

Hydrido Carbonyl Complexes of Osmium(II) and Ruthenium(II) Containing Polypyridyl Ligands

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Received October 19, 1983

Several different synthetic routes have been explored to produce hydrido complexes of Os(II) and Ru(II) containing polypyridyl ligands. The resulting complexes, the majority of which contain coordinated CO, are of three types: *cis*-[M(chelate)₂(CO)H]⁺, *trans*-[Os(chelate)(PPh₃)₂(CO)H]⁺, and [Os(chelate)(di-phos)(PR₃)H]⁺ (where M = Ru or Os and chelate is, for example, 2,2'-bipyridine or 1,10-phenanthroline or a related ligand). The electronic, infrared, and NMR spectral properties of the complexes are discussed along with the redox properties of their ground and excited states. An important observation is that the hydride ligand endows the metal to ligand charge-transfer (MLCT) excited states of some of the complexes with strong reducing properties. The ground-state chemistry of the complexes is discussed especially with regard to their use as synthetic precursors to new, highly oxidizing, long-lived MLCT excited states of Os(II), e.g., [Os^{III}(bpy⁻)(bpy)(CO)(CH₃CH)]²⁺.

The chemistry of polypyridyl complexes of Ru(II) and Os(II) has been extensively studied over a period of years, in particular for complexes containing 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen). Work in this area has been motivated in large part by the use of the complexes as stoichiometric and catalytic redox reagents,^{1,2} as the component parts in mixed-valence ions,³ and in the study of excited-state electron-transfer reactions.⁴ With regard to the latter point, the use of the long-lived metal to ligand charge-transfer (MLCT) excited states of Ru(bpy)₃²⁺ in a variety of energy conversion schemes is especially notable.^{4,5} The expansion of the study of excited-state redox reactions using photocatalysts has been hampered by a number of factors among which are photoinstability of the complexes and insufficient ranges of excited-state energies and associated redox potentials in complexes with long-lived MLCT excited states.

The recent discovery that systematically variable excited-state properties could be obtained in bpy and phen complexes of Os(II) has led to the development of synthetic routes for the preparation of a variety of complexes of the type Os(bpy)₂L₂²⁺, Os(phen)₂L₂²⁺, Os(bpy)L₄²⁺, and Os(phen)L₄²⁺ where L can be a wide variety of ancillary or "tuning" ligands that modify the properties of the Os-bpy or Os-phen chromophores in a predictable manner. In earlier work on Os(II) polypyridyl complexes the ancillary ligands have generally been phosphines, arsines, NH₃, or CN⁻.^{6,7} Here we report the development of new synthetic

routes to polypyridyl complexes of Os(II) and of Ru(II) to which the CO and hydride ligands are bound. Several of the Os complexes have the unusual feature, for a metal hydride, of having low-lying, emitting excited states that can be observed in fluid solution at room temperature. A portion of this work has appeared as a preliminary communication.⁸

Experimental Section

Instrumental Data. Cyclic voltammetric experiments were carried out by using a Princeton Applied Research 173 potentiostat with a home-built sweep generator and an HP7015B XY recorder. Samples were dissolved in high purity acetonitrile (Burdick-Jackson Labs) with 0.1 M tetra-*N*-ethylammonium perchlorate (TEAP) as the supporting electrolyte and were deoxygenated by N₂ bubbling for 5 min prior to use. The solutions were kept under a constant N₂ flow during the measurement. A single compartment cell utilizing a platinum bead working electrode, a platinum wire auxiliary electrode, and a saturated sodium chloride calomel reference electrode (SSCE) was used for all measurements. Potentials are all reported vs. the SSCE. All potentials are reported as *E*_{1/2} values where *E*_{1/2} = 1/2(*E*_p^a + *E*_p^c) and *E*_p^a and *E*_p^c are the anodic and cathodic peak potentials. Peak splittings were typically less than 70 mV, and unless stated otherwise, all couples were assumed to be chemically reversible.

NMR spectra were obtained on a Bruker AM250 instrument. ¹H spectral data (250 MHz) were acquired in either acetonitrile-*d*₃ or acetone-*d*₆ (Aldrich) at room temperature in 4-mm tubes with Me₄Si as an internal standard. In general ¹H NMR spectral data were used to define the stereochemistries of products containing alkylphosphine ligands. Due to the complexity of the aromatic bpy and phen resonances in the region δ 6-9 (particularly when arylphosphines are present) only peak resonances for alkyl groups will be reported unless the aromatic region is required in order to prove the structure.

Proton-decoupled ³¹P NMR spectral data (101 MHz) were obtained in either acetone-*d*₆/acetone (1:3) or CD₃CN/CH₃CN (1:2) in 10-mm tubes with 0.1 M phosphoric acid as an external

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standard. All shifts are reported under the modern convention with positive shifts being downfield. In some cases instead of transferring the external field from sample to sample the instrument was locked by using phosphoric acid and the most intense peak, which was due to PF_6^- , was used as an internal standard (-143.0 ppm) since all complexes were PF_6^- salts and therefore the standard was automatically present. Sample concentrations were typically 10^{-3} M in complex, and generally satisfactory spectra were obtained with 200–1000 pulses.

Electronic spectra were acquired by using either a Cary 17 or a Bausch and Lomb Spectronic 2000 spectrometer. Samples were contained in 1-cm quartz cells.

Infrared spectra were obtained on a Beckman IR 4250 recording spectrophotometer. Solution spectra (CH_2Cl_2) were run in 1-mm length NaCl cells.

Elemental analyses were provided by Integral Microanalytical Labs, Raleigh, NC, and are supplied as supplementary material.

Materials. All solvents were of reagent grade and were used as received. $[\text{OsCl}_6][\text{NH}_4]_2$ was from Engelhard. All ligands except phosphines and arsines (Strem Chemicals) were obtained from Aldrich. Neutral alumina was obtained from Fischer.

Preparations. **Preparation of $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}](\text{PF}_6)$.** A suspension of *cis*- $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (250 mg)¹ was heated at reflux in 35 mL of 2-methoxyethanol while a stream of CO gas was passed through the liquid. After 1.5 h the CO stream was discontinued and the vessel was cooled to room temperature. To the yellow solution was added 10 mL of saturated aqueous $(\text{NH}_4)\text{PF}_6$ solution and 35 mL of H_2O . The flocculent bright yellow precipitate was filtered, washed with H_2O , and Et_2O and dried by suction. The solid was then dissolved in 2:1 toluene/ CH_3CN solution and recrystallized using the solvent gradient. Bright yellow microcrystals were obtained in 93% yield (284 mg).

Preparation of *cis*- $[\text{Os}^{\text{II}}(\text{bpy})_2(\text{CO})\text{Cl}](\text{PF}_6)$ from Carbon Monoxide. A round-bottom flask equipped with a side-arm bubbler and reflux condenser was charged with 30 mL of ethylene glycol and 200 mg of $\text{Os}(\text{bpy})_2\text{Cl}_2$. In a well-ventilated hood CO gas was slowly bubbled through the mixture. The solution was then heated at reflux until all the starting complex had dissolved to give a reddish solution (ca. 2 h). At this point the reaction was cooled to room temperature and an excess of $(\text{NH}_4)\text{PF}_6$ (in H_2O) was added, along with ca. 30 mL of pure H_2O . The flocculent red to red-orange solid was filtered by suction, washed with copious amounts of H_2O followed by Et_2O , and air-dried. The complex was purified by column chromatography on alumina by using 1:1 CH_3CN /toluene as eluant; isolated yield 170 mg (69%).

Preparation of $[\text{M}(\text{bpy})_2(\text{CO})\text{O}_2\text{CH}](\text{PF}_6)$ ($\text{M} = \text{Ru}^{\text{II}}, \text{Os}^{\text{II}}$). In a typical preparation, 175 mg of $\text{M}(\text{bpy})_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$ ^{6d,9} was added to a round-bottom flask containing 30 mL of deoxygenated 90% formic acid. The mixture was heated at reflux for 1 h in the case of Ru and 3 h for Os. After the mixture was cooled to room temperature, the formic acid was removed on a rotary evaporator and the resultant sticky solid dissolved in 25 mL of cold water. To this solution was added 5 mL of saturated NH_4PF_6 solution. The solid precipitate that was bright yellow for Ru and red for Os was subsequently filtered and washed with water and then Et_2O . The complexes were dissolved in methylene chloride and slowly dripped into stirred Et_2O through a sintered glass frit. The yield was 151 mg in the case of Ru and 177 mg for Os (89% and 85%, respectively).

Preparation of *trans*- $\text{Os}(\text{phen})(\text{L})_2(\text{CO})\text{Cl}^+$ ($\text{L} = \text{PPh}_3, \text{PPh}_2\text{Me}, \text{PMe}_3$). In a typical reaction $\text{Os}(\text{phen})\text{Cl}_4^7$ (75 mg) was allowed to react with PPh_3 (200 mg, 5.2 equiv) at reflux in ethylene glycol under an atmosphere of CO for 1 h followed by standard workup and chromatography with 1:1 toluene/ MeCN as eluant. Typically, the yellow product, e.g., *trans*- $[\text{Os}(\text{phen})(\text{PPh}_3)_2(\text{CO})\text{Cl}](\text{PF}_6)$ was obtained in 85% yield.

Preparation of *cis*- $\text{Os}(\text{phen})(\text{L}_2)(\text{CO})\text{Cl}^+$ ($\text{L}_2 = \text{dppene}, \text{dppb}$ ($\text{dppene} = \text{cis-1,2-Bis(diphenylphosphino)ethylene}$; $\text{dppb} = \text{1,2-Bis(diphenylphosphino)benzene}$)). The complexes were prepared as described above for monodentate phosphines. In both cases the products were the isomer with CO *trans* to P.

Preparation of *cis*- $[\text{Os}(\text{phen})(\text{dppene})(\text{CO})\text{Cl}](\text{PF}_6)$ from Carbon Monoxide. The addition of CO was accomplished in

a similar manner to that described above in the preparation of $[\text{M}(\text{bpy})_2(\text{CO})\text{Cl}](\text{PF}_6)$. In a typical reaction 80 mg of *cis*- $\text{Os}(\text{phen})(\text{dppene})\text{Cl}_2$ ^{6d} was allowed to react with a stream of CO gas while the solution was heated at reflux for 30 min in 2-methoxyethanol. Purification was achieved as described for the $[\text{M}(\text{bpy})_2(\text{CO})\text{Cl}](\text{PF}_6)$ complexes. The yield was 72 mg (78%).

Reaction of $[\text{Os}(\text{bpy})_2(\text{CO})\text{Cl}](\text{PF}_6)$ with Nitrite Ion. $[\text{Os}(\text{bpy})_2(\text{CO})\text{Cl}](\text{PF}_6)$ (200 mg) was allowed to react at reflux with a 100-fold excess of NaNO_2 for 26 h in 1:1 ethylene glycol/ H_2O under an argon atmosphere. During the course of the reaction, the solution slowly changes color from red to yellow. The product was precipitated from solution by the addition of an excess of KPF_6 and isolated by filtration. Column chromatography on alumina with 2:1 toluene/acetonitrile as eluant gave the pure product $[\text{Os}(\text{bpy})_2(\text{CO})\text{NO}_2](\text{PF}_6)$ as a yellow solid.

***cis*- $[\text{Os}(\text{bpy})_2(\text{CO})\text{Cl}](\text{PF}_6)$ from Formic Acid.** Another convenient method for the preparation of $[\text{Os}(\text{bpy})_2(\text{CO})\text{Cl}](\text{PF}_6)$ involved the reaction between *cis*- $\text{Os}(\text{bpy})_2\text{Cl}_2$ (250 mg) and deoxygenated HCOOH (30 mL, 90% solution). The mixture was heated at reflux for 12 h under a N_2 atmosphere, after which time the formic acid was removed on a rotary evaporator. To the residue was added 25 mL of H_2O and 5 mL of saturated NH_4PF_6 solution, and the resultant red flocculent precipitate was collected by filtration. Purification was accomplished as described above for the CO reaction product. The yield was 262 mg (85%).

Reaction of $[\text{Os}(\text{phen})(\text{dppb})(\text{CO})\text{Cl}](\text{PF}_6)$ with PMe_2Ph . Substitution of CO by PMe_2Ph was achieved by the reaction of *cis*- $[\text{Os}(\text{phen})(\text{dppb})(\text{CO})\text{Cl}](\text{PF}_6)$ (75 mg) with excess PMe_2Ph (150 mg) in 30 mL of ethylene glycol heated at reflux for 1 h followed by the usual workup and chromatography. The red crystalline salt $[\text{Os}(\text{phen})(\text{dppb})(\text{PMe}_2\text{Ph})\text{Cl}](\text{PF}_6)$ was subsequently air-dried.

Alcohol and Base Procedure for the Preparation of $[\text{Os}(\text{chelate})_2(\text{CO})\text{H}](\text{PF}_6)$ (Chelate = bpy or phen). The hydrido complexes were prepared directly from the corresponding chloro derivatives. In a typical reaction $[\text{Os}(\text{bpy})_2(\text{CO})\text{Cl}](\text{PF}_6)$ (100 mg) was allowed to react with either PPh_3 (300 mg) or 2,6-lutidine (0.5 mL) in 30 mL of ethylene glycol at reflux for 12 h. The red starting material slowly deepened in color and following standard workup and chromatography $[\text{Os}(\text{bpy})_2(\text{CO})\text{H}](\text{PF}_6)$ was obtained in ca. 70% yield. The only impurities were starting material and, in the case of PPh_3 , a small amount of *trans*- $[\text{Os}(\text{bpy})(\text{PPh}_3)_2(\text{CO})\text{H}](\text{PF}_6)$, both of which are easily removed by chromatography.

$[\text{M}(\text{chelate})_2(\text{CO})\text{H}](\text{PF}_6)$ from the Metal Formate Complexes ($\text{M} = \text{Ru}, \text{Os}$; Chelate = bpy or phen). In a typical experiment $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{O}_2\text{CH})](\text{PF}_6)$ (100 mg) was added to 25 mL of deoxygenated 2-methoxyethanol. The mixture was heated at reflux for 5 h after which time the reaction mixture was cooled and 5 mL of saturated NH_4PF_6 solution and 35 mL of H_2O were added to the yellow-orange reaction solution. The yellow-orange flocculent product was filtered, washed with H_2O and Et_2O , and air-dried. Chromatography on alumina as described in the previous preparations with 2:1 toluene/acetonitrile yielded 45 mg (48%) of yellow-orange crystalline product. The osmium analogue was prepared and purified in the same manner except that the solvent used was ethylene glycol, and the reaction time was 45 min at reflux. In this case, the yield from 100 mg of carbonyl formate was 83 mg (88%).

***trans*- $[\text{Os}(\text{bpy})(\text{PPh}_3)_2(\text{CO})\text{H}]^+$ by the Alcohol and Base Method.** This complex can be prepared by a number of reactions. Prolonged reflux of $[\text{Os}(\text{bpy})_2(\text{CO})\text{Cl}](\text{PF}_6)$ with PPh_3 in ethylene glycol gives the yellow *trans*- $\text{Os}(\text{bpy})(\text{PPh}_3)_2(\text{CO})\text{H}^+$, apparently via $\text{Os}(\text{bpy})_2(\text{CO})\text{H}^+$ which is formed as an intermediate. The reaction of $\text{Os}(\text{bpy})\text{Cl}_4^7$ (1.0 equiv) with PPh_3 (4.0 equiv) in ethylene glycol at reflux for 15 min yielded the hydride in addition to an extremely insoluble brown material. Finally, the reaction of $\text{Os}(\text{PPh}_3)_3\text{Cl}_2$ (1.0 equiv) with bpy (1.05 equiv) in ethylene glycol at reflux for 12 h also yielded the hydride.

***trans*- $[\text{Os}(\text{chelate})(\text{PPh}_3)_2(\text{CO})\text{H}](\text{PF}_6)$ from *mer*- $\text{Os}(\text{PPh}_3)_3(\text{CO})\text{HCl}$ (Chelate = Bipyridine, Bipyrimidine, Bipyrazine, or 4,5,7,8-Tetramethyl-1,10-phenanthroline).** As a general procedure, 100 mg of *mer*- $\text{Os}(\text{PPh}_3)_3(\text{CO})\text{HCl}$ ¹⁰ was

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heated at reflux with a 5-fold molar excess of chelate ligand for 20 min in ca. 10 mL of ethylene glycol. The solution was then cooled to room temperature, and 20 mL of aqueous NH_4PF_6 was added. After the yellow to orange precipitate was washed with H_2O followed by ether, the complex was air-dried. Material of high purity could be obtained by slowly dropping a CH_2Cl_2 solution of the complex into stirred Et_2O followed by collection of the resulting solid and finally washing with ether and air-drying. The isolated yields were 90–95% based on the starting Os complex.

Preparation of PF_6^- Salts of $\text{Os}(\text{phen})(\text{dppb})(\text{PPh}_3)\text{H}^+$, $\text{Os}(\text{phen})(\text{dppene})(\text{PPh}_3)\text{H}^+$, and $\text{Os}(\text{phen})(\text{dppene})(\text{PEt}_3)\text{H}^+$. These complexes were prepared from *cis*- $[\text{Os}(\text{phen})(\text{dppb})(\text{CO})\text{Cl}](\text{PF}_6)$ and *cis*- $[\text{Os}(\text{phen})(\text{dppene})(\text{CO})\text{Cl}](\text{PF}_6)$, respectively. In a typical reaction the yellow $[\text{Os}(\text{phen})(\text{dppb})(\text{CO})\text{Cl}](\text{PF}_6)$ (70 mg) was allowed to react with PPh_3 (200 mg) for 30 min in 25 mL of ethylene glycol heated at reflux. Following standard workup and chromatography the red salt $[\text{Os}(\text{phen})(\text{dppb})(\text{PPh}_3)\text{H}](\text{PF}_6)$ was obtained in 75% yield.

Reaction of $[\text{Os}(\text{bpy})_2(\text{CO})\text{H}](\text{PF}_6)$ with $\text{CF}_3\text{SO}_3\text{H}$. In a 500-mL round-bottom flask containing 150 mL of 1,2-dichloromethane and 450 mg of $[\text{Os}(\text{bpy})_2(\text{CO})\text{H}](\text{PF}_6)$ 12 drops of $\text{CF}_3\text{SO}_3\text{H}$ were added by using a glass pipette. The mixture was stirred under a N_2 atmosphere for 40 min. The red color of the carbonyl hydride in solution slowly changed to yellow during this period. The mixture was heated at reflux for 30 min during which time the color changed to yellow-orange and some orange crystals deposited from the solution. After the mixture was cooled to room temperature, 300 mL of Et_2O was added in 50-mL aliquots with 5-min stirring time between each addition. After the addition was complete, the solution was stirred for another 30 min and then filtered. The yield was 540 mg (87%).

Reaction of $[\text{Os}(\text{bpy})_2(\text{CO})\text{H}](\text{PF}_6)$ with RCOOH ($\text{R} = \text{CH}_3, \text{CF}_3$). To a flask containing 100 mg of $[\text{Os}(\text{bpy})_2(\text{CO})\text{H}](\text{PF}_6)$ and 50 mL of 1,2-dichloroethane was added 1 mL of the appropriate acid under a N_2 blanket. The reaction was heated at reflux for 1 h and cooled, and the solvent was removed on a rotary evaporator. The resulting sticky, semisolid material was treated with H_2O followed by NH_4PF_6 (salt); the solid was collected, dried, and purified by chromatography on alumina. For the case of trifluoroacetic acid the yield was 85% (99 mg). For the case of acetic acid the crude mixture was not purified, but cyclic voltammetry showed partial conversion to the acetate complex as shown by the appearance of a wave at 1.18 V in CH_3CN vs. SSCE which can be associated with the carboxylato complex.

Reaction of $[\text{Os}(\text{bpy})_2(\text{CO})\text{H}](\text{PF}_6)$ with $(\text{C}_7\text{H}_7)(\text{PF}_6)$. To a stirred solution of 120 mg of $[\text{Os}(\text{bpy})_2(\text{CO})\text{H}](\text{PF}_6)$ in 15 mL of nitromethane was added dropwise a solution of 42 mg of $(\text{C}_7\text{H}_7)(\text{PF}_6)$ in 20 mL of CH_3NO_2 . The mixture was allowed to stir for 1 h at which time 100 mL of Et_2O was slowly added. The yellow to light yellow precipitate that formed was collected on a sintered glass funnel, washed with copious amounts of Et_2O , and air-dried. The yield was 129 mg (95%).

Thermolysis of $\text{Os}(\text{bpy})_2(\text{CO})(\text{OC}(\text{=O})\text{CF}_3)(\text{PF}_6)$. To a flask containing 150 mg of $\text{Os}(\text{bpy})_2(\text{CO})(\text{OC}(\text{=O})\text{CF}_3)(\text{PF}_6)$ was added 20 mL of ethylene glycol. The mixture was heated at reflux for 45 min.

Preparation of $[\text{Os}(\text{bpy})_2(\text{CO})(\text{OS}(\text{=O})_2\text{CF}_3)](\text{O}_3\text{SCF}_3)$ from $[\text{Os}(\text{bpy})_2(\text{CO})\text{Cl}](\text{PF}_6)$ and Trifluoromethanesulfonic Acid. To a round-bottom flask containing 500 mg of $[\text{Os}(\text{bpy})_2(\text{CO})\text{Cl}]\text{PF}_6$ was added 150 mL of 1,2-dichlorobenzene. The mixture was deoxygenated with a stream of N_2 , and after 15 min 10 drops of $\text{CF}_3\text{SO}_3\text{H}$ were added. Deoxygenation was continued for another 10 min at which time a reflux condenser was added and the mixture heated at reflux for 1.5 h while magnetic stirring was maintained under a N_2 atmosphere. After this period the reaction mixture was cooled to room temperature, 10 drops more $\text{CF}_3\text{SO}_3\text{H}$ was added (under N_2), and the mixture heated at reflux for 30 min. After the mixture was cooled to room temperature a second time, 300 mL of Et_2O was added to the reaction mixture slowly (ca. 50 mL at a time) while gentle magnetic stirring was maintained. The mixture was then allowed to stir for ca. 1 h to assure complete (or near complete) precipitation of the yellow-orange complex, after which time the microcrystalline product was filtered on a sintered glass funnel and washed with copious amounts of Et_2O . Purification was achieved by dissolving the complex in ca. 50–100 mL of dry dimethoxyethane and filtering

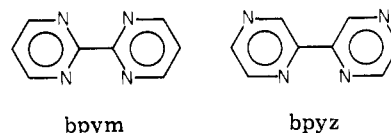
into stirred Et_2O (300 mL). In this manner a bright yellow insoluble impurity was removed. The yield was 524 mg (91%).

Reaction of $[\text{Os}(\text{bpy})_2(\text{CO})(\text{O}_3\text{SCF}_3)](\text{O}_3\text{SCF}_3)$ with $\text{C}_6\text{H}_5\text{N}$ and CH_3CN . To a 50-mL round-bottom flask containing 20 mL of the neat solvent was added 100 mg of the osmium complex. The reaction mixture was heated at reflux for 3 h under a blanket of dry N_2 while magnetic stirring was maintained. After the mixture was cooled, the solvent was removed on a rotary evaporator and 20 mL of H_2O was added until the yellowish residue had dissolved. Upon addition of 5 mL of a saturated NH_4PF_6 solution a flocculent yellow precipitate appeared that was collected in a sintered glass frit, washed with H_2O followed by Et_2O , and subsequently air-dried. Chromatography with 2:1 CH_3CN /toluene on alumina yielded yellow microcrystals in both cases. The yields were for CH_3CN 93 mg (88%) and for $\text{C}_6\text{H}_5\text{N}$ 96 mg (86%).

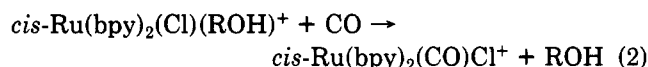
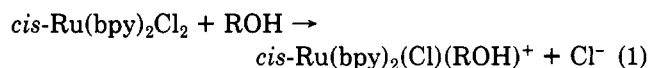
Reaction of $[\text{Os}(\text{bpy})_2(\text{CO})(\text{O}_3\text{SCF}_3)](\text{O}_3\text{SCF}_3)$ with NO_2^- . The reaction of $[\text{Os}(\text{bpy})_2(\text{CO})(\text{O}_3\text{SCF}_3)](\text{O}_3\text{SCF}_3)$ with NO_2^- (Na salt) was carried out on a spectroscopic scale, and the UV-vis spectrum (vide supra) was used to confirm the reaction product as $[\text{Os}(\text{bpy})_2(\text{CO})\text{NO}_2]^+$.

Results and Discussion

In the results and discussion which follow, the bis(diphenylphosphino) ligands *cis*- $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$ and *cis*-(Ph_2P) $_2\text{C}_6\text{H}_4$ are abbreviated as dppene and dppb, respectively, and the polypyridyl ligands 2,2'-bipyridine, 1,10-phenanthroline, 4,5,7,8-tetramethyl-1,10-phenanthroline, 2,2'-bipyrimidine, and 2,2'-bipyrazine as bpy, phen, 4,5,7,8-Me $_4$ phen, bpym, and bpyz, respectively.



Preparation of Polypyridyl Carbonyl Halide and Carbonyl Formate Complexes. The most simple and straightforward synthetic route to polypyridyl complexes of Ru(II) and Os(II) containing CO is the direct reaction of the dichloro precursors *cis*- $\text{Ru}(\text{bpy})_2\text{Cl}_2$, *cis*- $\text{Os}(\text{chelate})_2\text{Cl}_2$ (chelate = bpy or phen), and *cis*- $\text{Os}(\text{phen})(\text{dppene})\text{Cl}_2$ (dppene = 1,2-bis(diphenylphosphino)ethylene) with CO gas in a refluxing alcohol solution. For the complexes *cis*- $\text{Os}(\text{chelate})_2\text{Cl}_2$ the alcohol of choice is ethylene glycol while the remaining complexes can be prepared in 2-methoxyethanol solution. It is well-known, at least for the case of Ru, that in water or aqueous alcohol, halide substitution reactions proceed by intermediate solvento complexes. It is therefore probable that these syntheses occur by CO displacement of the alcohol and that the steps involved are as shown in eq 1 and 2.



Supporting evidence for reactions 1 and 2 come from the fact that the solvento complexes $\text{Ru}(\text{bpy})_2(\text{S})\text{Cl}^{+9}$ and $\text{Os}(\text{bpy})_2(\text{S})\text{Cl}^{+11}$ have been shown to be intermediates in other ligand substitution reactions ($\text{S} = \text{H}_2\text{O}$, acetone).

The conditions for the reactions between *cis*- $\text{Os}(\text{phen})_2\text{Cl}_2$ and *cis*- $\text{Os}(\text{phen})(\text{dppene})\text{Cl}_2$ with CO make an interesting contrast. In order to proceed, the former must be heated at reflux in ethylene glycol solution, while the latter occurs under milder conditions, in 2-methoxyethanol. As we have demonstrated previously for Ru(II)^{12,13} and

(11) Kober, E. M. Ph.D. Thesis, The University of North Carolina, Chapel Hill, NC, 1982.

Table I. Selected NMR Spectral Data for the Hydride-Containing Complexes

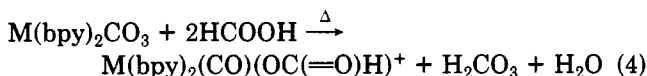
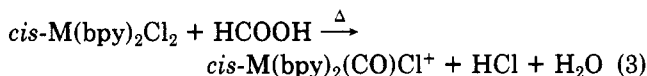
complex (as PF ₆ ⁻ salt)	¹ H (M-H) NMR ^a	³¹ P{ ¹ H} NMR, ^b ppm
[Ru(bpy) ₂ (CO)H] ⁺	-11.3 (s)	...
[Os(bpy) ₂ (CO)H] ⁺	-11.4 (s)	...
[Os(phen) ₂ (CO)H] ⁺	-11.5 (s)	...
[Os(phen)(dppb)(PPh ₃)H] ⁺	-14.7 (q, 17 Hz)	...
[Os(phen)(dppene)(PPh ₃)H] ⁺	-15.1 (d of t, 16 Hz, 20 Hz)	c
[Os(phen)(dppene)(PEt ₃)H] ⁺	-15.5 (d of t, 16 Hz, 21 Hz)	c
<i>trans</i> -[Os(bpy)(PPh ₃) ₂ (CO)H] ⁺	-12.1 (t, 37 Hz)	c
<i>trans</i> -[Os(bpy)(PPh ₃) ₂ (CO)H] ⁺	-12.3 (t, 37 Hz)	c
<i>trans</i> -[Os(bpy)(PPh ₃) ₂ (CO)H] ⁺	-12.3 (t, 37 Hz)	c
<i>trans</i> -[Os(4,5,7,8-Me ₄ phen)(PPh ₃) ₂ (CO)H] ⁺	-12.1 (t, 35 Hz)	c
[Os(phen)(dppb)(CO)Cl] ⁺	...	30.4 (s), 22.3 (s)
[Os(phen)(dppene)(CO)Cl] ⁺	...	36.1 (s), 27.3 (s)
<i>trans</i> -[Os(phen)(PMe ₂ Ph) ₂ (CO)Cl] ⁺	...	-24.4 (s)
<i>trans</i> -[Os(phen)(PMe ₃) ₂ (CO)Cl] ⁺	...	-35.0 (s)

^a Recorded in (CD₃)₂CO solution with Me₄Si as internal standard (δ scale). ^b Recorded in CH₃CN solution, shift relative to 85% H₃PO₄. ^c Not recorded.

Os(II)¹³ polyphosphine complexes, the rate enhancement is expected due to the kinetic *trans*-labilizing ability of the phosphine ligands.

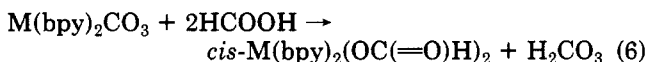
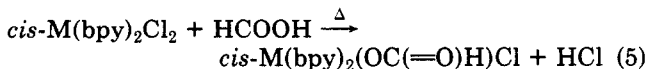
The carbonyl complexes [M(bpy)₂(CO)Cl]⁺ were shown to have the *cis* configuration by both ¹H and ¹³C NMR spectral data. The ¹³C NMR spectrum of Ru(bpy)₂(CO)Cl⁺ in CH₃CN solution shows clearly the magnetically inequivalent ortho, meta, and para carbon atoms that occur from ca. -160 to -120 ppm (from CH₃CN as internal standard, adjusted to Me₄Si at 0 ppm.) In addition, the carbonyl carbon resonance is clearly visible at -200.4 ppm.

A convenient source of CO for the synthesis of mono-carbonyl complexes of Ru(II) and Os(II) is formic acid,¹⁴ which, it should be noted, is simply hydrated CO. Thus, heating *cis*-M(bpy)₂Cl₂ or M(bpy)₂CO₃ in refluxing formic acid produces M(bpy)₂(CO)Cl⁺ and M(bpy)₂(CO)(OC(=O)H)⁺, respectively (see eq 3 and 4) in yields exceeding 80%. The carbonyl formate complexes have ¹H NMR

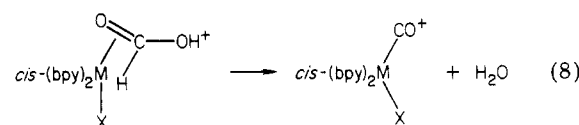
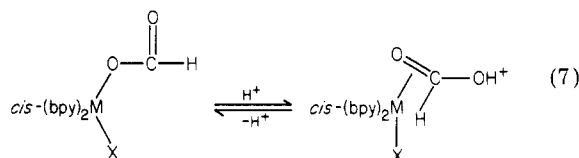


spectra characteristic of the *cis* bpy geometry,^{1,15,16} which is very similar to the spectrum of [Ru(bpy)₂(CO)Cl]⁺; however, a characteristic single resonance also appears that can be assigned to the aldehydic type proton at δ 7.85 for Ru and δ 7.63 for Os (CH₃CN solution vs. Me₄Si standard). Elemental analyses for the complexes reported here for the first time are supplied as supplementary material.

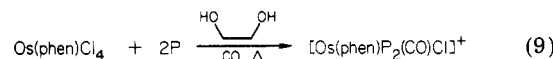
Although no mechanistic information is available for the formic acid reactions, reasonable pathways can be written involving initial formate binding forming mono- or bis-(formate) complexes (eq 5 and 6). The bis(formate)



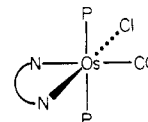
complex *cis*-Ru(bpy)₂(O₂CH)₂ has been isolated and characterized and will be discussed in a separate publication.¹⁷ The subsequent interconversion to the carbonyl hydrido complexes must be intramolecular reactions. It is conceivable that they involve as an intermediate a π -bound formic acid group like that shown in eq 7 and 8. There appears to be no direct precedence for such an intermediate; however, related η^2 -formaldehyde complexes of Os¹⁸ and Pt¹⁹ have been isolated.



Preparation of Mixed-Ligand Polypyridine Phosphine Carbonyl Chloride Complexes. A convenient "one-pot" synthesis of carbonyl chloride complexes can be achieved by direct reaction between Os^{IV}(phen)Cl₄, excess phosphine, and CO gas according to the general reaction shown in eq 9. The source of reducing equivalents necessary to reduce Os^{IV} to Os^{II} in eq 9 presumably comes from excess phosphine.



For the case of potentially chelating phosphines like dppene the product in eq 9 is the previously discussed complex Os(phen)(dppene)(CO)Cl⁺ made by direct reaction between *cis*-Os(phen)(dppene)Cl₂ and CO. For monodentate phosphines where P = PPh₃, PPh₂Me, PMe₂Ph, and PMe₃ the predominant product is the isomer shown below.



The assignment of the structure shown above is based on

(12) Sullivan, B. P.; Calvert, J. M.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 1404.

(13) Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 1037.

(14) For some examples of the use of formic acid as a carbonylating agent see: (a) Cleare, M. J.; Griffith, W. P. *J. Chem. Soc. A* **1969**, 372. (b) Douglas, P. G.; Shaw, B. L. *Ibid.* **1969**, 1491.

(15) Walsh, J. L.; Durham, B. *Inorg. Chem.* **1982**, *21*, 329.

(16) Birchall, J. D.; O'Donoghue, T. D.; Wood, J. R. *Inorg. Chim. Acta* **1979**, *37*, L461.

(17) Sullivan, B. P., work in progress.

(18) Head, R. A. *J. Chem. Soc., Dalton Trans.* **1982**, 1637.

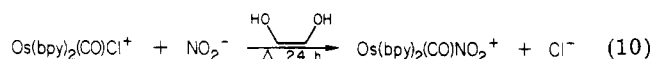
(19) Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Organomet. Chem.* **1982**, *231*, 335.

NMR spectra of the PMe_3 and PMe_2Ph derivatives where "virtually coupled" CH_3 resonances appear in the ^1H NMR spectrum, indicating trans phosphines. ^{31}P NMR spectral data for the carbonyl complexes are summarized in Table I. In these cases two magnetically distinct phosphorus nuclei appear with no observable spin-spin splitting.

Chemical Properties of the Carbonyl Chloride Complexes. The chemical properties of the complex $\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}^+$ have been discussed,²⁰ and the synthesis of the previously discussed Os carbonyl complexes allows some interesting comparisons to be made between the second- and third-row transition metal ions in equivalent coordination environments.

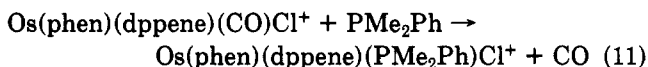
The reaction of $\text{Os}(\text{bpy})_2(\text{CO})\text{Cl}^+$ with Ag^+ in CH_3CN at reflux produces no change over prolonged heating times which contrasts with the Ru analogue which has previously been shown to undergo Cl^- displacement²⁰ to form $\text{Ru}(\text{bpy})_2(\text{CO})(\text{CH}_3\text{CN})^{2+}$.

As will be discussed later, reaction of $\text{Os}(\text{bpy})_2(\text{CO})\text{Cl}^+$ with PPh_3 in ethylene glycol results in Cl^- replacement to form predominantly carbonyl hydride products instead of the expected substitution product $\text{Os}(\text{bpy})_2(\text{CO})(\text{PPh}_3)^{2+}$. No CO displacement products are observed in the reaction under the conditions employed. Displacement of the chloride ion from $\text{Os}(\text{bpy})_2(\text{CO})\text{Cl}^+$ can be effected by anions under forcing conditions. While CN^- in refluxing ethylene glycol yields an intractable mixture of products, under the same conditions NO_2^- gives the carbonyl nitrite complex in good yield (eq 10), which is isolated as its hexafluorophosphate salt.



As mentioned above, displacement of CO by neutral ligands does not occur under forcing thermal conditions nor does it occur with visible photolysis, at least for $\text{Os}(\text{bpy})_2(\text{CO})\text{Cl}^+$ or $\text{Os}(\text{phen})_2(\text{CO})\text{Cl}^+$ in CH_3CN solution. The corresponding complexes of Ru undergo displacement of CO upon visible photolysis to give complexes like $\text{Ru}(\text{bpy})_2(\text{CH}_3\text{CN})\text{Cl}^+$.²⁰ The relative photochemical inertness of the Os complexes parallels that of $\text{Os}(\text{bpy})_3^{2+}$ or $\text{Os}(\text{bpy})_2\text{L}_2^{2+}$ vs. $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{bpy})_2\text{L}_2^{2+}$ where the general explanation is that for $\text{Ru}(\text{bpy})_3^{2+}$ the low-lying MLCT excited states have a thermally accessible d-d state or states from which substitutional photochemistry occurs. In the case of the Os^{II} polypyridyl complexes, 10Dq is ca. 30% higher, the d-d states are considerably higher in energy and apparently thermally inaccessible from the MLCT states, which makes the complexes photochemically stable toward ligand substitution.

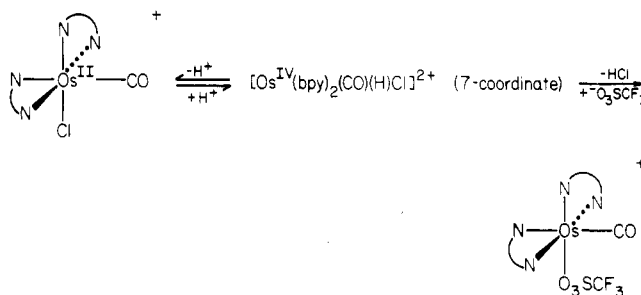
The complex $\text{Os}(\text{phen})(\text{dppene})(\text{CO})\text{Cl}^+$ is an example where CO substitution does occur with the good donor phosphine ligand PMe_2Ph as shown in eq 11. This is



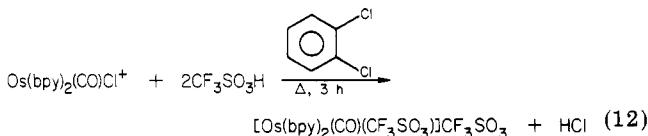
undoubtedly due to the trans-labilizing ability of the diphosphine ligand noted earlier, and it is important to note that the apparent trans effect applies not only to σ -donor ligands like Cl^- (vide supra) but also to π -acceptor ligands.

Protonation and subsequent reaction of $\text{Os}(\text{bpy})_2(\text{CO})\text{Cl}^+$ can be achieved by using high-temperature conditions and the strong acid $\text{CF}_3\text{SO}_3\text{H}$. With *o*-dichlorobenzene as

Scheme I



solvent the reaction shown in eq 12 proceeds in ca. 90% yield.²² No reaction is observed using HCOOH or CF_3C -



O_2H under identical conditions. The reaction may proceed by initial protonation of the $\text{Os}(\text{II})$ complex under the strongly acidic conditions used in the synthesis to yield a formal $\text{Os}(\text{IV})$ intermediate. In a subsequent step, the final product would appear by elimination of HCl concomitant with capture of the CF_3SO_3^- ligand (see Scheme I).

In fact, in a later paper we will present NMR spectral evidence in strong acid media for *stable* seven-coordinate hydrido species.²⁸ An alternate and clearly important possibility, if not here in other systems, is proton-assisted substitution via intermediates like $[(\text{bpy})_2(\text{CO})\text{Os}(\text{HCl})]^{2+}$.

Synthesis of Carbonyl Hydride Complexes and Phosphine Hydride Complexes from Phosphines and Ethylene Glycol. A useful aspect of the thermal substitution chemistry of osmium carbonyl chloride complexes is that reaction with excess PPh_3 in ethylene glycol provides a facile route to several new structural types of carbonyl hydride products. For the example of $[\text{Os}(\text{bpy})_2(\text{CO})\text{Cl}]^+$, a typical preparation yields both the red complex $\text{Os}(\text{bpy})_2(\text{CO})\text{H}^+$ and the bright yellow complex $[\text{Os}(\text{bpy})(\text{PPh}_3)_2(\text{CO})\text{H}]^+$ which account for over 85% of the reaction mixture (see Experimental Section).

The assignment of the trans stereochemistry to $[\text{Os}(\text{bpy})(\text{PPh}_3)_2(\text{CO})\text{H}]^+$ follows from both ^1H and ^{31}P NMR spectral studies which show that the bpy ligand has no magnetic symmetry while the phosphorus environments ($^{31}\text{P}\{^1\text{H}\}$) are magnetically symmetric. The hydride resonance is consistent with this formulation in that it is coupled to two equivalent phosphorus nuclei and thus appears as a triplet (see Table I). The structural characterization of *cis*- $[\text{Os}(\text{bpy})_2(\text{CO})\text{H}]^+$ is presented in a subsequent section of this paper.

By reaction of the complexes $[\text{Os}(\text{phen})(\text{diphos})(\text{CO})\text{Cl}]^+$ (diphos is either dppene or dppb) with either PPh_3 or PET_3 , non-carbonyl-containing hydrides are obtained. It is interesting that the same reaction with PMe_2Ph produces only the phosphine chloro derivative as shown in eq 11. Since PMe_2Ph is sterically a less demanding ligand than either PPh_3 or PET_3 but intermediate in basicity, we can only speculate that some degree of steric hindrance is

(20) Clear, J. M.; Kelly, J. M.; O'Connell, C. M.; Vos, J. G.; Cardin, S. J.; Coster, S. R.; Edwards, A. J. *J. Chem. Soc., Chem. Commun.* 1980, 750.

(21) (a) Durham, B.; Caspar, J. V.; Nagle, J. K.; Meyer, T. J. *J. Am. Chem. Soc.* 1982, 104, 4803. (b) VanHouten, J.; Watts, R. J. *Inorg. Chem.* 1980, 19, 2141.

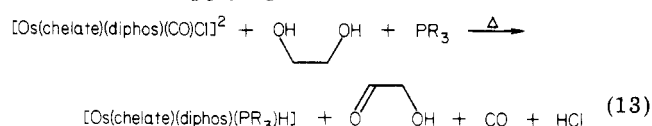
(22) The impetus for developing this synthetic intermediate comes from some very interesting and potentially very important Ru and Os triflate complex chemistry; see: Lay, P. A.; Magnuson, R. H.; Sen, J.; Taube, H. *J. Am. Chem. Soc.* 1982, 104, 7658. Note that in the articles above neat triflic acid was used which can cause oil formation and therefore necessitate in situ use of the metal triflate. In our preparation a high boiling electron poor solvent is used with only a moderate excess of triflic acid; the gain in terms of ease of workup and isolation is obvious.

Table II. Infrared Spectral, Electronic, and Cyclic Voltammetry Data for the Hydride, Carbonyl, and Carbonyl Hydride Complexes

no.	complex ^a	$E_{1/2}(\text{Ox}),^b$ V	$E_{1/2}(\text{Red}),^b$ V	$\nu_{\text{CO}}, \text{cm}^{-1}$	$\nu_{\text{H}}, \text{cm}^{-1}$	$\lambda_{\text{max}}, \text{nm}$ ($\epsilon, \text{M}^{-1} \text{cm}^{-1} \times 10^{-3}$) ^d
1	[Ru(bpy) ₂ (CO)H] ⁺	1.14 ^c	-1.45, -1.67	1941 (br)		22.47
2	[Os(bpy) ₂ (CO)H] ⁺	0.88 ^c	-1.40, -1.63	1911 (s)	2005 (m)	19.23 (4360)
3	[Os(phen) ₂ (CO)H] ⁺	0.90 ^c	-1.43, -1.65	1913 (s)	2006 (m)	20.05 (5320)
4	[Os(phen)(dppb)(PPh ₃)H] ⁺	0.83 ^c	-1.69 ^c		2075 (w)	27.29 (5320)
5	[Os(phen)(dppene)(PPh ₃)H] ⁺	0.80 ^c	-1.65		<i>e</i>	26.12 (5260)
6	[Os(phen)(dppene)(PEt ₃)H] ⁺	0.74 ^c	-1.64 ^c		<i>e</i>	25.13 (5730)
7	<i>trans</i> -[Os(bpy)(PPh ₃) ₂ (CO)H] ⁺	1.54 ^c	-1.47	1931 (s)	2060 (w)	23.91 (1820)
8	<i>trans</i> -[Os(bpy)(PPh ₃) ₂ (CO)H] ⁺	1.55 ^c	-1.04, -1.84	1931 (s)	<i>e</i>	22.17 (876)
9	<i>trans</i> -[Os(bpy)(PPh ₃) ₂ (CO)H] ⁺	1.54 ^c	-0.91, -1.70 ^c	1933 (s)	<i>e</i>	21.00 (1510)
10	<i>trans</i> -[Os(3,4,7,8-Me ₄ phen)(PPh ₃) ₂ (CO)H] ⁺	1.22 ^c	-1.69	1930 (s)	<i>e</i>	25.38 (2367)
11	[Os(phen)(dppb)(CO)Cl] ⁺	1.42	-1.33	1989 (s)		26.48 (3060)
12	[Os(phen)(dppene)(CO)Cl] ⁺	1.54	-1.33	1993 (s)		26.56 (1940)
13	<i>trans</i> -[Os(phen)(PMe ₂ Ph) ₂ (CO)Cl] ⁺	1.28	-1.40	1950 (s)		23.70 (2900), 28.16 (2270)
14	<i>trans</i> -[Os(phen)(PMe ₃) ₂ (CO)Cl] ⁺	1.25	-1.38?	1952 (s)		23.42 (2980), 28.69 (2640)
15	<i>trans</i> -[Os(phen)(PMePh ₂) ₂ (CO)Cl] ⁺	1.41	-1.30	1950 (s)		24.10 (2370), 28.76 (1820)
16	<i>trans</i> -[Os(phen)(PPh ₃) ₂ (CO)Cl] ⁺	1.50	-1.33	1948 (s)		24.37 (2180), 28.76 (2120)
17	[Os(phen)(dppene)(PMe ₂ Ph)Cl] ⁺	0.80	-1.50	...		21.33 (3050)
18	[Ru(bpy) ₂ (CO)Cl] ⁺	1.50	-1.32, -1.55 ^c	1984 (s)		
19	[Ru(bpy) ₂ (CO)(O ₂ CH)] ⁺	1.47	-1.32, -1.52 ^c	1984 (s)		24.51 (4550)
20	[Os(bpy) ₂ (CO)Cl] ⁺	1.18	-1.29, -1.50	1949 (s)		20.82 (3990)
21	[Os(bpy) ₂ (CO)(O ₂ CH)] ⁺	1.13	-1.26, -1.45	1958 (s)		20.64 (3670)
22	[Os(bpy) ₂ (CO)NO ₂] ⁺	1.54 ^c	-1.24, -1.44	1965 (s)		24.21
23	[Os(bpy) ₂ (CO)(O ₂ CCF ₃)] ⁺	1.26	-1.23, -1.43	1963 (s)		21.57 (2480)
24	[Os(bpy) ₂ (CO)(CF ₃ SO ₃)] ⁺	1.55	<i>e</i>	1973 (s)		22.37 (1310)
25	[Os(bpy) ₂ (CO)CF ₃] ⁺	0.99 ^c	-1.43, ^c -1.71 ^c	1921 (s)		19.27 (2110)
26	[Os(bpy) ₂ (CO)(CH ₃ CN)] ²⁺	1.80	-1.14, -1.31	1986 (s)		24.88 (2550)
27	[Os(bpy) ₂ (CO)py] ²⁺	1.67	-1.15, -1.33	1972 (s)		23.96 (1860)
28	[Os(bpy) ₂ (CO)(C ₆ H ₅)] ²⁺	<i>f</i>	<i>f</i>	1990 (s)		25.46 (1910)
29	[Os(bpy) ₂ (CO)(PPh ₃)] ²⁺ ^g	1.98	-1.09, -1.29	1988 (s)		25.71 ^g

^a All PF₆ salts except where noted. ^b Recorded in CH₃CN solution with 0.1 M [NEt₄](ClO₄) at a Pt bead working electrode, using a scan rate of 200 mV/s. Values cited are generally $E_{1/2}$ values calculated from $(E_{p,c} + E_{p,a})/2$, where $E_{p,c}$ and $E_{p,a}$ are the potentials at peak cathodic and anodic current for the waves. ^c Potentials at peak current for irreversible electrochemical processes. ^d Lowest energy λ_{max} in the visible. Molar extinction coefficients are given in parentheses. ^e Not found or not recorded. ^f Reacts too rapidly with CH₃CN to obtain data. ^g See ref 28.

required for the formation of the hydrido complexes by this route. In a general sense, it is easy to envision the accepted mechanism²³ for hydride formation in alcoholic base media as applying to our reactions, e.g., eq 13. In



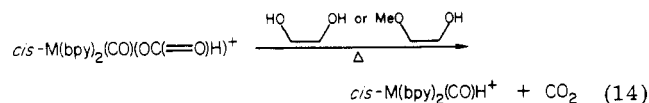
the case of the small phosphine PMe₂Ph, CO displacement must predominate so that the phosphino chloro complex is the major product (eq 11). However, with a sterically hindered phosphine, *trans* phosphorus ligand labilization of the CO group could lead to alcohol/alkoxide ion displacement of CO which is a key step in the mechanism of hydride formation. Since electronically similar complexes of the type *mer*-Os(PR₃)₃(bpy)Cl⁺ are completely inert to chloride substitution under identical conditions, initial phosphine displacement of CO would quench the hydride-forming chemistry.

The complexes *trans*-Os(bpy)(PR₃)₂(CO)Cl⁺ are incapable of forming hydrides from any phosphine reagent under the conditions appropriate for carrying out eq 13. In fact, the complexes are completely inert toward substitution by either PR₃ or by NO₂⁻ after prolonged reflux in ethylene glycol.

The structural assignment of the complexes [Os(phen)(diphos)(PR₃)H]⁺ as having the PR₃ and H group

as mutually *cis* is based on the following evidence, where [Os(phen)(dppb)(PPh₃)H]⁺ is used as a specific example: (1) the phen ligand lacks magnetic symmetry by ¹H NMR; (2) the hydride ligand resonance appears as two overlapping triplet patterns; (3) the ³¹P{¹H} NMR spectrum (CH₃CN solution) is consistent with three separate phosphorus magnetic environments (see Table I). It is important to note that the above structure is the least sterically crowded of the three possible isomers. All of the analogous complexes have the same structure as shown by the ¹H and ³¹P NMR spectral data in Table I.

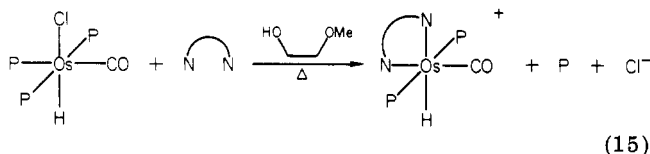
Synthesis of Carbonyl Hydride Complexes by Thermolysis of Carbonyl Formates. Carbon dioxide insertion into metal-hydrogen bonds to form metal formates and the reverse process of CO₂ extrusion to form metal hydrides have been observed for complexes of Mo,^{14b} W,^{14b} and Os.²⁴ The synthesis of the carbonyl formate complexes described above provided an opportunity for using such routes for the specific formation of carbonyl hydride complexes of Os(II) and Ru(II). Thus, thermolysis in a high boiling alcohol gave carbonyl hydrides in good to excellent yield (eq 14). For the case of M = Os, ethylene



glycol is necessary, but for M = Ru, 2-methoxyethanol has

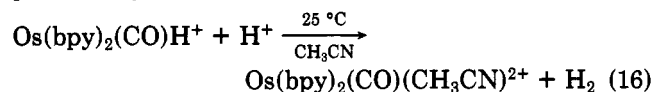
a sufficient thermal range which is convenient since the use of ethylene glycol results in extensive decomposition. The ^1H NMR spectra of the $\text{M}(\text{bpy})_2(\text{CO})\text{H}^+$ complexes are characterized by 16 magnetically nonequivalent bpy protons and sharp M-H resonances at -11.3 and -11.4 ppm for $\text{M} = \text{Ru}$ and $\text{M} = \text{Os}$, respectively (δ vs. Me_4Si as internal standard). The infrared spectra of both complexes in CH_2Cl_2 solution show a medium intensity metal-hydride stretch for $\text{Os}(\text{bpy})_2(\text{CO})\text{H}^+$ at 2005 cm^{-1} , but no apparent stretch is found for the Ru analogue; however, the carbonyl stretch in this compound, which occurs at 1941 cm^{-1} , is noticeably broadened.

Synthesis of Carbonyl Hydride Complexes from *mer*- $\text{Os}(\text{PPh}_3)_3(\text{CO})(\text{H})\text{Cl}$. Another synthetic route to the complex *trans*- $\text{Os}(\text{bpy})(\text{PPh}_3)_2(\text{CO})\text{H}^+$ is the direct reaction between bpy and the complex *mer*- $\text{Os}(\text{PPh}_3)_3(\text{CO})(\text{H})\text{Cl}$ in ethylene glycol (2-methoxyethanol will also work at longer reaction times). The advantages of this method are that a wide variety of heterocyclic ligands can be introduced, and the reactions are virtually quantitative. As shown in eq 15, the reaction takes place to give the expected *trans* product. For the reaction shown in eq 15 the heterocyclic ligand can be extremely electron withdrawing as in the case of 2,2'-bipyrazine (bpz) or 2,2'-bipyrimidine (bpym) or electron donating like 4,5,7,8-tetramethyl-1,10-phenanthroline (4,5,7,8- Me_4phen).



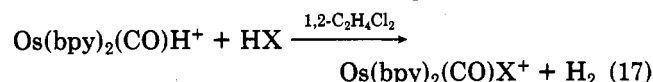
(15)

Chemical Properties of the Metal Hydrido Complexes and Related Derivatives. The complexes $\text{M}(\text{bpy})_2(\text{CO})\text{H}^+$ behave as mild hydride sources in solution. Thus, reaction with a noncoordinating acid such as HPF_6 in CH_3CN solution rapidly produces the solvento complex, presumably with the evolution of hydrogen (eq 16). For



the example shown in eq 16, the acetonitrile complex was isolated and characterized. The complexes $\text{Os}(\text{phen})(\text{diphos})(\text{PR}_3)\text{H}^+$ also react rapidly with HPF_6 in CH_3CN , but the less electron-rich system $\text{Os}(\text{chelate})(\text{PPh}_3)_2(\text{CO})\text{H}^+$ is apparently inert to acid at room temperature since it can be recovered quantitatively from the reaction solution.

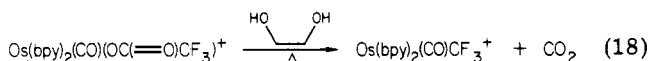
Acid derivatives can be made easily by reaction of the hydride with the coordinating acid in 1,2-dichloroethane solution. The reaction shown in eq 17 occurs with HCl ,



$\text{CF}_3\text{C}(=\text{O})\text{OH}$, or $\text{CF}_3\text{SO}_3\text{H}$ at relatively low temperatures. It is of some interest to note, however, that $\text{CH}_3\text{CO}_2\text{H}$ under the same conditions does not react, an observation which may provide a qualitative feeling for the basicity of the $\text{Os}(\text{II})$ center.

For the case of the CF_3SO_3^- derivative, an alternate preparative route is available by direct reaction between $\text{Os}(\text{bpy})_2(\text{CO})\text{Cl}^+$ and the acid at elevated temperatures, i.e., in refluxing 1,2-dichlorobenzene solution (vide supra). The difference in reactivity of the complexes $\text{Os}(\text{bpy})_2(\text{CO})\text{X}^+$ ($\text{X} = \text{CF}_3\text{CO}_2^-, \text{CF}_3\text{SO}_3^-$) is marked; while the CF_3SO_3^- group can be displaced by pyridine or CH_3CN even at room temperature, the CF_3CO_2^- complex is substitution inert under the same conditions. In refluxing

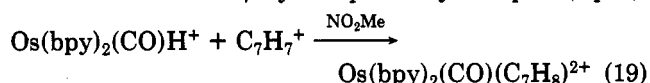
ethylene glycol the CF_3SO_3^- derivative undergoes CF_3 group transfer to the metal (eq 18), much like the formate



complex in eq 12. The reaction in eq 18 provides a new entry route into $\text{Os}(\text{II})$ and $\text{Ru}(\text{II})$ alkyls containing polypyridyl ligands and will be the subject of a forthcoming paper.²⁵

The complex $[\text{Os}(\text{bpy})_2(\text{CO})(\text{O}_3\text{SCF}_3)]^+$ will undergo substitution reactions in aqueous, aqueous alcoholic, or aqueous DMF solutions with anionic donors such as NO_2^- to form $[\text{Os}(\text{bpy})_2(\text{CO})\text{NO}_2]^+$, while the BD_4^- ion at reflux in D_2O allowed the deuterium-substituted derivative $[\text{Os}(\text{bpy})_2(\text{CO})\text{D}]^+$ to be isolated.

A formal insertion reaction between $\text{Os}(\text{bpy})_2(\text{CO})\text{H}^+$ and tropylium ion occurs quantitatively in nitromethane solution to form the η^7 -cycloheptatrienyl complex (eq 19).



This same formal insertion reaction has been recently observed by Sweet and Graham for the complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CO})\text{H}]^+$.²⁶ The Os product contains a bound C_7H_8 ligand that is strongly activated toward attack by nucleophiles. The chemistry of this and related cationic alkene and alkyne complexes will also be described in a later publication. The reaction with tropylium ion may proceed via an initial electron-transfer step since $\text{Os}(\text{bpy})_2(\text{CO})\text{H}^+$ is very stable thermally in the presence of added neutral ligands, which would appear to rule out pathways involving lower coordinate intermediates. Also consistent with an electron-transfer mechanism is the fact that the complex *trans*- $\text{Os}(\text{bpy})(\text{PPh}_3)_2(\text{CO})\text{H}^+$, which has an $\text{Os}(\text{III})/\text{Os}(\text{II})$ reduction potential ca. 500 mV more positive than for $\text{Os}(\text{bpy})_2(\text{CO})\text{H}^+$ (note below), fails to react with C_7H_7^+ even at reflux in nitromethane.

NMR Spectral Studies. Although NMR spectral techniques (^1H , ^{13}C , and ^{31}P) were used to assign structures to all the complexes discussed above, the spectral feature of most interest was the hydridic resonance. Table I shows the M-H chemical shifts for all of the hydrides. The most noticeable result is that, as the $\text{Os}(\text{II})$ complexes become more substituted with phosphine ligands, the hydrido resonance shifts to higher field. An example is found in the series $\text{Os}(\text{bpy})_2(\text{CO})\text{H}^+$ ($\delta -11.4$), *trans*- $\text{Os}(\text{bpy})(\text{PPh}_3)_2(\text{CO})\text{H}^+$ ($\delta -12.1$), and $\text{Os}(\text{phen})(\text{dppb})(\text{PPh}_3)\text{H}^+$ ($\delta -14.7$). Another feature of the data is that, in equivalent coordination environments, the shift is insensitive to both the nature of the metal (compare $\text{Ru}(\text{bpy})_2(\text{CO})\text{H}^+$ ($\delta -11.3$) and $\text{Os}(\text{bpy})_2(\text{CO})\text{H}^+$ ($\delta -11.4$)) and to the nature of the heterocyclic ligand in the complexes *trans*- $\text{Os}(\text{chelate})(\text{PPh}_3)_2(\text{CO})\text{H}^+$ (where the chelate is 4,5,7,8- Me_4phen , bpy, bpym, or bpyz). It has been noted that the metal-hydrogen chemical shift occurs at higher field with ligands of larger trans influence.²⁷ If this is true for our complexes, the order of trans influence is phosphine > nitrogen heterocycles, which is the same ordering as found for trans ligand substitution labilities in some d^6 ruthenium complexes.¹²

Table I also shows $^{31}\text{P}\{^1\text{H}\}$ NMR spectral shifts that have been used in previous sections in conjunction with the structural assignments for the complexes.

(25) Sullivan, B. P.; Smythe, R.; Meyer, T. J. *J. Am. Chem. Soc.* 1982, 104, 4701.

(26) Sweet, J. R.; Graham, W. A. G. *Organometallics* 1982, 1, 982.

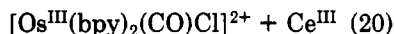
(27) Sullivan, B. P.; Kober, E. M.; Meyer, T. J. *Organometallics* 1982, 1, 1011.

Table III. Emission Maxima and Excited-State Properties of Some Carbonyl and Hydrido Complexes of Os(II)

complex ^a	$\lambda_{\text{max}}, \text{nm}$ ($E_{\text{em}}, \text{cm}^{-1} \times 10^{-3}$)	τ, ns	$E^\circ(\text{Os}^{\text{III/II}*}),^c$ V	$E^\circ(\text{Os}^{\text{II}*/\text{I}}),^c$ V
[Os(bpy) ₂ (CO)H] ⁺	740 (1.675)	42	<-0.80	0.28
[Os(phen) ₂ (CO)H] ⁺	729 (1.701)	192	<-0.80	0.27
[Os(phen)(dppene)(PEt ₃)H] ⁺	731 (1.696)	21	<-0.96	0.01
[Os(phen)(dppene)(PPh ₃)H] ⁺	637 (1.946)	<10	<-1.15	0.30
[Os(phen)(dppb)(PPh ₃)H] ⁺	700 (1.772)	<10	<-0.94	0.08
[Os(bpy) ₂ (CO)Cl] ⁺	682 (1.818)	92	-0.62	0.53
[Os(phen) ₂ (CO)Cl] ⁺	700 (1.772)	425	-0.59	0.50
[Os(phen) ₂ (CO)(py)] ²⁺	590 (2.10)	7010	-0.45	0.97
[Os(bpy) ₂ (CO)(py)] ²⁺	596 (2.10)	1190	-0.43	0.95
[Os(bpy) ₂ (CO)(CH ₃ CN)] ²⁺	563 (2.20)	2400	-0.42	1.06

^a As PF₆⁻ salts. ^b Deoxygenated CH₃CN solution at room temperature. ^c Calculated from data in Table III using eq 21 and 22.

Cyclic Voltammetry of the Complexes. Cyclic voltammetry of the osmium carbonyl complexes in CH₃CN solution with 0.1 M tetraethylammonium perchlorate as supporting electrolyte using a Pt bead electrode shows for all cases an oxidative wave that is in most cases electrochemically and chemically reversible (see Table II). A typical example is that of [Os^{II}(bpy)₂(CO)Cl]⁺ which undergoes a clear reversible oxidation with Ce^{IV} in CH₃CN solution to yield the Os(III) derivative (eq 20).¹¹ All of [Os^{II}(bpy)₂(CO)Cl]⁺ + Ce^{IV} →



the hydrido complexes, including [Ru(bpy)₂(CO)H](PF₆), exhibit irreversible cyclic voltammograms (no return wave) or in the case of the non-carbonyl-containing complexes like [Os(phen)(dppene)(PPh₃)H]⁺, a partially reversible wave, which implies for these latter complexes that a transiently stable Os^{III} hydride is accessible. It is interesting to note that the analogous alkyl complexes [Os(bpy)₂(CO)R]⁺ (R = CF₃, CH₂Ph) are also irreversible upon oxidation.

All of the complexes show one or two heterocycle-based reduction waves that for bpy or phen are in the range of ca. -1.15 to -1.70 depending upon the charge type of the complex.

Two comments of note can be made concerning the ligand-based reduction. The first is that a remarkable variation in redox potential is observed across the series *trans*-[Os(chelate)(PR₃)₂(CO)H]⁺ where bpz > bpym > bpy > 4,5,7,8-Me₄phen. The second is that the range of 0.8 V has profound effects on the variation of excited-state potentials of the complexes, as noted below.

An additional point germane to the problem of ground-state electronic structure is that the first ligand-based reduction for a given heterocyclic ligand can change by ca. 0.4 V through variations in the four remaining ligands in the coordination sphere. This is demonstrated, for example, in the series *trans*-[Os(phen)(PMe₂Ph)₂(CO)Cl]⁺ (-1.30 V) > [Os(phen)(dppene)(PMe₂Ph)Cl]⁺ (-1.50 V) > [Os(phen)(dppb)(PPh₃)H]⁺ (-1.69 V). This dramatic variation is probably not due to solvation energy differences since the complexes are all of the same charge type and have similar molecular radii. Specific electronic effects that induce stronger metal-chelate mixing at one end of the above series would appear to be a likely explanation. Thus, for the above series, phen-based ligand reductions occur at more negative potentials as the ligands used are made more electron rich, that is, as PR₃ replaces CO and H⁻ replaces Cl⁻. The net effect of such an exchange in ligands would be to raise the level of the zero-

order dπ(Os) levels nearer those of π*(phen), resulting in enhanced dπ-π* mixing and more antibonding character in π*(phen) redox levels. Further support for enhanced dπ-π* mixing comes from the fact that the molar extinction coefficient for the lowest lying MLCT band, which is predominantly π*(phen) ← Os(dπ) in nature, systematically increases from 2300 to 5400 M⁻¹ across the above series.

Turning now to the variation in the oxidative processes for the osmium complexes, it is easily seen by reference to Table II that the values vary by about 1.1 V (from ca. 0.7 to 1.8 V) depending upon the ligand content of the coordination sphere. As we have shown previously, the M(III)/M(II) potentials for a series of complexes of the type *cis*-[M(bpy)₂LL']ⁿ⁺ (M = Ru(II), Os(II); n = 0, 1, or 2) vary in a systematic manner with L and L'. As L and L' become better π-acids, the potential for the M^{III/II} redox couple moves to more positive values.^{1,6a} For the carbonylosmium complexes the CO group has the effect of drastically removing electron density from the metal center and thus complexes like Os^{II}(bpy)₂(CO)(CH₃CN)²⁺ and Os^{II}(bpy)₂(CO)(PPh₃)²⁺ are noticeably difficult to oxidize.

Comparison of potentials for the metal-based oxidations for the series *cis*-Os(bpy)₂(CO)X⁺ provides an unprecedented opportunity to demonstrate the relative σ-donor ability of a series of anionic ligands (X). From the data shown in Table III the ability of the ligand X to move the osmium oxidation potential to negative values follows the order H⁻ > -OC(=O)H > -OC(=O)Me > Cl⁻ > -OC(=O)CF₃ > -OS(=O)₂CF₃, which is roughly the order of decreasing basicity of the anion.

For the ruthenium complexes [Ru(bpy)₂(CO)Cl]⁺ and [Ru(bpy)₂(CO)H]⁺ the oxidative wave is displaced positively by ca. 400 mV more than the osmium analogues. This difference between Ru- and Os-based couples in equivalent coordination environments has been noted and discussed previously.¹¹

Absorption, Emission, and Excited-State Properties of Osmium(II) Carbonyl and Osmium(II) Hydrido Complexes. All of the carbonyl and hydrido complexes reported here are red to yellow in color (see Table II). The visible portion of their electronic spectra are dominated by one or more intense dπ → π*(bpy) or -(phen), metal to ligand charge-transfer (MLCT) bands. Intense transitions occur above ~320 nm (~3.13 V) that arise from bpy-localized π → π* transitions and, where present, to phenyl-localized π → π* transitions. In this regard the complexes are very similar to other complexes of Os(II) and Ru(II).¹

A basis for the assignment of the lowest energy, visible absorption bands (E_{op} ; see Figure 1) as predominantly dπ(Os) → π*(bpy) in nature for all the complexes is that plots of E_{op} vs. $\Delta E_{1/2}$ (where $\Delta E_{1/2} = E_{1/2}(\text{Os}^{\text{III/II}}) - E_{1/2}$ -

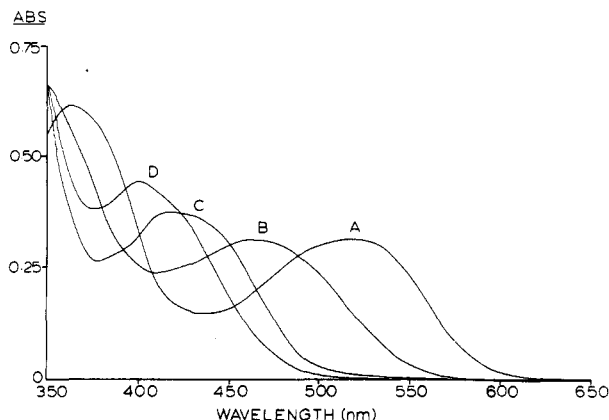


Figure 1. Visible spectra in CH_3CN solution of (a) $[\text{Os}(\text{bpy})_2(\text{CO})\text{CH}_2\text{Ph}](\text{PF}_6)_2$, (b) $[\text{Os}(\text{bpy})_2(\text{CO})(\text{OC}(=\text{O})\text{CF}_3)](\text{PF}_6)_2$, (c) $[\text{Os}(\text{bpy})_2(\text{CO})(\text{py})](\text{PF}_6)_2$, and (d) $[\text{Os}(\text{bpy})_2(\text{CO})(\text{CH}_3\text{CN})](\text{PF}_6)_2$. Notice that the series shows a general trend to higher MLCT transition energy as a function of the ligand cis to CO (see text).

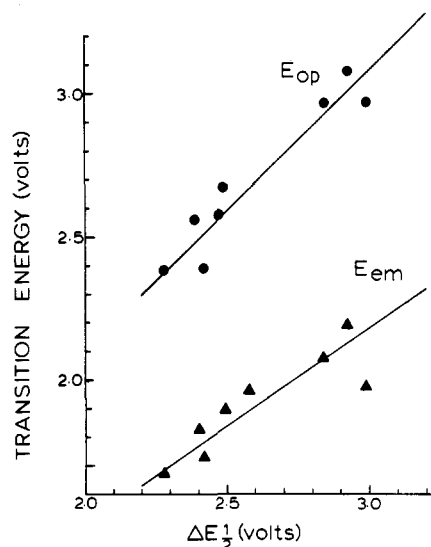


Figure 2. Plot of the lowest energy MLCT spectral transition maximum, E_{op} , and the MLCT emission maximum, E_{em} , vs. the quantity $\Delta E_{1/2}$ for a series of complexes $[\text{Os}(\text{bpy})(\text{CO})(\text{L}, \text{L}', \text{L}'')^{n+}]$ where $n = 1+$ or $2+$ (see text for complexes). The quantity $\Delta E_{1/2}$ is the difference between the metal-based oxidation potential and the ligand- (bpy-) based reduction potential. All measurements refer to CH_3CN solution. The complexes and values used in the comparisons are listed in Table III and conditions detailed in Table III.

(bpy/bpy $^{\cdot-}$) or $E_{1/2}(\text{phen}/\text{phen}^{\cdot-})$ give linear relationships for both the bpy and phen series $[\text{Os}^{\text{II}}(\text{heterocycle})(\text{CO})\text{LL}'\text{L}'']^{n+}$ (heterocycle is bpy or phen; L, L', and L'' are given in Table III; $n = 1$ or 2).^{6a} The linear relationship is demonstrated for a series of bpy complexes in Figure 2. Usually plots such as that in Figure 2a do not exhibit much scatter, but since $\Delta E_{1/2}$ in this case must be determined from kinetic instead of thermodynamic data, i.e., E_p instead of $E_{1/2}$ values, a less satisfactory result is obtained. Figure 2 also shows the same type of plot involving the emission energy, E_{em} , of the MLCT excited state for the same series of complexes.

Absorption and emission energies for the complexes can be dramatically altered by varying the chromophoric, heterocyclic acceptor ligand as shown in Figures 3 and 4 for the series $\text{trans}-[\text{Os}(\text{chelate})(\text{PPh}_3)_2(\text{CO})\text{H}]^+$ where the chromophoric ligands are 4,5,7,8-Me $_4$ phen, bpy, bpyz, and bpym. In Figure 3 are shown visible MLCT spectra of the four complexes, and Figure 4 shows the lowest MLCT absorption and emission energies plotted against the reduction potential for the chelate-localized reduction. It

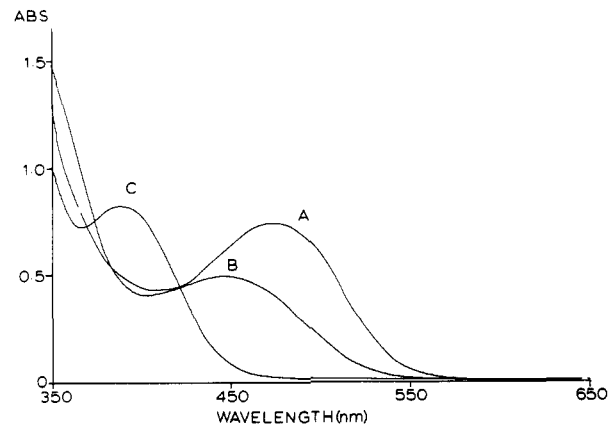


Figure 3. Electronic spectra of $\text{trans}-[\text{Os}(\text{chelate})(\text{PPh}_3)_2(\text{CO})\text{H}](\text{PF}_6)$ in CH_3CN solution: (a) chelate is 2,2'-bipyrazine; (b) chelate is 2,2'-bipyrimidine; (c) chelate is 3,4,7,8-tetramethyl-1,10-phenanthroline. Note the trend to lower energy for the transition as the acceptor ligand becomes electron deficient.

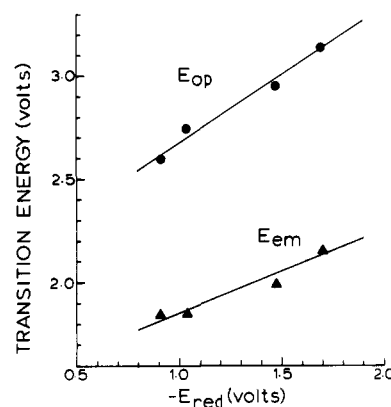


Figure 4. Plots of transition energies vs. $E_{1/2}$ for chelate-based reduction for $\text{trans}-[\text{Os}(\text{chelate})(\text{PPh}_3)_2(\text{CO})\text{H}](\text{PF}_6)$ where in the order shown from left to right chelate is 2,2'-bipyrazine, 2,2'-bipyrimidine, 2,2'-bipyridine, or 3,4,7,8-tetramethylphenanthroline: (a) emission energy vs. $E_{1/2}$ ($-E(\text{Red})$) is shown in the bottom line; (b) energy of the lowest energy MLCT band maximum vs. $-E(\text{Red})$ is shown in the top line. Data refer to CH_3CN solution (see Table III).

is apparent from these data that the presence of chromophoric ligands that are easily reduced leads to a shift in the transition energies to the red.

Table III also lists excited-state lifetime (τ_0) and calculated excited-state redox potentials in deoxygenated CH_3CN solution at room temperature. The τ_0 values vary from <10 ns for the phosphine-rich hydride complexes like $[\text{Os}(\text{phen})(\text{dppene})(\text{PET}_3)\text{H}]^+$ to over $7 \mu\text{s}$ for a carbonyl dication. The latter values are exceptional in that they are the longest known for Os(II) polypyridyl complexes, an observation which can be explained in terms of restricted rates of radiationless decay of the MLCT states due to the relatively large energy gap between the ground and excited states.^{29,30}

Excited-state redox potentials for the complexes were calculated directly from E_{em} and ground-state potential data using eq 21 and 22, which have been shown to give

$$E^\circ(\text{Os}^{\text{II}*}/\text{I}) = E_{\text{em}} + E_{1/2}(\text{bpy}/\text{bpy}^{\cdot-}) \quad (21)$$

$$E^\circ(\text{Os}^{\text{III}}/\text{II}^*) = E_{\text{em}} - E_{1/2}(\text{Os}^{\text{III}}/\text{II}) \quad (22)$$

(29) Caspar, J. V. Ph.D. Thesis, The University of North Carolina, Chapel Hill, NC, 1982.

(30) (a) Caspar, J. V.; Sullivan, B. P.; Kober, E. M.; Meyer, T. J. *J. Chem. Phys. Lett.* 1982, 91, 91. (b) Caspar, J. V.; Meyer, T. J. *J. Phys. Chem.* 1983, 22, 1407. (c) Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* 1983, 105, 5583. (d) Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* 1983, 22, 2444.

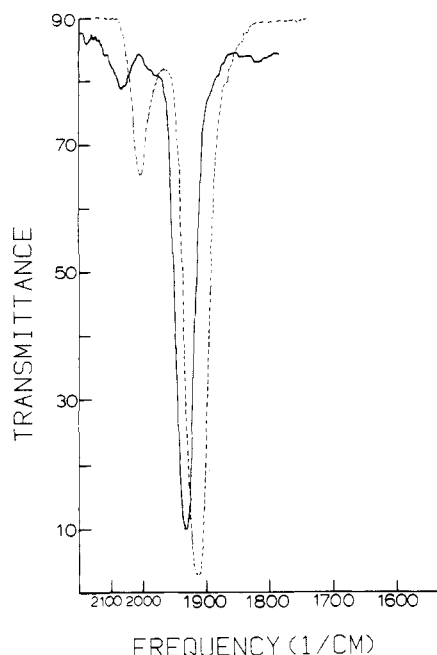


Figure 5. Infrared spectra of *cis*-[Os(bpy)₂(CO)H](PF₆) (---) and *trans*-[Os(bpy)(PPh₃)₂(CO)H](PF₆) (—) in CH₂Cl₂ solution. The weak absorption at higher frequency is assigned as the Os-H stretch while the intense low-frequency absorption is the CO stretch.

reasonably accurate estimates.^{4c,31} Note that in several cases only estimates for the Os(III)/Os(II*) complexes are available because it was necessary to use E_p values for irreversible Os(III)/Os(II) ground-state couples. Perhaps the most important feature of the excited-state potentials listed in Table III is that of the carbonyl dications Os-(bpy)₂(CO)L²⁺ (L = py, CH₃CN, PPh₃) in that all are extremely powerful excited-state oxidants. This is especially true for Os(bpy)₂(CO)PPh₃²⁺ which has an excited-state oxidation potential of ca. +1.2 V.

Another notable feature of the excited-state redox potential data is that the donating ability of the hydride ligand can lead to excited states that are strongly reducing; see, for example, [Os(phen)(dppene)(PPh₃)H]⁺ in Table III.

An important aspect in the design of molecular excited states with specific redox properties is illustrated in the series *trans*-[Os(chelate)(PPh₃)₂(CO)H]⁺ where the nature of the chelate ligand dramatically alters the excited-state redox potential as oxidant. This is easily seen by comparing the electron poor chelate 2,2'-bipyrazine and the relatively electron-rich 4,5,7,8-tetramethyl-1,10-phenanthroline system where $E_{1/2}(\text{Os}^{\text{II}/\text{I}})$ is 0.47 V vs. 0.93 V. It is also apparent that the ability of the excited state to act as a reductant follows the order 4,5,7,8-Me₄phen > bpy > bpym ≈ bpyz but quantitative comparisons are not meaningful since an irreversible peak potential was used for the Os(III)/Os(II) potential calculation in eq 22. The photochemical properties of the hydrido complexes are currently under investigation.³²

Infrared Spectral Studies. Infrared spectral data were recorded where possible in CH₃CN solutions of all the complexes in the ν_{CO} and $\nu_{\text{M-H}}$ stretching region. For all of the Os(II) complexes a strong ν_{CO} absorption band occurs at ca. 1910–1990 cm⁻¹ (see Table I) while a weak

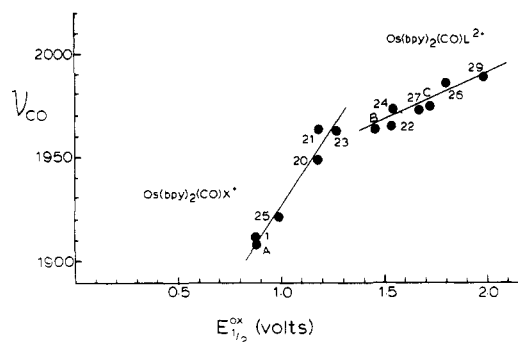


Figure 6. Graphical relationship between carbonyl stretching frequency, ν_{CO} , and the metal-based, M(III/II) reduction potential $E_{1/2}(\text{Ox})$ for a series of complexes of the type [Os(bpy)₂(CO)-X](PF₆) and [Os(bpy)₂(CO)L](PF₆)₂ in CH₃CN solution. The numbers of the points refer to complexes in Table II with the exception of A, B, and C, which represent [Os(bpy)₂(CO)-(CH₂Ph)](PF₆), [Os(bpy)₂(CO)(O₂CCF₃)]PF₆, and [Os(bpy)₂(CO)(4,4'-bpy)](PF₆)₂.

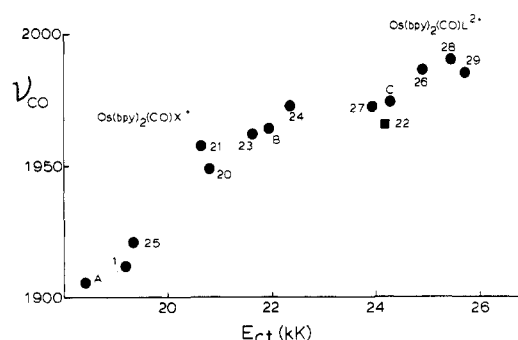


Figure 7. Graphical relationship between carbonyl stretching frequency, ν_{CO} , and the charge-transfer band maximum, E_{op} , for a series of complexes of the types [Os(bpy)₂(CO)X](PF₆) and [Os(bpy)₂(CO)L](PF₆)₂ in CH₃CN solution. See Figure 6 for the designations used for the complexes.

to very weak $\nu_{\text{M-H}}$ stretch is always found above 2000 cm⁻¹. This is particularly well illustrated by Figure 5. In several cases the $\nu_{\text{M-H}}$ band was not located due to its low intensity, although for each structural class, examples having well-defined $\nu_{\text{M-H}}$ bands were found.

For the few examples shown in Table I the metal hydride resonance frequency in the ¹H NMR spectrum shifts to higher field as $\nu_{\text{M-H}}$ increases; compare, for example, [Os(bpy)₂(CO)H]⁺ where $\nu_{\text{M-H}}$ is 2005 cm⁻¹ and the chemical shift is δ -11.4; *trans*-[Os(bpy)(PPh₃)₂(CO)H]⁺ where $\nu_{\text{M-H}}$ is 2060 cm⁻¹ and the chemical shift is δ -12.1, and [Os(phen)(dppb)(PPh₃)H]⁺ where $\nu_{\text{M-H}}$ is 2075 cm⁻¹ and the shift is δ -14.7. This effect has been discussed recently by Olgemöller and Beck³³ for a series of Ir(III) hydrides where the variation in chemical shift and $\nu_{\text{M-H}}$ was seen for different ligands *trans* to the Ir-H bond. The origin of this effect in our complexes is not obvious since it does not seem to correlate with the electron density at the metal.

Considerably more interesting correlations are found between ν_{CO} and the electrochemical or MLCT spectral properties of complexes of the type [Os(bpy)₂(CO)X]⁺ and [Os(bpy)₂(CO)L]²⁺, as shown in Figures 6 and 7. For example, in Figure 6 ν_{CO} is plotted vs. the M^{III/II} potential at the metal while in Figure 7 a plot is shown of ν_{CO} and the lowest energy MLCT transition (E_{op}). It is obvious that both $E_{1/2}(\text{Ox})$ or $E_p(\text{Ox})$ and E_{op} are good predictors of ν_{CO} , but in a nonlinear fashion in both cases. Reasonable linear relationships can be found, however, if complexes of the

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same charge type are considered; only $[\text{Os}(\text{bpy})_2(\text{CO})\text{NO}_2]^+$ and $[\text{Os}(\text{bpy})_2(\text{CO})\text{O}_3\text{SCF}_3]^+$ are exceptions, in that both fall on the dication line.

Although the nonlinear form of the correlations can not be explained in detail, several qualitative observations are revealing. First, since $E_{1/2}(\text{Ox})$ and E_{op} both reflect the amount of electron density at the Os(II) center, more specifically both measure the relative energy of the $d\pi$ orbitals, a decrease in $d\pi-\pi^*(\text{CO})$ mixing is anticipated as $E_{1/2}(\text{Ox})$ and E_{op} increase. Second, these correlations could be nonlinear from one or more of the following factors: (a) differing solvation energy contributions to $E_{1/2}(\text{Ox})$ and stabilization of the transition dipole (for both E_{op} and ν_{CO}); (b) for the E_{op} correlation the $\pi^*(\text{bpy})$ levels slowly become more stable as E_{op} increases, as shown from the electrochemical results.

Acknowledgment is made to the Department of Energy under Grant No. DAAG29-82-KO111 for support of this research.

Registry No. $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}](\text{PF}_6)$, 79850-20-7; $[\text{Os}(\text{bpy})_2(\text{CO})\text{Cl}](\text{PF}_6)$, 80502-54-1; $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{O}_2\text{CH})](\text{PF}_6)$, 84117-41-9; $[\text{Os}(\text{bpy})_2(\text{CO})(\text{O}_2\text{CH})](\text{PF}_6)$, 84117-43-1; *trans*- $[\text{Os}(\text{phen})(\text{PMe}_3)_2(\text{CO})\text{Cl}](\text{PF}_6)$, 89689-48-5; *trans*- $[\text{Os}(\text{phen})(\text{PPh}_3)_2(\text{CO})\text{Cl}](\text{PF}_6)$, 89689-50-9; *trans*- $[\text{Os}(\text{phen})(\text{PMePh}_2)_2(\text{CO})\text{Cl}](\text{PF}_6)$, 89689-52-1; $[\text{Os}(\text{phen})(\text{dppene})(\text{CO})\text{Cl}](\text{PF}_6)$, 89689-54-3; $[\text{Os}(\text{phen})(\text{dppb})(\text{CO})\text{Cl}](\text{PF}_6)$, 84117-39-5; $[\text{Os}(\text{bpy})_2(\text{CO})\text{NO}_2](\text{PF}_6)$, 89689-56-5; $[\text{Os}(\text{phen})(\text{dppene})(\text{PMe}_3)_2\text{Cl}](\text{PF}_6)$, 89689-58-7; $[\text{Os}(\text{bpy})_2(\text{CO})\text{H}](\text{PF}_6)$, 84117-35-1; $[\text{Os}(\text{phen})_2(\text{CO})\text{H}](\text{PF}_6)$, 84117-33-9; $[\text{Ru}(\text{bpy})_2(\text{CO})\text{H}](\text{PF}_6)$, 82414-89-9; $[\text{Ru}(\text{phen})_2(\text{CO})\text{H}](\text{PF}_6)$, 89689-60-1; *cis*- $\text{Ru}(\text{bpy})_2\text{Cl}_2$, 19542-80-4; $\text{Os}(\text{bpy})_2\text{Cl}_2$, 15702-72-4; *trans*- $[\text{Os}(\text{bpy})(\text{PPh}_3)_2(\text{CO})\text{H}](\text{PF}_6)$, 84117-37-3; *trans*- $[\text{Os}(\text{bpy})(\text{PPh}_3)_2(\text{CO})\text{H}](\text{PF}_6)$, 89689-62-3; *trans*- $[\text{Os}(\text{bpy})(\text{PPh}_3)_2(\text{CO})\text{H}](\text{PF}_6)$, 89689-64-5; *trans*- $[\text{Os}(3,4,7,8\text{-Me}_4\text{phen})(\text{PPh}_3)_2(\text{CO})\text{H}](\text{PF}_6)$, 89689-66-7; $[\text{Os}(\text{phen})(\text{dppb})(\text{PPh}_3)_2\text{H}](\text{PF}_6)$, 84117-29-3; $[\text{Os}(\text{phen})(\text{dppe})\text{ne}(\text{PEt}_3)_2\text{H}](\text{PF}_6)$, 84117-31-7; $[\text{Os}(\text{phen})(\text{dppe})\text{ne}(\text{PPh}_3)_2\text{H}](\text{PF}_6)$, 89689-68-9; $[\text{Os}(\text{bpy})_2(\text{CO})(\text{O}_2\text{CCF}_3)](\text{PF}_6)$, 89689-70-3; $[\text{Os}(\text{bpy})_2(\text{CO})(\text{CF}_3\text{SO}_3)](\text{O}_3\text{SCF}_3)$, 89689-72-5; $[\text{Os}(\text{bpy})_2(\text{CO})\text{CF}_3](\text{PF}_6)$, 89689-74-7; $[\text{Os}(\text{bpy})_2(\text{CO})(\text{CH}_3\text{CN})](\text{PF}_6)$, 89689-76-9; $[\text{Os}(\text{bpy})_2(\text{CO})(\text{C}_7\text{H}_8)](\text{PF}_6)$, 89689-78-1; $[\text{Os}(\text{bpy})_2(\text{CO})\text{py}](\text{PF}_6)$, 89689-80-5; *trans*- $[\text{Os}(\text{phen})(\text{PMe}_2\text{Ph})_2(\text{CO})\text{Cl}](\text{PF}_6)$, 89689-82-7; $\text{Ru}(\text{bpy})_2\text{CO}_3$, 59460-48-9; $\text{Os}(\text{bpy})_2\text{CO}_3$, 89689-83-8; $\text{Os}(\text{phen})\text{Cl}_4$, 89689-84-9; *cis*- $\text{Os}(\text{phen})(\text{dppe})\text{Cl}_2$, 89689-85-0; $\text{Os}(\text{bpy})\text{Cl}_4$, 57288-05-8; *mer*- $\text{Os}(\text{PPh}_3)_3(\text{CO})\text{HCl}$, 36007-23-5; HCOOH , 64-18-6.

Supplementary Material Available: Table of elemental analysis for the hydride and carbonyl complexes (2 pages). Ordering information is given on any current masthead page.

Palladium(II)-Catalyzed Exchange and Isomerization Reactions. 12.¹ Isomerization and Water Exchange of Allyl Alcohol in Aqueous Solution Catalyzed by PdCl_4^{2-}

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Received September 23, 1983

The isomerization of allyl-1,1- d_2 alcohol (**5a**) into an equilibrium mixture of **5a** and allyl-3,3- d_2 alcohol (**5b**) in aqueous solution was studied by ^1H NMR at various palladium(II), proton, and chloride concentrations. The rate expression was found to be $\text{rate} = k_1[\text{PdCl}_4^{2-}][\text{5a}]/[\text{Cl}^-]$. The exchange of nondeuterated allyl alcohol with oxygen-18 enriched water was studied by mass spectrum under one set of reaction conditions. The exchange rate was the same, within experimental error, as the isomerization rate. This result is consistent with both isomerization and exchange occurring by a hydroxypalladation-dehydroxypalladation route rather than by π -allyl intermediates. The rate expression for isomerization is consistent with exterior attack of water on a trichloropalladium(II)-allyl alcohol π complex to give *trans* stereochemistry. The isomerization rate equation is quite different from that for oxidation of allyl alcohol to carbonyl products, indicating that hydroxypalladation leading to oxidation is a different process from that leading to exchange. Furthermore, under the conditions (high chloride concentration in the presence of cupric chloride) that chloroethanol is produced from ethene, the hydroxypalladation leading to exchange is faster than that leading to oxidation to aldehydes and ketones. By analogy ethene would be expected to undergo the same type of nonoxidative hydroxypalladation as allyl alcohol with the same rate expression. All the evidence is consistent with the hydroxypalladation adduct *not* leading to aldehydes and ketones being the one captured by cupric chloride to give chloroethanol. Thus, the observed *trans* stereochemistry for the oxidation of ethene-1,2- d_2 to chloroethan-1,2- d_2 -ol does not reflect the stereochemistry of the hydroxypalladation in the Wacker reaction.

Introduction

In recent years there has been considerable discussion concerning the stereochemistry of the hydroxypalladation step that is generally agreed to be operative in the palladium(II)-catalyzed oxidation of acyclic olefins to aldehydes and ketones.³ The rate expression for eq 1 over a certain $\text{PdCl}_4^{2-} + \text{C}_n\text{H}_{2n} + \text{H}_2\text{O} \rightarrow \text{Pd}(\text{O}) + \text{C}_n\text{H}_{2n}\text{O} + 2\text{HCl} + 2\text{Cl}^-$ (1)

range of reaction conditions ($[\text{Pd}(\text{II})] = 0.005\text{--}0.04\text{ M}$; $[\text{Cl}^-] = 0.1\text{--}1.0\text{ M}$; $[\text{H}^+] = 0.04\text{--}1.0\text{ M}$) is given by eq 2.³

$$\frac{-d[\text{olefin}]}{dt} = \frac{k_1[\text{PdCl}_4^{2-}][\text{olefin}]}{[\text{H}^+][\text{Cl}^-]^2} \quad (2)$$

With ethene as the simplest example the rate expression has been interpreted in terms of the two hydroxy-

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(2) (a) University of Guelph. (b) Loyola University of Chicago.

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