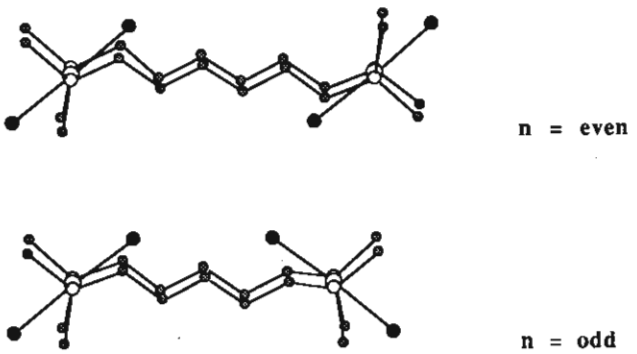
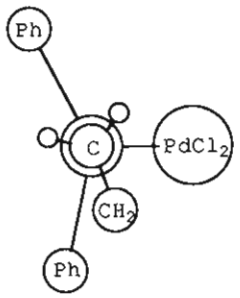


Figure 7. Schematic structures of **6** (determined) and **7** (proposed) that are representative of complexes of the type *trans*-$[(Ph_2P(CH_2)_nPPh_2)PdCl_2]_2$ with even- and odd-membered carbon backbones. Only the ispo carbon of each Ph ring is shown, and H atoms are omitted.

interactions with the phosphorus-attached substituents (Figure 7). A projection along the $C_{\alpha\text{-}CH_2}$–P bond



reveals that the arrangement of substituents in **6** is the same as in *trans*-$[(^tBu_2P(CH_2)_nP^tBu_2)PdCl_2]_2$ (n = 5, 7),[21] indicating that the phenyl and *tert*-butyl groups exhibit similar steric requirements in these dimetallic ring systems.

Trends in torsion angles for the backbones of bis(phosphine) ligands supporting dipalladium(II) complexes deserve a comment. Shaw et al. have previously observed that in *trans*-$[(^tBu_2P(CH_2)_{10}P^tBu_2)PdCl_2]_2$ torsion angles for the two even-membered organic chains deviate significantly from 180°; twisting of the central part of each C_{10} chain is in accord with that in a regular long-chain alkane.[39] On the other hand, the odd-membered polymethylene chains of *trans*-$[(^tBu_2P(CH_2)_5P^tBu_2)PdCl_2]_2$ and *trans*-$[(^tBu_2P(CH_2)_7P^tBu_2)PdCl_2]_2$ are fully extended.[21] The present data illustrate an extended-chain conformation for an even-membered organic chain. We suggest that, whether containing an odd or even number of methylene groups, the organic backbone of the ligand will tend to adopt an extended conformation thus minimizing interactions that involve the L_2PdCl_2 groups. With "long" ($n \geq 10$)[39] polymethylene chains, a number of twisted conformations exhibiting *gauche*- rather than *anti*-C–C–C–C, but which retain minimal interactions involving the L_2PdCl_2 units, are possible. The conformation of each polymethylene chain in *trans*-$[(R_2P(CH_2)_nPR_2)PdCl_2$ (n = 8, 9; R = Ph, ^{t}Bu) remains to be crystallographically established.

We propose that **7** has a molecular structure analogous to that of **6**, but as detailed above, the molecule is expected to exhibit a crystallographic mirror plane rather than a center of inversion. This structural expectation contrasts with the monomeric nature of *cis*-(dppp′)$PtCl_2$.[35] It is difficult to rationalize this difference on steric grounds. In the latter complex, the Pt–P distances of 2.237 (3) and 2.256 (3) Å are very similar to those in *cis*-L_2PdCl_2 (L_2 = dppm, dppe, dppp), and similarly, Pt–Cl bond lengths in *cis*-(dppp′)$PtCl_2$ are close to those in the cis-palladium complexes.[14] Our own observations underline phenomena considered by Shaw[21] and by Hill and McAuliffe,[19] namely that the preference for the formation of a monomeric, dimeric, or higher oligomeric structure may be a marginal one for a complex containing a bis(diphenylphosphino)(*n*-alkane) ligand and especially for a molecule in which the ligand exhibits a backbone with either five or six carbon atoms.

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Supplementary Material Available: Tables S1–S5, containing complete crystallographic data, bond distances, bond angles, thermal parameters, and H atom coordinates (4 pages); Table S6, listing structure factors (22 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113

Generalized Synthesis of *cis*- and *trans*-Dioxorhenium(V) (Bi)pyridyl Complexes

M. S. Ram and Joseph T. Hupp*

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Efficient new synthetic routes to *trans*-$(O)_2Re(py\text{-}X)_2(py\text{-}Y)_2^+$ and *cis*-$(O)_2Re(bpy\text{-}Y_2)(py\text{-}X)_2^+$ complexes have been devised (py = pyridine; bpy = 2,2′-bipyridine). The new routes make use of labile *cis*-$(O)_2Re(py\text{-}X)_2(I)$ species as preparative intermediates. The most useful new features of the synthetic chemistry are (1) the ability to prepare trans species containing electron-withdrawing substituents, (2) the ability to prepare mixed-ligand *trans*-dioxorhenium species, and (3) generalization of the *cis*-dioxorhenium preparation.

Introduction

trans-Tetrakis(pyridine)dioxorhenium(V) and related complexes have attracted considerable attention in the last 8 years on account of their redox catalytic activity,[1,2] persistent photophysical activity,[2,4] and multielectron electrochemical behavior.[1,5] We have been particularly interested in the last characteristic, especially as it relates to multielectron transfer *kinetics* at electrochemical interfaces. In kinetics studies, we have found it desirable to manipulate (or attempt to manipulate) reactivity by systematically varying the pyridyl ligand substituents. Brewer and Gray have expressed a similar interest in ligand tunability from the point of view of $(O)_2ReL_4^+$ photophysical studies.[6] Unfortunately, apart

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from Brewer's report,[6] the available synthetic routes to tetrakis(pyridyl) complexes[7] lack synthetic versatility and are incapable of yielding the desired complexes.

A related development in rhenium chemistry has been the successful synthesis and characterization of a *cis*-dioxo complex, $(O)_2Re(bpy)(py)_2^+$ (bpy = 2,2′-bipyridine; py = pyridine).[5,8] The seemingly trivial trans to cis conversion has significant chemical consequences.[5] Most notably: (1) photophysical activity disappears, (2) redox energetics (formal potentials) shift by several hundred millivolts, and (3) interfacial-electron-transfer rates are accelerated. Here also there is a need to introduce systematic reactivity changes via ligand substituent effects. Unfortunately, the existing synthetic route[5] has proven unsuccessful with substituted bipyridyl ligands. Furthermore, even where it does succeed (i.e. with the parent bpy ligand), the synthesis is lengthy, cumbersome, and inefficient. There is an obvious need, therefore, for a more satisfactory and general route to the *cis*-dioxo complex.

We wish to report here efficient new synthetic routes to *trans*-$(O)_2Re(py\text{-}X)_4^+$ and *cis*-$(O)_2Re(bpy\text{-}Y_2)(py\text{-}X)_2^+$. The new routes rely upon labile five-coordinate Re(V) species as preparative intermediates—a strategy used also in the Brewer and Gray synthesis.[6] From the new syntheses, seven new cis complexes have been obtained as have six trans complexes (two of which were previously known). The most useful new features of the synthetic chemistry are (1) the ability to prepare trans species containing electron-withdrawing substituents on the pyridyl ligands, (2) the ability to prepare mixed-ligand *trans*-dioxorhenium species, and (3) generalization of the *cis*-dioxorhenium preparation. As noted under Results and Discussion, a few complexes remain inaccessible. The majority of the species needed for systematic electrochemical studies, however, have been obtained. A discussion of electrochemical properties is contained in a forthcoming report.[9]

Experimental Section

Materials. All starting materials were reagent grade chemicals from Aldrich or Mallinckrodt and were used without further purification. The ligand 4,4′-dichloro-2,2′-bipyridine (4,4′-Cl_2-bpy) was prepared via literature methods[10,11] involving 4,4′-dichloro-2,2′-bipyridine *N,N′*-dioxide as an intermediate. The ligand 4,4′-dimethoxy-2,2′-bipyridine (4,4′-$(MeO)_2$-bpy) was also obtained from 2,2′-bipyridine, initially via literature methods.[10,11] These methods utilized 4,4′-dinitro-2,2′-bipyridine *N,N′*-dioxide as an intermediate.[11] *Safety note: The precautions outlined in refs 10 and 11 should be strictly followed. In particular, to avoid explosion hazards, the precursor material 2,2′-bipyridine N,N′-dioxide must be very thoroughly rinsed to remove any traces of* H_2O_2 *prior to addition of nitric acid.*[12] Both ligand syntheses had to be repeated several times to collect sufficient material (generally 6–7 g) as neither could be safely scaled up (owing to the extreme exothermicity of the preparative reactions).

Subsequent to these experiments, the following modified synthesis of 4,4′-$(MeO)_2$-bpy was developed. Its advantages are (1) higher yield and (2) absence of contamination with highly colored side-reaction products. The modified synthesis required suspension of 6 g (~23 mmol) of 4,4′-Cl_2-bpy-*N,N′*-dioxide in 400 mL of methanol with 1.5 g (~27 mmol) of sodium methoxide. This mixture was refluxed for 45 min. An additional 1.6 g of sodium methoxide was added, and refluxing was continued for another 1 h. The mixture was filtered while hot, and the solid was washed with CH_3OH. The filtrate and washings were then rotary-evaporated to near dryness. The desired 4,4′-$(MeO)_2$-bpy-*N,N′*-dioxide was precipitated by addition of ether and collected by filtration. No attempt was made to remove residual NaCl and/or NaOMe. Instead, the crude material was reacted directly with $PCl_3/CHCl_3$ to effect removal of oxygen and yield the 4,4′-dimethoxy-2,2′-bipyridine product.

Metal Complexes. Both the cis and trans (mixed-ligand) complexes were prepared via the synthetic intermediacy of $Re(O)(OEt)(py\text{-}X)_2(I)_2$,[7c,13] which evidently exists under reactive conditions as the five-coordinate $(O)_2Re(py\text{-}X)_2(I)$.[7c] The precursors to these species were prepared by slight modifications to known syntheses as detailed below. With one exception, the yields from the ethoxy intermediates to purified final products were in the 60–73% range.

***trans*-$[(O)_2Re(py)_4]Cl$.** Although there are other methods of synthesis for this complex,[6,7] we found the following, a modification of Johnson's procedure,[7b] the most convenient. A 6-g sample of $ReOCl_3(PPh_3)_2$ was mixed with 12 mL of pyridine and 6 mL of water in 120 mL of acetone.[14] The mixture was heated at reflux for 90 min and cooled in ice water for 30 min. The orange-yellow complex (which precipitates even while refluxing) was collected by filtration and washed with two 20-mL portions of toluene and two 20-mL portions of ether. Yield: 3.7 g (90%). In our hands, this procedure proved to be superior (with respect to time and yields) to those described in the existing literature.

***trans*-$[(O)_2Re(3\text{-}Cl\text{-}py)_4)]NO_3$.** Neither the procedure above nor the available literature procedures succeeded here. The complex was obtained in good yield (>80%), however, by combining 2 g of $Re(O)(Cl)_3(PPh_3)_2$ with 10 mL of 3-chloropyridine and 130 mL of water.[14] This mixture was heated at reflux with stirring for 1 h. The layers were allowed to separate, and to the yellow aqueous solution was added 5 mL of saturated aqueous sodium nitrate solution. The solution was cooled in ice water and the bright yellow solid filtered out, washed with three 20-mL portions of toluene and three 20-mL portions of 90% ether/10% acetone, and vacuum-dried. Anal. Found: C, 32.2; H, 2.21; N, 9.45; Cl, 18.9. Calc: C, 32.6; H, 2.27; N, 9.52; Cl, 19.3. ^1H NMR (acetone-d_6) (ppm): 9.26 (m, 8 H), 8.04 (d, 4 H), 7.75 (t, 4 H). ^{13}C NMR (CD_3OD) (ppm): 151.0, 150.7, 143.3, 135.5, 128.5. IR: ν(O=Re=O) = 814 cm^{-1}.

We were unable to prepare the analogous complexes containing 4-chloropyridine[15] or 3,5-dichloropyridine by this method (however, see below).

$Re(O)(OEt)(py\text{-}X)_2(I)_2$. These species were prepared essentially by the method of Freni et al.[7c] except that some modifications in the timing and in the amount of added HI were necessary in order to drive the syntheses toward completion. For X = H, 2 g of $[(O)_2Re(py)_4]Cl$ was dissolved in 60 mL of refluxing ethanol. A 3-mL portion of 57% HI was added, and the mixture was refluxed with stirring for 15 min. (Longer reaction times led to decomposition.) The solution was then cooled in ice water for 45 min. The precipitated complex was filtered out and washed with three 20-mL portions of ethanol. Inasmuch as the material had been prepared previously[7c,13] and was used here only as a synthetic intermediate, no further purification or characterization was undertaken. It should be noted, however, that any trace of starting material (*trans*-dioxorhenium(V), λ_{max} = 331 nm) is readily evident (by UV–vis absorption) in the ultimate *cis*-dioxorhenium(V) products; this particular preparation shows no evidence of starting material.

The synthesis was employed also for X = 3-Cl, 4-MeO, and 4-NMe_2 except that the refluxing times were 5, 25, and 60 min, respectively. The first two reactions evidently went to completion (based on ultimate product purity). The third appeared to go only 60–70% toward completion, on the basis of 30–40% contamination of the ultimate *cis*-dioxorhenium product (see below) with *trans*-$(O)_2Re(4\text{-}NMe_2\text{-}py)_4^+$.

***trans*-$[(O)_2Re(3\text{-}Cl\text{-}py)_2(py)_2](NO_3)\cdot H_2O$.** A 1-g sample of $Re(O)(OEt)(py)_2(I)_2$ was mixed with 3 mL of 3-chloropyridine, 36 mL of acetone, and 4 mL of water. The mixture was stirred for 45 min and then cooled in ice water. The precipitated yellow solid, $[(O)_2Re(3\text{-}Cl\text{-}py)_2(py)_2](I)$, was filtered out, washed with two 20-mL portions of toluene and two 20-mL portions of 80% ether/20% acetone, and redissolved in a minimal amount of 50% aqueous methanol. A 1.2-equiv amount of $AgNO_3$ was then added. After 20 min of stirring, the precipitated AgI was removed by filtration. The filtered solution was evaporated until the first crystals of the nitrate complex appeared. A 5-mL quantity of saturated $NaNO_3$ was added, and the resulting solution was then cooled in ice water. The precipitated yellow complex was filtered out and

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(14) The key ingredient here is water. We find, for example, that $(O)_2Re(py)_4^+$ is *not* obtained when the synthesis is attempted strictly as specified in the original report,[7b] i.e. with 100% ethanol as solvent; trace amounts of water are required for any reaction and more substantial amounts for completion.
(15) The failure of the synthesis with 4-chloropyridine appears to be due to the occurrence of a competing ligand-based oligomerization reaction: *Pyridine and Its Derivatives*; Klingsberg, E., Ed.; Interscience: New York, 1961; Part 2, p 345.

washed with toluene and then with ether/acetone. Anal. Found: C, 34.6; H, 2.63; N, 10.27; Cl, 10.0. Calc: C, 35.1; H, 2.92; N, 10.2; Cl, 10.4. ^{1}H NMR (CD_3OD) (ppm): 9.11 (d, 4 H), 9.07 (d, 4 H), 7.94 (q, 4 H), 7.64 (m, 6 H). ^{13}C NMR (CD_3OD) (ppm): 152.5, 151.0, 150.6, 143.3, 143.1, 135.3, 128.4, 128.0. IR: ν(O=Re=O) = 819 cm^{-1}.

***trans*-[$(O)_2$Re(py)$_2$(4-NMe$_2$-py)$_2$](PF_6)·H_2O.** A 1-g sample of Re(O)(OEt)(py)$_2$(I)$_2$ was stirred with 3 g of 4-(dimethylamino)pyridine in 50 mL of 80% aqueous acetone for 30 min. The mixture was cooled in ice water for 30 min. The precipitated iodide complex was filtered out, washed with toluene and ether/acetone, and redissolved in a minimum volume of 70% methanol/30% water mixture. (Removal of iodide with Ag^+ was not successful.) A 5-mL portion of saturated NH_4PF_6 solution was added to reprecipitate the complex, which was then washed with toluene and an ether/acetone mixture and dried in a vacuum oven. Anal. Found: C, 36.3; H, 3.86; N, 10.72. Calc: C, 36.6; H, 3.83; N, 10.60. ^{1}H NMR (acetone-d_6) (ppm): 9.14 (d, 4 H), 8.55 (d, 4 H), 7.87 (d, 2 H), 7.65 (t, 4 H), 6.73 (d, 4 H), 3.15 (s, 12 H). IR: ν(O=Re=O) = 813 cm^{-1}.

***trans*-[$(O)_2$Re(py)$_2$(4-Cl-py)$_2$](PF_6).** A 0.6-g quantity of 4-Cl-py·HCl in 10 mL of water was partially neutralized by the slow addition (with stirring) of 0.3 g of $NaHCO_3$. The resulting solution was added to 2 g of Re(O)(OEt)(py)$_2$(I)$_2$ in 20 mL of acetone, and the mixture was stirred for 15 min. Addition of solid NH_4PF_6 precipitated the complex [$(O)_2$Re(py)$_2$(4-Cl-py)$_2$](PF_6). The precipitate was collected on a glass frit and washed thoroughly with an acetone/ether mixture. Purification was achived by column chromatography on alumina using 5% 2-propanol/95% CH_2Cl_2 as eluent. Anal. Found: C, 31.5; H, 2.40; N, 7.26. Calc: C, 32.0; H, 2.40; N, 7.47. ^{1}H NMR (acetone-d_6) (ppm): 9.21 (t, 8 H), 7.97 (t, 2 H), 7.78 (d, 4 H), 7.69 (t, 4 H). ^{13}C NMR (acetone-d_6) (ppm): 152.9, 152.2, 147.1, 142.7, 127.7, 127.4. IR: ν(O=Re=O) = 817 cm^{-1}.

This method was not successful with 3,5-dichloropyridine.

***trans*-[$(O)_2$Re(4-CONH$_2$-py)$_4$](ClO_4).** This complex was prepared analogously to [$(O)_2$Re(py)$_4$](Cl) except that the initially formed chloride salt required purification (Bio-Gel P2 column, elution with water) prior to its conversion to the perchlorate. *Caution! Perchlorates of heavy-metal ions with organic ligands are potentially explosive. It is advisable to handle or store only small amounts of this material and then also with the usual precautions to avoid mixing with concentrated acids. Furthermore, the material should not be subjected to mechanical or thermal stress.* The complex was found to be very highly soluble in water but entirely insoluble in ethanol or acetone. Anal. Found: C, 35.4; H, 3.06; N, 13.41. Calc: C, 35.7; H, 2.97; N, 13.80. IR: ν(O=Re=O) = 817 cm^{-1}. ^{1}H NMR (D_2O): 9.12 (d, 8 H), 7.93 (d, 8 H).

***cis*-[$(O)_2$Re(bpy)(3-Cl-py)$_2$](PF_6).** A 1-g sample of Re(O)(OEt)(3-Cl-py)$_2$(I)$_2$ was combined with 1 g of bpy in 50 mL of acetone containing 5 mL of water, and the mixture was stirred for 30 min, after which it was filtered. To the filtrate was added 5 g of NH_4PF_6. This solution was heated slightly (35 °C) and rotary-evaporated until substantial amounts of product had precipitated. The mixture was cooled, ether was added to precipitate additional product, and the entire product was collected on a glass frit. The product was purified by column chromatography on alumina with 95% dichloromethane/5% 2-propanol as the eluent. Anal. Found: C, 31.9; H, 2.07; N, 7.41. Calc: C, 32.1; H, 2.41; N, 7.50. ^{1}H NMR (acetone-d_6) (ppm): 10.89 (d, 2 H), 8.71 (d, 2 H), 8.38 (m, 4 H), 8.04 (t, 2 H) 7.96 (t, 2 H), 7.75 (m, 4 H). IR: ν(O=Re=O) = 840, 908 cm^{-1}.

***cis*-[$(O)_2$Re(4,4′-Cl$_2$-bpy)(py)$_2$](ClO_4)·H_2O.** This compound was prepared and purified as described above for [$(O)_2$Re(bpy)(3-Cl-py)$_2$](PF_6)·H_2O except that 4,4′-Cl$_2$-bpy and Re(O)(OEt)(py)$_2$(I)$_2$ were used and, for solubility reasons, a perchlorate counterion was employed. (See safety note above.) Even so, the final product was found to be far less soluble (in water) but far more stable than the bpy/3-Cl-py analogue. Anal. Found: C, 33.2; H, 2.22; N, 7.85; Cl, 14.6. Calc: C, 33.3; H, 2.50, N, 7.78; Cl, 14.8. ^{1}H NMR (acetone-d_6) (ppm): 10.82 (d, 2 H), 8.91 (d, 2 H), 8.43 (d, 4 H), 8.05 (d, 2 H), 7.78 (t, 3 H), 7.86 (t, 3 H). IR: ν(O=Re=O) = 847, 909 cm^{-1}.

***cis*-[$(O)_2$Re(4,4′-Cl$_2$-bpy)(4-MeO-py)$_2$](PF_6).** A 0.3-g quantity of Re(O)(OEt)(4-MeO-py)$_2$(I)$_2$ was stirred with 0.5 g of 4,4′-Cl$_2$-bpy in 20 mL of acetone containing 5 mL of water. After 1 h the mixture was filtered. A crude product was isolated by addition of solid NH_4PF_6, followed by rotary evaporation of part of the solvent. The complex was purified by alumina column chromatography as described above. Anal. Found: C, 32.78; H, 2.48; N, 6.93. Calc: C, 32.7; H, 2.52; N, 6.94. ^{1}H NMR (acetone-d_6) (ppm): 10.73 (d, 2 H), 8.93 (s, 2 H), 8.16 (d, 4 H), 7.96 (d, 2 H), 7.17 (d, 4 H), 3.99 (s, 6 H). IR: ν(O=Re=O) = 905 cm^{-1}, ν(P—F) = 836 cm^{-1}.

***cis*-[$(O)_2$Re(4,4′-Cl$_2$-bpy)(3-Cl-py)$_2$](PF_6).** A 1-g sample of Re(O)(OEt)(3-Cl-py)$_2$(I)$_2$ was stirred with 3 g of 4,4′-Cl$_2$-bpy in 50 mL of acetone containing 5 mL of water. After 2 h the solution was rotary-evaporated to 20 mL. Addition of ether precipitated the complex. (With any of the cis complexes, attempts to remove iodide with Ag^+ led to partial decomposition—perhaps because of oxidation of Re(V) by Ag(I).) The crude complex was dissolved in a minimal amount of 30% aqueous methanol. One-tenth volume of saturated aqueous NH_4PF_6 was added to precipitate the PF_6^- salt. Purification and isolation followed the procedure described above. Anal. Found: C, 29.1; H, 1.71; N, 6.87; Cl, 18.8. Calc: C, 29.4; H, 2.45; N, 6.86; Cl, 17.4. ^{1}H NMR (acetone-d_6) (ppm): 10.86 (d, 2 H), 8.92 (d, 2 H), 8.38 (m, 4 H), 8.12 (m, 2 H), 7.83 (m, 2 H), 7.72 (m, 2 H). IR: ν(O=Re=O) = 908 cm^{-1}, ν(P—F) = 836 cm^{-1}.

***cis*-[$(O)_2$Re(bpy)(4-MeO-py)$_2$](PF_6).** A 1-g quantity of Re(O)(OEt)(4-MeO-py)$_2$(I)$_2$ was stirred with 1 g of 2,2′-bipyridine in 40 mL of acetone containing 10 mL of water. After 30 min the acetone was removed and the complex was precipitated by addition of 5 mL of a saturated aqueous NH_4PF_6 solution. The precipitated complex was washed first with water and then with a 95/5 v/v ether/acetone mixture. The crude product was then dissolved in CH_2Cl_2, and the solution was placed on an alumina column and eluted with 5% 2-propanol in CH_2Cl_2. The purified product was precipitated by addition of ether. Anal. Found: C, 35.9; H, 2.93; N, 7.50. Calc: C, 35.8; H, 2.98; N, 7.59. ^{1}H NMR (acetone-d_6) (ppm): 3.98 (s, 6 H), 7.17 (d, 4 H), 7.77 (t, 2 H), 8.16 (d, 4 H), 8.71 (d, 2 H), 10.78 (d, 2 H). IR: ν(O=Re=O) = 904 cm^{-1}, ν(P—F) = 836 cm^{-1}.

***cis*-[$(O)_2$Re(4,4′-(MeO)$_2$-bpy)(py)$_2$](PF_6).** This complex was prepared and purified as described above for [$(O)_2$Re(bpy)(4-MeO-py)$_2$](PF_6) except that 4,4′-(MeO)$_2$-bpy and Re(O)(OEt)(py)$_2$(I)$_2$ were used. Anal. Found: C, 35.8; H, 3.02; N, 7.61. Calc: C, 35.8; H, 2.98; N, 7.59. ^{1}H NMR (acetone-d_6) (ppm): 4.17 (s, 6 H), 7.67 (m, 8 H), 8.12 (d, 2 H), 8.34 (d, 4 H), 10.61 (d, 2 H). IR: ν(O=Re=O) = 900 cm^{-1}, ν(P—F) = 836 cm^{-1}.

***cis*-[$(O)_2$Re(bpy)(4-NMe$_2$-py)$_2$](PF_6).** This complex was prepared by the reaction of bpy with [$(O)_2$Re(4-NMe$_2$-py)$_4$]Cl or with Re(O)(OEt)(4-NMe$_2$-py)$_2$(I)$_2$ by following the procedure described above or the procedure given in ref 5. In both these procedures, heavy contamination of the product by $(O)_2$Re(4-NMe$_2$-py)$_4$ was observed. (The compound Re(O)(OEt)(4-NMe$_2$-py)$_2$(I)$_2$ was always found to be contaminated with Re$(O)_2$(4-NMe$_2$-py)$_4^+$.) Partial purification of the chloride salt (first method) was achieved by repeated alumina column chromatography using CH_2Cl_2 containing 2% 2-propanol as eluent. (Unfortunately, the complex could not be eluted with less polar solvents and was insufficiently soluble in aqueous solutions to be purified by cation-exchange chromatography.[5]) ^{1}H NMR (acetone-d_6) (ppm): 10.68 (d, 2 H), 8.73 (d, 2 H), 7.75 (m, 2 H), 7.61 (m, 2 H), 6.69 (–), 3.255 (s).

Measurements. IR spectra were obtained from KBr pellets in a Mattson FTIR instrument. NMR spectra were obtained in acetone-d_6 or methanol-d_4 with a Varian 400 spectrometer. In the spectra, CHD_2COCD_3 and CHD_2OD resonances at 2.04 and 3.6 ppm were used as the proton references. The $^{13}CD_3OD$ resonance at 49 ppm and $^{13}CD_3OCD_3$ resonance at 29.8 ppm were used as ^{13}C references. (^{13}C experiments were performed only for those trans complexes for which ambiguous H NMR data were obtained. The cis complexes did not yield ^{13}C data of useful quality.) Elemental analyses were obtained from Northwestern's Analytical Services Laboratory or from Galbraith Laboratories.

Results and Discussion

The present results show that a number of new *cis*-dioxo and mixed-ligand *trans*-dioxo pyridyl-type complexes of rhenium(V) can be prepared from Re(O)(OEt)(py-X)$_2$(I)$_2$ intermediates. Following Freni,[7c] we propose the following general reaction sequence:

$$(O)_2\text{Re(py-X)}_4^+ \xrightarrow{\text{HI, EtOH}} \text{Re(O)(OEt)(py-X)}_2\text{(I)}_2 + 2\text{Hpy-X}^+ \quad (1)$$

$$\text{Re(O)(OEt)(py-X)}_2\text{(I)}_2 \xrightarrow{H_2O} \textit{cis}\text{-(O)}_2\text{Re(py-X)}_2\text{(I)} + \text{EtOH} + \text{HI} \quad (2)$$

$$\textit{cis}\text{-(O)}_2\text{Re(py-X)}_2\text{(I)} \xrightarrow{\text{py-Y}} \textit{trans}\text{-(O)}_2\text{Re(py-X)}_2\text{(py-Y)}_2 \quad (3a)$$

$$\textit{cis}\text{-(O)}_2\text{Re(py-X)}_2\text{(I)} \xrightarrow{\text{bpy-Y}_2} \textit{cis}\text{-(O)}_2\text{Re(py-X)}_2\text{(bpy-Y}_2\text{)} \quad (3b)$$

The first reaction—the formation of the ethoxide from $(O)_2$Re(py-X)$_4^+$—is known, at least for X = H.[7c] We find that it can

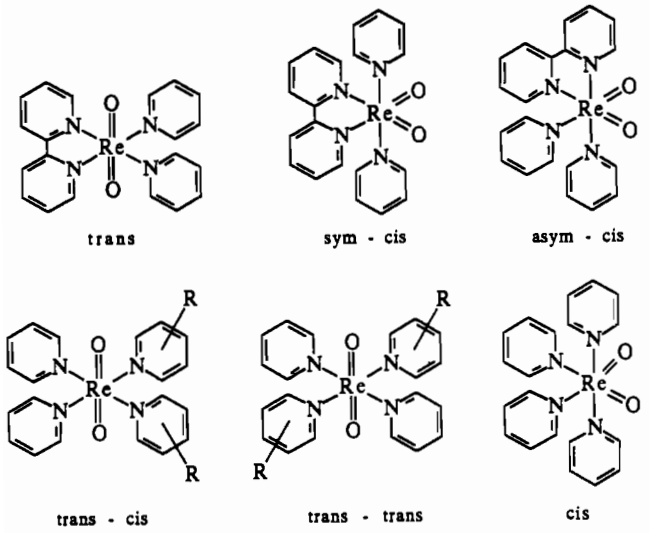

Figure 1. Potential geometric configurations for *cis*- and *trans*-dioxorhenium(V) (bi)pyridyl complexes. Note that the structures labeled trans, cis, and asym-cis have been ruled out by NMR and X-ray crystallographic studies.

easily be extended to X = 3-Cl or 4-methoxy but only with difficulty to X = 4-NMe_2. Evidently, the (dimethylamino)pyridine ligand is too basic to permit rupturing of the rhenium–nitrogen bond under ordinary conditions. Attempts to force the reaction by increasing the concentration of hydriodic acid proved only partially successful because of increased protonation of an oxo ligand; evidently, the resulting oxo–hydroxo complex is subject to moderately rapid decomposition to give unknown products. On the other hand, if the pyridyl ligands are too lacking in basicity (e.g., 3,5-Cl_2-py), the initial $(O)_2Re(py\text{-}X)_4^+$ complex is not formed.[15]

The reaction sequence apparently proceeds by ethoxide hydrolysis and iodide ligand loss (eq 2). (Note that in the rigorous absence of water, and therefore hydrolysis, no ligand substitution occurs.) Although we have not chosen to isolate the proposed five-coordinate intermediate, it has been isolated previously (and partially characterized) by Freni et al.[7c] This species is key because it presents both an open coordination site and an easily lost ligand (I^-). It is possible, therefore, to incorporate relatively poorly coordinating species like 4-Cl-py. It should be noted that the potential synthetic value of five-coordinate rhenium species has previously been recognized by Brewer and Gray[6] and that our work can reasonably be viewed as complementary to their study.

Reactions 3a and 3b proceed to yield *cis*- and *trans*-dioxo species, respectively.[16] The gross geometries (see Figure 1) have been previously established by X-ray crystal structural studies of the parent compounds, $[(O)_2Re(py)_4](X)$ and $[(O)_2Re(bpy)(py)_2](X)$.[5,17] These geometries have been confirmed for the derivatized complexes by magnetic and vibrational spectroscopy. Thus, all tetrakis(pyridyl) species (including mixed-ligand species) display a single O=Re=O stretching mode (asymmetrical) near 815 cm^{-1}, consistent with a *trans*-dioxo geometry. On the other hand, the bipyridyl species show two oxo–rhenium stretches (symmetric and asymmetric, at ca. 905 and 845 cm^{-1}),[5] consistent with a cis geometry. (The hexafluorophosphate salts, however, suffer interference from a P—F stretch in the asymmetric O=Re=O stretching region and only one band is observed.) As discussed previously, the A–B coupling patterns in ^1H NMR spectra also indicate a *cis*-$[(O)_2Re(bpy\text{-}Y_2)(py\text{-}X)_2](PF_6)$ geometry.[5] These further indicate a sym-cis rather than asym-cis configuration. For the $(O)_2Re(py\text{-}X)_2(py\text{-}Y)_2^+$ complexes, the ^1H coupling pattern indicates a *trans*-dioxo geometry. In a few cases where spectral congestion occurs we have also employed ^{13}C magnetic resonance to confirm the mixed-ligand nature of the complexes. Unfortunately, neither the ^1H nor ^{13}C NMR experiments (nor the IR measurements) have permitted us to distinguish between the trans,trans and trans,cis possibilities for the four equatorial pyridyl ligands (see Figure 1). The ^{13}C data do indicate, however, that only one isomeric form is obtained. Very recent X-ray structural results for $[(O)(OMe)Re(py)_2(dmapy)_2](PF_6)_2$ (which is obtained directly from *trans*-$(O)_2Re(py)_2(dmapy)_2^+$) now indicate that trans,trans isomers are obtained.[18]

To summarize, *cis*-$(O)_2Re(bpy\text{-}Y_2)(py\text{-}X)_2^+$ and *trans*-$(O)_2Re(py\text{-}X)_2(py\text{-}Y)_2^+$ complexes featuring both electron-donating and electron-withdrawing substituents have been obtained in good yields via the synthetic intermediacy of $(O)_2Re(py\text{-}Y)_2(I)_2$ species. The availability of these complexes should provide the necessary breadth of structure to permit the multielectron reactivity (kinetics) of these species to be understood quantitatively. The first steps in that direction—systematic studies of one- and two-electron redox thermodynamics—will be reported in a following paper.[9]

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(16) It is worth mentioning that the *cis*-dioxo formation reaction (eq 2 + eq 3b) was found to be reversible. In other words, in the presence of excess HI and ethanol, the chelate bpy is substituted in preference to the monodentate pyridine ligands.

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