Long-Lived Osmium(II) Chromophores Containing 2,3,5,6-Tetrakis(2-pyridyl)pyrazine

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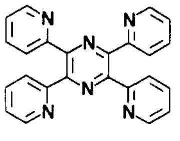
A series of complexes of the form $[\mathrm{Os(tpypz)(LLL)}]^{2+}$, $[\mathrm{Os(tpypz)(dppe)X}]^{n+}$, and $[\mathrm{Os(tpypz)(PPh_3)_2X}]^{n+}$ (tpypz = 2,3,5,6-tetrakis(2-pyridyl)pyrazine; tpy = 2,2′,2″-terpyridine; LLL = tpy, tpypz; dppe = bis(diphenylphosphino)ethane; X = $\mathrm{Cl^-}$, $\mathrm{CH_3CN}$) have been prepared and characterized. These complexes represent the first polyazine bridging ligand complexes in which the polyazine ligand is capable of bridging and the light-absorbing metal is also coordinated to a phosphine ligand. The incorporation of the phosphine ligands into the osmium tpypz framework has lead to interesting reactivity. Even in the presence of a diphosphine ligand, trans substitution is observed to yield two dangling diphosphine ligands although the cis chelated product is also formed. In the $[\mathrm{Os(tpypz)(PPh_3)_2X}]^{n+}$ series, cis–trans isomerization is observed upon production of the solvato complex. The incorporation of the tpypz ligand into the osmium framework has resulted in the production of a series of complexes with relatively long-lived metal-to-ligand charge-transfer excited states, hundreds of nanoseconds in fluid solution at room temperature. The synthesis and characterization of this new class of osmium phosphine complexes are outlined herein. An ESR study of the singly reduced form of one of these complexes, $[\mathrm{Os(tpypz^-)(PPh_3)_2Cl}]$, indicates that the electrochemically occupied orbital is based on the pyrazine portion of the tpypz ligand. It is this orbital that represents the LUMO in all of the complexes reported herein. These systems are of interest due to their long excited state lifetime coupled to the presence of the tpypz ligand which makes possible their incorporation into stereochemically defined supramolecular complexes. In addition, the solvato species are designed to facilitate synthetic variation and coupling to additional fragments in these supramolecular complexes.

Introduction

Since the discovery of $[\mathrm{Ru(bpy)_3}]^{2+}$ (bpy = 2,2′-bipyridine), a large number of studies have concentrated on the excited-state properties of this and related systems.[1,2] Much of this effort has concentrated on intermolecular electron-transfer quenching of the ruthenium-based MLCT (metal-to-ligand charge transfer) excited state.[2] Extension of this chemistry to the utilization of osmium chromophores has been somewhat limited due to the shorter lifetimes of analogous osmium systems.[3,4] Osmium polypyridine complexes tend to be more photostable than their ruthenium analogs, due to the higher energy of their LF (ligand field) excited states.[4] It is these LF states that are responsible for photodecomposition in ruthenium complexes.[5,6]

Utilization of tridentate ligands, such as tpy (tpy = 2,2′,2″-terpyridine), has slightly enhanced the lifetimes of osmium polypyridyl complexes.[7] Replacement of some of the bpy ligands with chelating phosphines has produced a series of long-lived osmium chromophores.[8] Application of these chromophores to excited-state electron-transfer schemes is limited due to the inherent inefficiency of intermolecular electron transfer. A few examples of osmium complexes containing polyazine bridging ligands have appeared in the literature.[9–11] Within this framework we have prepared and studied a series of osmium chromophores which contain the tridentate ligand 2,3,5,6-tetrakis(2-pyridyl)pyrazine (tpypz). In this study, the tpypz ligand is bound to only one metal center in a nonbridging mode. The presence of the remote nitrogens makes possible the development of polymetallic complexes utilizing these chromophores. The complexes studied herein are of the form $[\mathrm{Os(tpypz)(LLL)}]^{2+}$, $[\mathrm{Os(tpypz)(dppe)X}]^{n+}$, and $[\mathrm{Os(tpypz)(PPh_3)_2X}]^{n+}$ (LLL = tpy, tpypz; dppe = bis(diphenylphosphino)ethane; X = $\mathrm{Cl^-}$, $\mathrm{CH_3CN}$). These represent the first polyazine complexes in which the polyazine ligand is capable of bridging and the light-absorbing metal is coordinated to a phosphine ligand. This synthetic design gives rise to osmium complexes with a polyazine ligand capable of



tpypz

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bridging possessing the highest energy MLCT excited state observed to date. The excited-state lifetimes of these tpypz systems are all in excess of 200 ns in fluid solution at room temperature.

Experimental Section

Materials. The acetonitrile used in these studies was high-purity Burdick and Jackson and dried over activated molecular sieves. The osmium trichloride was purchased from Johnson Matthey, and the ligand tpypz from GFS Chemical. The supporting electrolyte TBAH (tetrabutylammonium hexafluorophosphate) was prepared from the metathesis of tetrabutylammonium bromide using potassium hexafluorophosphate. All other reagents were purchased from Fisher Scientific or Aldrich Chemical Co. and used without further purification.

Syntheses. [Os(tpy)Cl$_3$][12] and [Os(tpypz)$_2$]$^{2+}$ [10] were prepared as described in the literature.

[Os(tpypz)Cl$_3$] was prepared by a modification of the preparation of [Os(tpy)Cl$_3$] substituting tpypz for tpy. A 0.347-g amount (0.99 mmol) of OsCl$_3$·3H$_2$O and 0.446 g (1.15 mmol) of tpypz were heated at reflux in 100 mL of 95% EtOH for 2 h. The solution was allowed to cool to room temperature, and the product was removed by vacuum filtration and washed with water and EtOH to remove excess reactants as well as slight amounts of [Os(tpypz)$_2$]Cl$_2$ which form during this procedure. The product that is isolated contains a small amount of the bimetallic [Cl$_3$Os(tpypz)OsCl$_3$]. Due to the lack of solubility of these neutral species, this product is used as isolated and this bimetallic impurity is easily removed from the products of the reactions that utilize this starting material. A typical yield for this reaction is 70%.

[Os(tpypz)(tpy)](PF$_6$)$_2$. During the preparation of this manuscript, Abruna et al. published a manuscript outlining the preparation and characterization of [Os(tpypz)$_2$]$^{2+}$ and [Os(tpypz)(tpy)]$^{2+}$.[10] Our method for the preparation of [Os(tpypz)(tpy)](PF$_6$)$_2$ is quite similar to that reported by Abruna et al.; however, in our hands this method yields three products that require extensive chromatographic separation as described below. A 0.322-g amount (0.61 mmol) of [Os(tpy)Cl$_3$] and 0.379 g (0.98 mmol) of tpypz were heated at reflux in 20 mL of ethylene glycol for 30 min. This solution was added to 100 mL of saturated aqueous KPF$_6$ to induce precipitation of the product which was removed from the solution by vacuum filtration. This complex was chromatographed on neutral alumina in a 5:2 toluene/acetonitrile solvent mixture. Careful monitoring of the electronic spectra of the species as they eluted allowed for the separation and isolation of three brown monometallic products [Os(tpy)$_2$]$^{2+}$, [Os(tpy)(tpypz)]$^{2+}$, and [Os(tpypz)$_2$]$^{2+}$ as well as the purple bimetallic {[(tpy)Os]$_2$(tpypz)}$^{4+}$. Each of these species were rechromatographed to ensure product purity. A typical yield for the desired mixed-ligand complex is 55%. It is also possible to prepare this complex under less rigorous conditions (i.e. refluxing EtOH); however, the yield is decreased and the additional monometallic products still persist. Attempts to prepare this complex from the reaction of [Os(tpypz)Cl$_3$] and tpy were also successful but led to similar product distributions.

[Os(tpypz)(dppe)Cl](PF$_6$), *trans*-[Os(tpypz)(dppe)$_2$Cl](PF$_6$), and {[(dppe)ClOs]$_2$(tpypz)}(PF$_6$)$_2$ were prepared by the reaction of 0.615 g (0.90 mmol) of [Os(tpypz)Cl$_3$] with 0.481 g (1.21 mmol) of dppe. These two reactants were combined and heated at reflux for 90 min in 30 mL of ethylene glycol. The solution was added to 100 mL of saturated aqueous KPF$_6$, and the solid that formed was removed by vacuum filtration. This crude product was chromatographed on neutral alumina using a 5:2 toluene/acetonitrile solvent mixture. Three products eluted from the column, a brown product with a chelated phosphine, [Os(tpypz)(dppe)Cl](PF$_6$), followed by a purple product, {[(dppe)ClOs]$_2$(tpypz)}(PF$_6$)$_2$, with the final brown band being the species with two dangling phosphine ligands, [Os(tpypz)(dppe)$_2$Cl](PF$_6$). Typical yields for these products are 45%, 15%, and 30%, respectively, based on the [Os(tpypz)Cl$_3$] starting material.

[Os(tpypz)(dppe)(CH$_3$CN)](PF$_6$)$_2$ can be prepared in ca. 95% yield by the reaction of [Os(tpypz)(dppe)Cl](PF$_6$) with an excess of AgPF$_6$ in refluxing 1:1 CH$_3$CN/H$_2$O. A 0.288-g amount of [Os(tpypz)(dppe)Cl](PF$_6$) and 0.570 g of AgPF$_6$ were dissolved in 35 mL of CH$_3$CN, and 35 mL of H$_2$O was added. This solution was heated at reflux for 48 h and the acetonitrile removed to induce precipitation of the product. The solid that resulted was dissolved in 2:1 toluene/acetonitrile and chromatographed on neutral alumina to yield the desired product in 95% yield.

***trans*-[Os(tpypz)(PPh$_3$)$_2$Cl](PF$_6$)** was prepared by substituting 2 equiv of PPh$_3$ for the dppe used in the synthesis of [Os(tpypz)(dppe)Cl](PF$_6$). This reaction yielded only one major product, [Os(tpypz)(PPh$_3$)$_2$Cl](PF$_6$), with a typical yield of 60%.

***cis*- and *trans*-[Os(tpypz)(PPh$_3$)$_2$(CH$_3$CN)](PF$_6$)$_2$** can be prepared as above by substituting [Os(tpypz)(PPh$_3$)$_2$Cl](PF$_6$) for [Os(tpypz)(dppe)Cl](PF$_6$) in the synthesis of [Os(tpypz)(dppe)(CH$_3$CN)](PF$_6$)$_2$. Purification on alumina yields two products, *cis*- and *trans*-[Os(tpypz)(PPh$_3$)$_2$(CH$_3$CN)](PF$_6$)$_2$ with an overall yield of 95%. Variation of the time of the reaction can selectively produce a majority of the cis or trans isomer.

Physical Measurements. The configurations for the electronic spectroscopy and electrochemistry have been described in detail elsewhere.[13] All electrochemical measurements were made in acetonitrile, and potentials are reported versus Ag$^+$/AgCl.

NMR Spectroscopy. All NMR measurements were made on saturated solutions of the complexes in deuterated acetone utilizing a Varian Unity 400-MHz instrument.

Emission Spectroscopy and Lifetime Apparatus. Emission spectroscopy was recorded on a customized single-photon-counting Alpha Scan fluorometer modified to detect red-shifted emissions which utilizes a thermoelectrically cooled Hamamatsu R666-S photomultiplier tube.

The system for obtaining emission lifetimes utilizes a Continuum Q-switched NY61-10 Nd/YAG excitation source which can be frequency doubled or tripled and passed through a nanosecond dye head for wavelength selection. The emission is detected at right angles by a thermoelectrically cooled R666-S photomultiplier tube, digitized by a LeCroy 6880B digitizer, and transferred to a computer for data analysis.

ESR Spectroscopy. The samples utilized in the ESR studies were electrolyzed in an H-cell inside of a Vacuum Atmospheres glovebox. These acetonitrile solutions were approximately 1 mM in the electroactive species and contained 0.1 M TBAH as the supporting electrolyte. Upon completion of the electrolysis, the sample was transferred to an ESR sample tube under a nitrogen atmosphere and capped for transport to the spectrophotometer. The ESR spectrum was obtained immediately following completion of the electrochemical conversion.

The ESR spectrophotometer is an IBM ER200-D-SRC, X-band, operating at 9.6 GHz.

Results and Discussion

Synthetic Routes. The synthetic aspects of this study revealed some interesting reactivity patterns. The preparation of the mixed-ligand complex, [Os(tpypz)(tpy)]$^{2+}$, from either the tpypz or tpy trihalide complex yields a mixture of all possible combinations of these two ligand types as outlined in Scheme 1. This result indicates that these tridentate ligands are somewhat substitutionally labile under these reaction conditions such that scrambling of the ligands results. A recent paper describing the preparation of this complex did not mention this type of behavior.[10] Since this extensive chromatography is needed, the mixed-ligand complex could also be prepared by the reaction of equimolar amounts of tpy, tpypz, and OsCl$_3$·3H$_2$O.

The incorporation of phosphine ligands into the osmium tpypz framework has resulted in the preparation of a novel series of complexes. The reaction of [Os(tpypz)Cl$_3$] with the diphosphine ligand dppe resulted in the production of two monometallic complexes as outlined in Scheme 2. These two species represent the chelated phosphine complex, [Os(tpypz)(dppe)Cl]$^+$, as well as a species which contains two dangling diphosphine units in a trans geometry, *trans*-[Os(tpypz)(dppe)$_2$Cl]$^+$. The presence of the trans complex indicates a preference for the two phosphine ligands to substitute trans to each other consistent with the higher trans-directing ability of the phosphine versus the pyrazine moiety. This effect has been observed in a similar study by Meyer et al. in which *cis*-[Ru(tpy)(PPh$_3$)Cl$_2$] is shown to substitute the chloride ligand trans to the phosphine ligand more readily than *trans*-[Ru(tpy)(PPh$_3$)Cl$_2$], a species in which the two chloride ligands are trans to each other.[8e] Our isolation of the chelated species indicates that the chelate effect is competitive with this trans-

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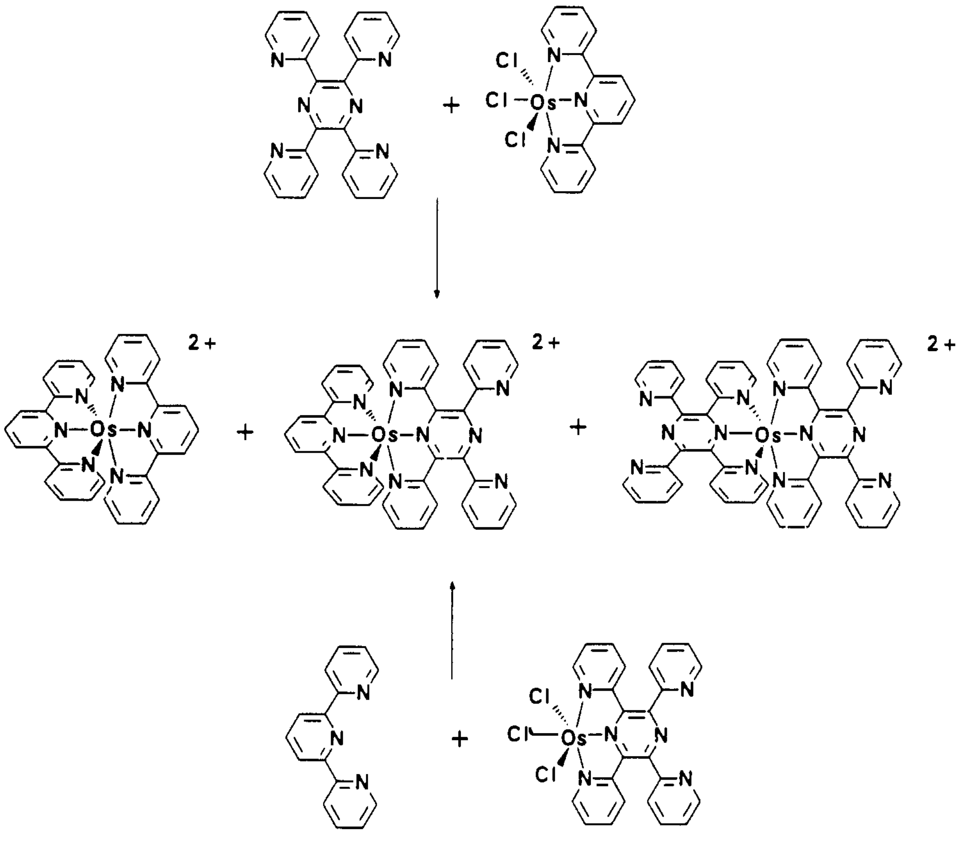
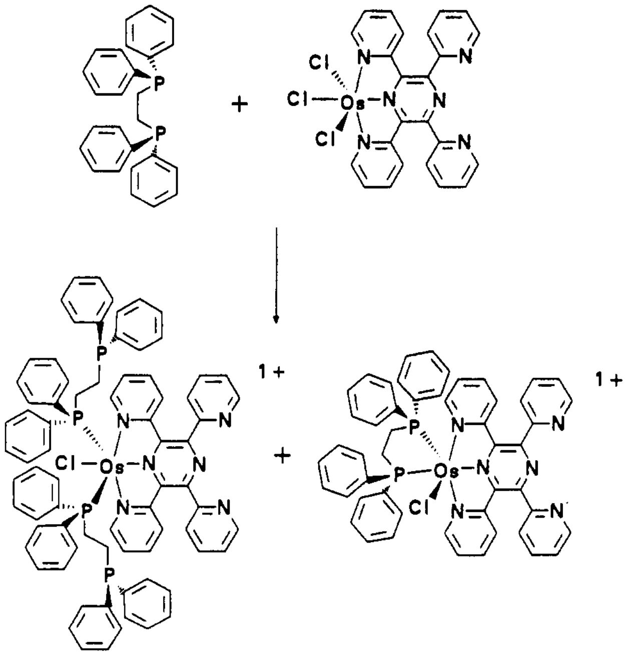
Scheme 1



Scheme 2



directing effect. Abstraction of the chloride ligand from the species with the chelated phosphine utilizing silver hexafluorophosphate to yield the acetonitrile complex, $[Os(tpypz)(dppe)(CH_3CN)]^{2+}$, can be accomplished in nearly quantitative yields.

Utilization of the monodentate phosphine, PPh_3, in the above reactions yields only the trans-disubstituted product, *trans*-$[Os(tpypz)(PPh_3)_2Cl]^+$. This confirms the assertion that the trans diphosphine species prepared in the dppe reaction is the preferred kinetic product, since this reaction eliminates chelation effects. Upon removal of the chloride ligand by treatment with silver hexafluorophosphate, two products are observed, *cis*- and *trans*-$[Os(tpypz)(PPh_3)_2(CH_3CN)]^{2+}$. This indicates that stereochemical rearrangement is possible under the conditions of this reaction, presumably due to the lability of the coordinated acetonitrile. Reactions that are allowed to proceed for longer times result in the formation of more of the cis isomer. This thermodynamic preference for the cis species could result from the enhanced π back-bonding available to the phosphine ligand when it is trans to a pyrazine versus another phosphine ligand.

NMR Spectroscopy. All of the phosphine complexes prepared have been analyzed by ^1H and ^{31}P NMR spectroscopy. The chelated species $[Os(tpypz)(dppe)Cl]^+$ shows two ^{31}P signals at 19.4 and 16.0 ppm due to the presence of two inequivalent phosphorus atoms. The ^1H NMR reveals two types of protons in the ethylene bridge of the chelated phosphine consistent with the nonequivalency of those sites due to the coordination of the phosphorus atoms.

One of the phosphorus signals, 19.4 ppm, is significantly broadened. This phosphorus atom is trans to a chloride ligand and should experience coupling to this nucleus to produce a multiplet. Substitution of the chloride by acetonitrile results in a significant shift in this signal and a dramatic sharpening. $[Os(tpypz)(dppe)(CH_3CN)]^{2+}$ exhibits two sharp ^{31}P signals at 27.8 and 16.4 ppm.

The identity of the species with the two dangling diphosphine ligands was confirmed by NMR. $[Os(tpypz)(dppe)_2Cl]^+$ shows two types of ^{31}P signals centered at 29.9 and -13.6 ppm consistent with coordinated and free phosphorus atoms. Each signal appears as a virtual triplet, consistent with a trans geometry of the two diphosphine ligands.

The ^{31}P NMR of $[Os(tpypz)(PPh_3)_2Cl]^+$ shows one signal at -18.8 ppm, consistent with a trans geometry of the two coordinated phosphine ligands. The aromatic region of the ^1H NMR is also consistent with the protons on the tpypz ligand appearing as sets of two equivalent nuclei, consistent with a trans stereochemistry. Substitution of acetonitrile for the chloride ligand gives rise to the production of both the *cis*- and *trans*-$[Os(tpypz)(PPh_3)_2(CH_3CN)]^{2+}$. The trans isomer exhibits one ^{31}P signal at -5.5

Table 1. Cyclic Voltammetric Data for a Series of Osmium Complexes Incorporating 2,3,5,6-Tetrakis(2-pyridyl)pyrazine[a]

	$E_{1/2}$ (V)	
complex	$\mathrm{Os^{II}/Os^{III}}$	$\mathrm{tpypz/tpypz^-}$
$[\mathrm{Os(tpypz)_2}]^{2+}$	+1.26	–0.80
$[\mathrm{Os(tpypz)(tpy)}]^{2+}$	+1.12	–0.93
$[\mathrm{Os(tpypz)(dppe)Cl}]^{+}$	+1.06	–0.85
$[\mathrm{Os(tpypz)(dppe)_2Cl}]^{+}$	+0.91	–0.99
$[\mathrm{Os(tpypz)(dppe)(CH_3CN)}]^{2+}$	+1.43	–0.77
trans-$[\mathrm{Os(tpypz)(PPh_3)_2Cl}]^{+}$	+0.78	–1.11
trans-$[\mathrm{Os(tpypz)(PPh_3)_2(CH_3CN)}]^{2+}$	+1.43	–0.89
cis-$[\mathrm{Os(tpypz)(PPh_3)_2(CH_3CN)}]^{2+}$	+1.34	–0.84

[a] Potentials are recorded in acetonitrile with 0.1 M TBAH at a scan rate of 200 mV/s and are reported versus $\mathrm{Ag^+/AgCl}$.

ppm consistent with trans stereochemistry. ^{1}H NMR in the aromatic region exhibits protons on the tpypz ligand that occur as sets of two equivalent nuclei. The cis isomer shows inequivalent phosphorus nuclei which exhibit two signals at –5.1 and –5.2 ppm. The ^{1}H NMR of this isomer is consistent with the lowered symmetry of this cis configuration.

Electrochemistry. These complexes have been analyzed by cyclic voltammetry, and the results of these studies are given in Table 1. $[\mathrm{Os(tpypz)_2}]^{2+}$ and $[\mathrm{Os(tpypz)(tpy)}]^{2+}$ have been reported by Abruna et al., but the numbers in the table are those measured under our conditions to make comparisons among the different systems more valid.[10] It is interesting to note that substitution of a tpypz ligand for a tpy ligand in these two complexes leads to a shift of the osmium-based oxidation to a significantly more positive potential (140 mV). The magnitude of this shift is large for this type of substitution of a polypyridyl ligand and reflects the significantly enhanced π acidity of the tpypz ligand.

An ESR study of the singly reduced $[\mathrm{Os(tpypz^-)(PPh_3)_2Cl}]$ has been accomplished. The single unpaired electron displays coupling to one nitrogen atom. This is consistent with a tpypz-based reduction in which the newly occupied orbital is based on the pyrazine portion of the tpypz ligand and is polarized toward the nitrogen bound to the electropositive Os metal center. The nature of this orbital is important in understanding the electrochemical properties of this series of complexes.[14]

Comparison of the species containing a chelated dppe diphosphine ligand with that possessing two dangling phosphines illustrates that the species with the chelated phosphine is harder to oxidize by 150 mV. The previously prepared *cis*-$[\mathrm{Ru(tpy)(PPh_3)Cl_2}]$ is harder to oxidize by 120 mV than the trans isomer.[8e] This is a result of the change in the stereochemistry allowing for an enhanced degree of Ru to phosphine π back-bonding in the cis complex. A similar effect is seen in our complexes. The chelated system, having two phosphine ligands cis, experiences enhanced back-bonding to the phosphine ligands relative to the species with the two dangling phosphine ligands, in which the two coordinated P are trans to each other. This is manifested in the metal oxidation potentials. Inspection of the tpypz-based reductions indicates that the species with the cis-chelated dppe is easier to reduce by 140 mV. The species with the chelated dppe has a phosphine trans to the pyrazine moiety of the tpypz ligand, whereas the dangling trans complex has a chloride ligand trans to this pyrazine. The greater π-accepting ability of the phosphine could diminish the π back-bonding from the Os to the pyrazine on the tpypz ligand. This would give rise to the observed shift of this reduction to more positive potentials. This result is consistent with the LUMO involved in the reduction of tpypz being primarily localized on the pyrazine portion of the ligand. Substitution of acetonitrile for the chloride ligand in the species containing the chelated phosphine gives rise to a shift of the metal oxidation potential to 370 mV more positive potential consistent with the lower σ-donating and better π-accepting ability of the coordinated acetonitrile ligand. It is interesting to note that the tpypz reduction in this solvato complex occurs at a much more positive potential. This is consistent with the less electron-rich osmium center displaying a significantly decreased degree of π back-bonding to the tpypz ligand. Similar effects are seen in the previously reported tpy-based systems. $[\mathrm{Os(tpy)(dppene)Cl}]^+$ (dppene = $\mathrm{Ph_2PCH{=}CHPPh_2}$) is easier to oxidize by 470 mV and harder to reduce by 170 mV than $[\mathrm{Os(tpy)(dppene)(CH_3CN)}]^{2+}$.[8d]

Utilization of the monodentate phosphine $\mathrm{PPh_3}$ gives a chloro species that is easier to oxidize than the dangling dppe complex by 130 mV. A similar shift of the metal oxidation potential is seen in comparing the previously reported $[\mathrm{Os(bpy)_2(dppe)}]^{2+}$ to $[\mathrm{Os(bpy)_2(PPh_2Me)_2}]^{2+}$. The species with the monodentate methyldiphenylphosphine ligands is easier to oxidize than the chelated system by 90 mV.[8c] The tpypz ligand in our complexes is harder to reduce in the tpypz reduction for the $\mathrm{PPh_3}$ system as compared to the dppe system. This is consistent with the osmium center in $[\mathrm{Os(tpypz)(PPh_3)_2Cl}]^+$ being more electron rich and enhancing its π back-bonding to the tpypz ligand. Formation of the acetonitrile complex leads to similar results in the electrochemistry as exhibited by the dppe system. Namely, the metal oxidation shifts to significantly more positive potential and the tpypz becomes easier to reduce. The magnitude of this shift in the $\mathrm{PPh_3}$ complex which involves a substitution trans to the pyrazine moiety is 140 mV larger than in the dppe system where the substitution is trans to a phosphine. This supports the assertion that the pyrazine moiety dominates the LUMO occupied in tpypz reduction.

Production of a cis acetonitrile complex is also observed in the $\mathrm{PPh_3}$ reaction. This system has the same stereochemical arrangement as the dppe complex and makes comparisons between these two species more valid. The chelated dppe solvato complex is harder to oxidize than the analogous $\mathrm{PPh_3}$ system. This is consistent with the decreased σ donation ability of the chelated dppe ligand. A concurrent shift of the tpypz reduction is also observed in comparing these two complexes. This is likely the result of the lower electron density on the Os in the dppe complex giving rise to decrease π back-bonding to the tpypz ligand.

Electronic Absorption Spectroscopy. The electronic spectra of these osmium complexes are shown in Figure 1 and summarized in Table 2. The spectra of the previously prepared $[\mathrm{Os(tpypz)_2}]^{2+}$ and $[\mathrm{Os(tpy)(tpypz)}]^{2+}$ are shown for comparison since the earlier report only gives a tabulation of the results. It is interesting to note that our mixed-ligand species which was purified by a slightly different technique exhibits somewhat higher ϵ than reported by Abruna et al.[10] The ultraviolet region of the spectrum for all of these tpypz containing complexes exhibits very similar band shapes and ϵ values, consistent with this region being dominated by tpypz-based $\pi \rightarrow \pi^*$ transitions.

The visible region of the electronic spectra of these complexes contains intense bands centered between 420 and 468 nm. These transitions represent the lowest lying ^{1}MLCT which is Os(dπ) $\rightarrow$ tpypz(π^*) in nature in all of the complexes prepared. Due to the high degree of spin–orbit coupling in osmium, transitions that are formally spin forbidden exhibit enhanced intensity. These ^{3}MLCT transitions appear as tails on the low-energy end of the more intense ^{1}MLCT transitions.

The energy of the Os → tpypz MLCT transition in the solvato complexes is clearly blue-shifted as compared to the analogous chloro complexes. This is consistent with the electrochemical results which indicate that the Os-based HOMO (highest-occupied molecular orbital) is stabilized upon substitution of acetonitrile for the chloride ligand. Comparison of the phosphine complexes to the species with two tridentate polyazine ligands illustrates that, for the solvato complexes, the Os → tpypz MLCT is shifted to significantly higher energy upon incorporation of the

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(14) Yanochko, G.; Dorn, H.; Brewer, K. J. Work in progress.

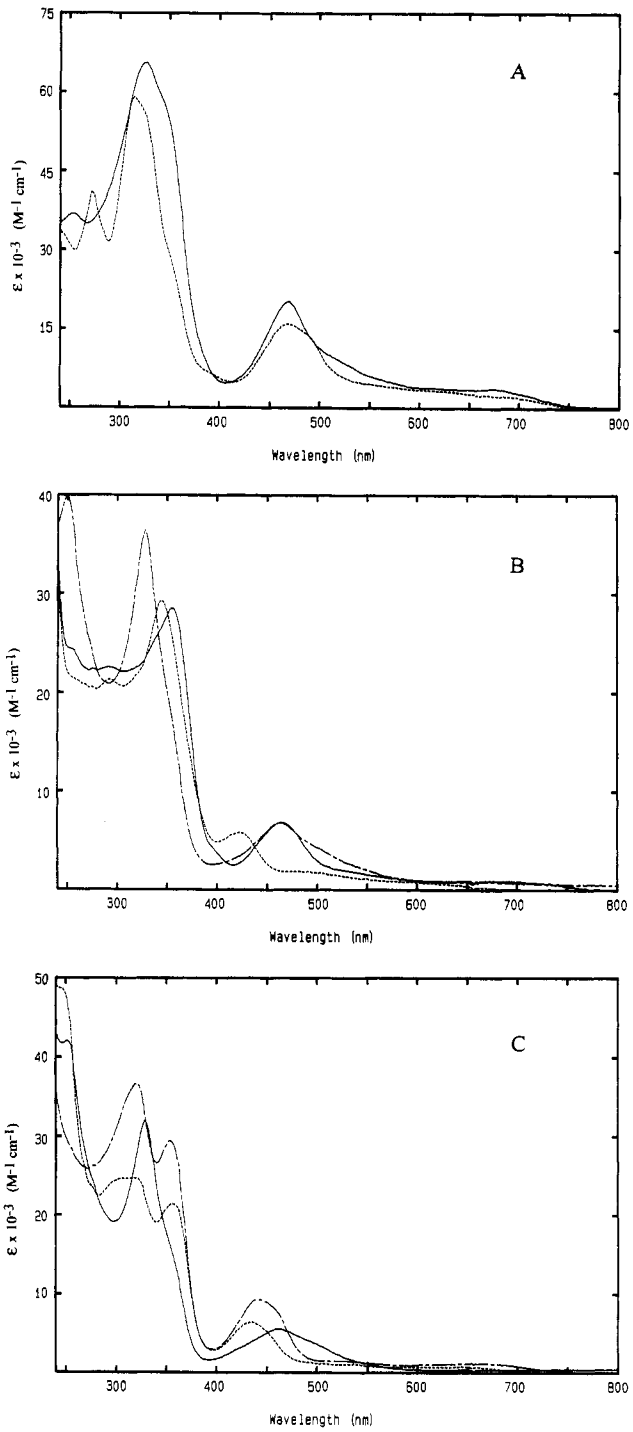

Figure 1. Electronic spectra in acetonitrile of a series of osmium complexes containing 2,3,5,6-tetrakis(2-pyridyl)pyrazine: (A) (—) [Os(tpypz)$_2$](PF$_6$)$_2$ and (- -) [Os(tpypz)(tpy)](PF$_6$)$_2$; (B) (—) [Os(tpypz)(dppe)Cl](PF$_6$), (- -) [Os(tpypz)(dppe)(CH$_3$CN)](PF$_6$)$_2$, and (- - -) *trans*-[Os(tpypz)(dppe)$_2$Cl](PF$_6$); (C) (—) *trans*-[Os(tpypz)(PPh$_3$)$_2$Cl](PF$_6$), (- -) *trans*-[Os(tpypz)(PPh$_3$)$_2$(CH$_3$CN)](PF$_6$)$_2$, and (- - -) *cis*-[Os(tpypz)(PPh$_3$)$_2$(CH$_3$CN)](PF$_6$)$_2$.

phosphine ligand. This is analogous to the results of Meyer et al. upon substitution of phosphine ligands for some of the bpy ligands in the [Os(bpy)$_3$]$^{2+}$ framework.[8] This shift is the result of a stabilization of the Os-based dπ HOMO upon coordination to the phosphine ligands.

[Os(tpypz)(dppe)(CH$_3$CN)]$^{2+}$ displays a lowest lying ^{1}MLCT absorption at 422 nm. This is the highest energy absorption for an osmium complex incorporating a polyazine ligand capable of bridging reported to date. This is a direct result of the incorporation of the phosphine ligand into the osmium tpypz framework.

Table 2. Electronic Absorption Spectroscopy and Photophysical Data for a Series of Osmium(II) Complexes Incorporating 2,3,5,6-Tetrakis(2-pyridyl)pyrazine[a]

complex	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	τ (ns)
[Os(tpypz)$_2$]$^{2+}$	468	750	600
[Os(tpypz)(tpy)]$^{2+}$	468	775	260
[Os(tpypz)(dppe)Cl]$^+$	464	800	250
[Os(tpypz)(dppe)$_2$Cl]$^+$	462	750	200
[Os(tpypz)(dppe)(CH$_3$CN)]$^{2+}$	422	720	344
trans-[Os(tpypz)(PPh$_3$)$_2$Cl]$^+$	462		
trans-[Os(tpypz)(PPh$_3$)$_2$(CH$_3$CN)]$^{2+}$	434	720	240
cis-[Os(tpypz)(PPh$_3$)$_2$(CH$_3$CN)]$^{2+}$	442	760	320

[a] Measured in deoxygenated acetonitrile solution at room temperature.

Emission Spectroscopy and Excited-State Lifetimes. All of the complexes reported herein are emissive at room temperature in fluid solution except [Os(tpypz)(PPh$_3$)$_2$Cl]$^+$, which probably emits beyond the detection limit of our system. The emission maxima and lifetimes for this series of osmium complexes are outlined in Table 2. Similar trends are seen in the emission energies and the absorption spectroscopy. Namely, substitution of the coordinated chloride by acetonitrile leads to a blue shift in the emission in both the dppe and PPh$_3$ complexes.

All of the complexes studied have excited-state lifetimes in excess of 200 ns. This is in contrast to the 90- and 60-ns lifetimes of [Os(dpp)$_3$]$^{2+}$ and [Os(bpy)$_2$(dpp)]$^{2+}$ (dpp = 2,3-bis(2-pyridyl)pyrazine), the only other osmium complexes with polyazine ligands capable of bridging which have reported emission lifetimes in the literature.[11] [Os(tpypz)$_2$]$^{2+}$ exhibits a much longer lifetime than the other complexes prepared. This may be due to the difference in acceptor modes in this complex.

[Os(tpy)(tpypz)]$^{2+}$ displays a single exponential decay of its emission in fluid solution at room temperature with a lifetime of 260 ns. This is somewhat surprising given that Abruna et al. stated in a previous report that this mixed-ligand complex displays emissions based on both ligands.[8] At 77 K, they report emission bands at 643 and 746 nm and a shoulder at 698 nm. Analysis of our complex under the same conditions (77 K, 4:1 EtOH/MeOH) yields only the band at 746 nm. No intensity is observed at 643 nm. A study of the effect of pH variation on the observed 77 K emission yielded the following results. At low pH (20% concentrated HCl in 4:1 EtOH/MeOH), no emission is observed. In pH regions above this level, the peak at 746 nm is seen. Within the pH region 2–10, we did not observe the additional peak at 643 reported by Abruna et al. The difference in our results may come from our more extensive chromatographic workup and the utilization of crystalline samples for our emission studies.

Conclusions

The preparation of this new class of osmium phosphine complexes has lead to the discovery of some interesting reactivity. The tendency of the diphosphine ligand to substitute trans to itself has lead to the formation of a species with two dangling dppe ligands. The behavior of the bis(triphenylphosphine) solvato complex, converting to the cis isomer from the trans species, indicates that the favored kinetic product involves phosphines trans to each other and the thermodynamic product has the two phosphines in a cis arrangement.

The longer lifetimes and higher energy excited states of these osmium chromophores make them useful building blocks for the construction of supramolecular systems which utilize their light-absorbing ability. The application of the tpypz ligand defines the stereochemical arrangement of additional metal centers which can be coordinated through the utilization of the free tridentate site in these complexes. The phosphine ligands provide a convenient NMR handle to probe stereochemistry. The presence of the coordinated acetonitrile will make possible the further synthetic modification and tuning of these chromophores. Our

ESR studies indicate that the LUMO in these complexes is primarily localized on the pyrazine portion of the tpypz ligand. Efforts are currently in progress to use these building blocks in an array of photochemical molecular devices.

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