featureless. Typical spectra have been published previously,[19,21,22] and only band maxima are included in Tables IV and V. Like the absorption band energies, the emission band maxima also track the reduction potentials for the analogous Os(III/II) couples, which supports the assignment of the emission as being from Os ($d\pi$)

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→ bpy, phen (π^*) MLCT excited states. At lower temperatures (77 K), the emission spectra typically exhibit a vibrational progression with $h\nu = \sim 1350$ cm^{-1},[14,22] which is characteristic of emissions from metal → bpy,phen(π^*) MLCT excited states.

The emissions observed overlap at least slightly with the low-energy "triplet" absorption bands and in that sense can be assigned as a triplet emission. The relative intensities of the high- and low-energy MLCT absorption bands suggest that the emitting triplet states may be as much as 30–40% singlet in character. Both excited-state lifetimes and the quantum yields for emission increase dramatically with the emission energy, the origins of which have been discussed in detail elsewhere.[22,41]

The majority of complexes investigated here exhibited no conspicuous photolability and were routinely handled in solution under room light with no substitution or degradation observed. Specifically, *cis*-$[Os(bpy)_2(PPh_3)Cl]^+$, $[Os(bpy)_2(dppm)]^{2+}$, and $[Os(bpy)(das)_2]^{2+}$ were photolyzed in CH_3CN solution in quartz cuvettes for 6 h by using a 500-W sunlamp and a 380-nm cutoff filter without any change in their spectral properties. Photochemical substitution behavior was only noted for the three complexes *cis*-$[Os(bpy)_2(DMSO)_2]^{2+}$, *cis*-$[Os(bpy)_2(norb)]^{2+}$, and $[Os(bpy)(dppm)_2]^{2+}$ in CH_3CN. For the first two complexes, spectral data at the end of photolysis indicated the formation of *cis*-$[Os(bpy)_2(CH_3CN)_2]^{2+}$. For the $(dppm)_2$ complex, the spectral changes upon photolysis suggest the formation of a "dangling" phosphine with CH_3CN occupying the open coordination site. The photochemical properties of the Os(III) complexes were not examined.

The photolability of the Ru complexes has been attributed to the occurrence of dd excited states that lead to ligand loss and are at energies similar to those of the MLCT excited states.[44] The results of temperature-dependent lifetime studies suggest that good thermal communication exists between the two types of states. For the third-row transition metal Os, the dd states should be ~30% higher in energy because of the greater values of $10Dq$ found for third-row vs second-row transition metals,[45] and only when the MLCT states are commeasurably higher in energy are the Os complexes expected to exhibit photolability. In accordance with the prediction, the three photolabile complexes all have quite high-energy MLCT excited states. An additional observation of relevance is the reported photolability of osmium(II) terpyridine complexes. For the trpy-containing complexes, ligand loss has been attributed to the unfavorable bite angle of the terpyridine ligand, which lowers the energy of the dd states by $d\sigma^*$–$d\pi$ mixing.[46]

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Registry No. $Os(bpy)Cl_4$, 57288-05-8; $Os(phen)Cl_4$, 89689-84-9; $Os(bpy)(PPhMe_2)Cl_3$, 89656-72-4; $Os(bpy)(PPh_3)Cl_3$, 116862-95-4; *cis*-$Os(bpy)(dppm)Cl_2$, 116862-96-5; *cis*-$Os(phen)(dppb)Cl_2$, 116862-97-6; *cis*-$Os(phen)(dppy)Cl_2$, 89689-85-0; $Os(phen)(dppb)(CO_3)$, 116862-98-7; *mer*-$[Os(bpy)(PEt_3)_3Cl](PF_6)$, 116863-00-4; *mer*-$[Os(bpy)(PMe_3)_3Cl](PF_6)$, 116863-02-6; *mer*-$[Os(bpy)(PPhMe_2)_3Cl](PF_6)$, 116863-04-8; $Os(phen)(py)_4(PF_6)_2$, 80502-72-3; *mer*-$[Os(bpy)(PPh_2Me)_3Cl](PF_6)$, 116863-06-0; *mer*-$[Os(bpy)(PPhMe_2)_3(NO_2)](PF_6)$, 116863-08-2; $[Os(bpy)(das)_2](PF_6)_2$, 80502-68-7; $[Os(phen)(das)_2](PF_6)_2$, 106373-21-1; $[Os(bpy)(dppm)_2](PF_6)_2$, 116863-10-6; $[Os(bpy)(dppy)_2](PF_6)_2$, 116863-11-7; $[Os(phen)(dppy)_2](PF_6)_2$, 116946-78-2; $Os(bpy)_2Cl_2$, 79982-56-2; $Os(phen)_2Cl_2$, 115793-18-5; $Os(bpy)_2CO_3$, 81831-23-4; $[Os(bpy)_2(py)Cl](PF_6)$, 116946-80-6; $[Os(bpy)_2(4,4'\text{-}bpy)Cl](PF_6)$, 116946-82-8; $[Os(bpy)_2(CH_3CN)Cl](PF_6)$, 81831-14-3; $[Os(bpy)_2(pz)Cl](PF_6)$, 116946-84-0; $[Os(bpy)_2(AsPh_3)Cl](PF_6)$, 116863-13-9; $[Os(bpy)_2(PPh_3)Cl](PF_6)$, 81831-16-5; $[Os(phen)_2(py)_2](PF_6)_2$, 115304-15-9; $[Os(bpy)_2(py)_2](PF_6)_2$, 115304-13-7; $[Os(bpy)_2(4,4'\text{-}bpy)_2](PF_6)_2$, 116887-34-4; $[Os(bpy)_2(py)(pz)](PF_6)_2$, 116863-15-1; $[Os(phen)_2(CH_3CN)_2](PF_6)_2$, 116946-86-2; $[Os(bpy)_2(PPh_2Me)(NO_2)](PF_6)$, 116863-17-3; $[Os(bpy)_2(CH_3CN)_2](PF_6)_2$, 116946-88-4; $[Os(bpy)_2(pz)_2](PF_6)_2$, 116946-90-8; $[Os(bpy)_2(PPh_3)(NO_2)](PF_6)$, 116863-19-5; $[Os(bpy)_2(PPh_2Me)(CH_3CN)](PF_6)_2$, 80502-91-6; *trans*-$[Os(phen)_2(PPhMe_2)_2](PF_6)_2$, 80558-60-7; *trans*-$[Os(bpy)_2(PPh_2Me)_2](PF_6)_2$, 80502-56-3; $[Os(bpy)_2(das)](PF_6)_2$, 80502-60-9; $[Os(phen)_2(das)](PF_6)_2$, 80502-80-3; $[Os(phen)_2(CO)Cl](PF_6)_2$, 80502-76-7; $[Os(bpy)_2(CO)Cl](PF_6)$, 80502-54-1; *cis*-$[Os(bpy)_2(PPh_2Me)_2](PF_6)_2$, 80558-58-3; $[Os(bpy)_2(dppm)](PF_6)_2$, 75441-73-5; $[Os(phen)_2(dpae)](PF_6)_2$, 80502-86-9; $[Os(bpy)_2(dppe)](PF_6)_2$, 80514-60-9; $[Os(phen)_2(dppe)](PF_6)_2$, 80502-84-7; $[Os(phen)_2(dppm)](PF_6)_2$, 75446-25-2; $[Os(bpy)_2(dppb)](PF_6)_2$, 80502-64-3; $[Os(bpy)_2(dppy)](PF_6)_2$, 75441-75-7; $[Os(phen)_2(dppy)](PF_6)_2$, 75446-27-4; $[Os(bpy)_2(CNMe)_2](PF_6)_2$, 81831-22-3; $[Os(bpy)_2(CNCH_2Ph)_2](PF_6)_2$, 116946-92-0; $[Os(bpy)_2(CO)(NO_2)](PF_6)$, 89689-56-5; $[Os(bpy)_2(norb)](PF_6)_2$, 81846-94-8; $[Os(bpy)_2(DMSO)_2](PF_6)_2$, 80502-70-1; $Os(phen)_2CO_3$, 116863-20-8; $(NH_4)_2OsCl_6$, 12125-08-5; *cis*-$Os(bpy)_2(CN)_2$, 73610-95-4; HCN, 74-90-8; MeI, 74-88-4; *cis*-$[Os(bpy)_2(PPh_2Me)Cl](PF_6)$, 116863-22-0; $Os(bpy)Cl_4^-$, 116863-23-1; $Os(phen)Cl_3^-$, 116863-24-2; $Os(bpy)(PPhMe_2)Cl_3^+$, 116863-25-3; $Os(bpy)(PPhMe_2)Cl_3^-$, 116863-26-4; $Os(bpy)(PPh_3)Cl_3^+$, 116863-27-5; $Os(bpy)(PPh_3)Cl_3^-$, 116863-28-6; *cis*-$Os(bpy)(dppm)Cl_2^+$, 116863-29-7; *cis*-$Os(phen)(dppb)Cl_2^+$, 116863-30-0; *cis*-$Os(phen)(dppy)Cl_2^+$, 116863-31-1; $Os(phen)(dppb)(CO_3)^+$, 116887-35-5; *mer*-$[Os(bpy)(PEt_3)_3Cl]^{2+}$, 116863-32-2; *mer*-$[Os(bpy)(PMe_3)_3Cl]^{2+}$, 116863-33-3; *mer*-$[Os(bpy)(PPhMe_2)_3Cl]^{2+}$, 116863-34-4; $Os(phen)(py)_4^{3+}$, 116863-35-5; *mer*-$[Os(bpy)(PPh_2Me)_3Cl]^{2+}$, 116863-36-6; *mer*-$[Os(bpy)(PPhMe_2)_3(NO_2)]^{2+}$, 116863-37-7; $[Os(bpy)(das)_2]^{3+}$, 116863-38-8; $[Os(phen)(das)_2]^{3+}$, 116863-39-9; $[Os(bpy)(dppm)_2]^{3+}$, 116863-40-2; $[Os(bpy)(dppy)_2]^{3+}$, 116863-41-3; $[Os(phen)(dppy)_2]^{3+}$, 116863-42-4; $Os(bpy)_2Cl_2^+$, 116863-43-5; $Os(phen)_2Cl_2^+$, 116946-93-1; $[Os(bpy)_2(py)Cl]^{2+}$, 116863-44-6; $[Os(bpy)_2(4,4'\text{-}bpy)Cl]^{2+}$, 116863-45-7; $[Os(bpy)_2(CH_3CN)Cl]^{2+}$, 116863-46-8; $[Os(bpy)_2(pz)Cl]^{2+}$, 116863-47-9; $[Os(bpy)_2(AsPh_3)Cl]^{2+}$, 116863-48-0; $[Os(bpy)_2(PPh_3)Cl]^{2+}$, 85370-12-3; $[Os(phen)_2(py)_2]^{3+}$, 115304-19-3; $[Os(bpy)_2(py)_2]^{3+}$, 115304-17-1; $[Os(bpy)_2(4,4'\text{-}bpy)_2]^{3+}$, 116863-49-1; $[Os(bpy)_2(py)(pz)]^{3+}$, 116863-50-4; $[Os(phen)_2(CH_3CN)_2]^{3+}$, 116863-51-5; $[Os(bpy)_2(PPh_2Me)(NO_2)]^{3+}$, 116863-53-7; $[Os(bpy)_2(CH_3CN)_2]^{3+}$, 116946-94-2; $[Os(bpy)_2(pz)_2]^{3+}$, 116863-54-8; $[Os(bpy)_2(PPh_3)(NO_2)]^{2+}$, 116863-55-9; $[Os(bpy)_2(PPh_2Me)(CH_3CN)]^{3+}$, 116863-56-0; *trans*-$[Os(phen)_2(PPhMe_2)_2]^{3+}$, 116863-57-1; *trans*-$[Os(bpy)_2(PPh_2Me)_2]^{3+}$, 116863-58-2; $[Os(bpy)_2(das)]^{3+}$, 115246-11-2; $[Os(phen)_2(das)]^{3+}$, 115246-29-2; $[Os(phen)_2(CO)Cl]^{2+}$, 116863-52-6; $[Os(bpy)_2(CO)Cl]^{2+}$, 116863-59-3; *cis*-$[Os(bpy)_2(PPh_2Me)_2]^{3+}$, 116946-95-3; $[Os(bpy)_2(dppm)]^{3+}$, 115246-13-4; $[Os(phen)_2(dpae)]^{3+}$, 116863-60-6; $[Os(bpy)_2(dppe)]^{3+}$, 97107-00-1; $[Os(phen)_2(dppe)]^{3+}$, 116863-61-7; $[Os(phen)_2(dppm)]^{3+}$, 115246-33-8; $[Os(bpy)_2(dppb)]^{3+}$, 115246-15-6; $[Os(bpy)_2(dppy)]^{3+}$, 115246-17-8; $[Os(phen)_2(dppy)]^{3+}$, 115246-35-0; $[Os(bpy)_2(CNMe)_2]^{3+}$, 116863-62-8; $[Os(bpy)_2(CNCH_2Ph)_2]^{3+}$, 116863-63-9; $[Os(bpy)_2(CO)(NO_2)]^{2+}$, 116863-64-0; $[Os(bpy)_2(norb)]^{3+}$, 116863-65-1; $[Os(bpy)_2(DMSO)_2]^{3+}$, 116863-66-2; 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