are representative of complexes of the type \textit{trans}-(DBU-P(CH2)0PBu2)-PdCl2 with even- and odd-membered carbon backbones. Only the isopropyl 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=CH2-P bond reveals that the arrangement of substituents in 6 is the same as in \textit{trans}-(DBU-P(CH2)0PBu2)-PdCl2 (n = 5, 7), indicating that the phenyl and tert-butyl groups exhibit similar steric requirements in these dimetallocene 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 \textit{trans}-(DBU-P(CH2)0PBu2)-PdCl2 torsion angles for the two even-membered organic chains deviate significantly from 180°; twisting of the central part of each C10 chain is in accord with that in a regular long-chain alkane. On the other hand, the odd-membered polymethylene chains of \textit{trans}-(DBU-P(CH2)0PBu2)-PdCl2 and \textit{trans}-(DBU-P(CH2)0PBu2)-PdCl2 are fully extended. 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 L2PdCl2 groups. With "long" (n \geq 10) polymethylene chains, a number of twisted conformations exhibiting gauche- rather than anti-C-C-C-C, but which retain minimal interactions involving the L2PdCl2 units, are possible. The conformation of each polymethylene chain in \textit{trans}-(R,P(CH2)0PR2)-PdCl2 (n = 8, 9; R = Ph, '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 \textit{cis}-(dpmm)-PdCl2. 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-L2PdCl2 (L2 = dpmm, dppe, dpdp), and similarly, Pt-Cl bond lengths in cis-(dpdp)-PdCl2 are close to those in the cis-palladium complexes. Our own observations underline phenomena considered by Shaw and by Hill and McAuliffe, 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(di-phenylphosphino)(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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\textbf{Supplementary Material Available:} Tables SI–SS, 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.

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\textbf{Generalized Synthesis of cis- and trans-Dioxorhenium(V) (Bi)pypyridyl Complexes}

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Efficient new synthetic routes to \textit{trans}-(O)2Re(ppy-X)2(ppy-Y)4 and \textit{cis}-(O)2Re(bpy-Y)2(ppy-X)4 complexes have been devised (ppy = pyridine; bpy = 2,2'-bipyridine). The new routes make use of labile \textit{cis}-(O)2Re(ppy-X)2(1) 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 \textit{cis}-dioxorhenium preparation.

\textbf{Introduction}

\textit{trans}-Tetrakis(pyridine)dioxorhenium(V) and related complexes have attracted considerable attention in the last 8 years on account of their redox catalytic activity, persistent photophysical activity, and multielectron electrochemical behavior. We have been particularly interested in the last characteristic, especially as it relates to multielectron transfer \textit{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 \textit{O}2ReL4+ photophysical studies. Unfortunately, apart from...
from Brewer's report,4 the available synthetic routes to tetra-
kis(pyridyl) complexes 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, \((\text{O}_2)\text{Re}((\text{py}-X))_2\), \(\text{py} = \text{pyridine}\).5,6 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 route7 has proven unsuccessful with substituted pyridyl ligands. Furthermore, even where it does succeed (i.e. with the parent bypy 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-\((\text{O}_2)\text{Re}((\text{py}-X))_2\) and cis-\((\text{O}_2)\text{Re}((\text{py}-Y))_2((\text{py}-X))_2\). The new routes rely upon labile five-coordinate \(\text{Re}V\) 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, containing six trans dioxo 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 \((4,4'\text{-Cl}_2\text{-bpy})\) 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 \((4,4'\text{-MeO}_2\text{-bpy})\) 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 ref. 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 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'-\(\text{MeO}_2\text{-bpy}\) 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 (\(~23 \text{ mmol}\)) of 4,4'-\(\text{Cl}_2\text{-bpy}\)-\(N,N'\)-dioxide in 250 mL of ethanol and 1.5 \(g\) \((\sim 27 \text{ mmol})\) 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 \(\text{CH}_3\text{OL}\). The filtrate and washings were then rotary-evaporated to near dryness. The desired 4,4'-\(\text{MeO}_2\text{-bpy}\)-\(N,N'\)-dioxide was precipitated by addition of ether. The reaction was allowed to separate, and to the yellow aqueous solution was added 5 mL of 1.1 M acetone \((\text{Ac}_2\text{O})\). The solution was cooled in ice water and the bright yellow solid filtered off, 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, 2.77; N, 9.52; Cl, 19.7.

\[N,N'-\text{dioxide} \rightarrow \text{ligand} = \text{no further purification or characterization was undertaken. It should be noted, however, that any trace of starting material (trans-dioxorhenium(V),} \lambda_{\text{max}} = 331 \text{ nm}) \text{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 3, 5, and 5 h, respectively. The first two reactions evidently went to completion (based on ultimate product purity). The third (a) appeared to go only 60–70% toward completion, on the basis of 30–40% contamination of the ultimate cis-di-oxorhenium product (see below) with trans-\((\text{O}_2)\text{Re}(3-\text{Cl-py})\) \((\text{py})_2\).\]

\[\text{trans-}\((\text{O}_2)\text{Re}(3-\text{Cl-py})\)\((\text{py})_2(\text{NO}_3)_2\). \text{A 1-g sample of Re(O)\text{OEI}(\text{py})_2(\text{py})_2(\text{NO}_3)_2 \text{was mixed with 3 mL of 3-chloropyridine, 11 mL of acetonitrile, and 4 mL of water. The mixture was stirred for 45 min and filtered off. The precipitated yellow solid, (} \text{O}_2\text{Re}(3-3\text{Cl-py})\)\((\text{py})_2(\text{py})_2(\text{NO}_3)_2 \text{was filtered, 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% acetonitrile/methanol. The solution was then filtered and the AgCl was removed by filtration. The 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}

(13) The key ingredient here is water. We find, for example, that (} \text{O}_2\text{Re}(3-3\text{Cl-py})\) \((\text{py})_2(\text{py})_2(\text{NO}_3)_2 \text{is not obtained when the reaction is attempted strictly according to the original report, i.e. with 100% \text{HNO}_3 as solvent; trace amounts of water are required for any reaction and more substantial amounts for completion. 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; Klingeberg, E.; Ed.: Interscience; New York, 1961; Part 2, p 345.}
washed with toluene and then with ether/acetone. Anal. Found: C, 35.4; H, 2.93; N, 7.50. Calc: C, 35.9; H, 2.93; N, 7.50. IR: v(O=Re=O) = 847 cm⁻¹.

cis-(O)₂Re(3-Cl-py)₂(PF₆). A 0.5-g quantity of trans-(O)₂Re(py)₂(PF₆) was dissolved in 10 mL of water, and the mixture was stirred for 30 min, after which the mixture was filtered. The filtrate was evaporated to 2 mL. Addition of ethyl ether precipitated the complex. The precipitate was collected by mechanical or thermal evaporation of the ether and acetone mixture, and the solution was filtered. The supernatant was evaporated to a volume of 35% methanol/30% water mixture. (Removal of iodide with Ag⁺ was not successful.) A 5-mL portion of saturated NH₄PF₆ solution was added to reprecipitate the complex, which was then washed with water and acetone containing 5 mL of 80% aqueous acetone for 30 min. The mixture was cooled in an ice bath for 30 min. The precipitated iodide complex was filtered out, washed with toluene and ether/acetone, and redisolved in a minimum volume of 70% methanol/30% water mixture. The precipitate was collected by centrifugation, washed with toluene and then with an ether/acetone mixture and dried in a vacuum oven. Anal. Found: C, 35.9; H, 2.93; N, 7.50. Calc: C, 35.8; H, 2.98; N, 7.59. IR: v(O=Re=O) = 840 cm⁻¹.

cis-(O)₂Re(4,4'-MeO-py)₂(PF₆). This compound was prepared by the reaction of bpy with [O]₂Re(4,4'-MeO-py)₂Cl₂ or Cl⁻ with Re(0)⁴(4,4'-MeO-py)₄⁺. Partial purification of the chloride salt (first method) was achieved by repeated alumina column chromatography using CH₂Cl₂ 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.) IR: v(O=Re=O) = 904 cm⁻¹, v(P-F) = 836 cm⁻¹.

cis-(O)₂Re(CI₂-py)₂(PF₆). This complex was prepared by the reaction of bpy with Re(0)⁴(4,4'-Cl₂-py)₂Cl₂ or Cl⁻ with Re(0)⁴(4,4'-Cl₂-py)₂⁺. Partial purification of the product by the reaction of Re(0)(OEt)(3,3'-Cl₂-py)₂ and Cl⁻ with [Re(0)(OEt)(3,3'-Cl₂-py)₂]⁺ was observed. (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.) IR: v(O=Re=O) = 904 cm⁻¹, v(P-F) = 836 cm⁻¹.

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(0)(OEt)(py-X)₂(1₂) intermediates following Fremi, they propose the following general reaction sequence:

\[
\begin{align*}
\text{cis-(O)₂Re(py-X)₂(PF₆)} & \xrightarrow{H₂O} \text{cis-(O)₂Re(py-X)₂(PF₆)} + \text{H₂O} \\
\text{cis-(O)₂Re(py-X)₂(PF₆)} & \xrightarrow{H₂O} \text{cis-(O)₂Re(py-X)₂(PF₆)} + \text{H₂O} \\
\text{cis-(O)₂Re(py-X)₂(PF₆)} & \xrightarrow{H₂O} \text{cis-(O)₂Re(py-X)₂(PF₆)} + \text{H₂O} \\
\end{align*}
\]

The first reaction—the formation of the ethoxide from [Re(0)²Re(0)(py-X)₂]—is known, at least for X = H. It can...
Dioxorhenium(V) (Bi)pyridyl Complexes

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.

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. This species is key because it presents both an open coordination site and an easily lost ligand (F−). It is possible, therefore, to incorporate relatively poorly coordinating species like 4-Cl-py. It should be noted that the gross geometries (see Figure 1) have been previously established by X-ray crystal structural studies of the parent compounds, [(O)Re(py)4](X) and [(O)Re(bpy)-(py)2](X). 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 bipyrindyl species show two oxo-rhenium stretches (symmetric and asymmetric, at ca. 905 and 845 cm⁻¹), 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)Re(bpy-Y)3(py-X)]PF₆ geometry. These further indicate a sym-cis rather than asym-cis configuration. For the (O)₄Re(py-X)₃(py-Y)² complexes, the ¹H coupling pattern indicates a trans-dioxo geometry. In a few cases where spectral congestion occurs we have also employed ¹⁳C magnetic resonance to confirm the mixed-ligand nature of the complexes. Unfortunately, neither the ¹H nor ¹³C NMR experiments (nor the IR measurements) have permitted us to distinguish between the trans,trans and trans,cis isomers possibilities for the four equatorial pyridyl ligands (see Figure 1). The ¹³C data do indicate, however, that only one isomeric form is obtained. Very recent X-ray structural results for [(O)(OMe)Re(py)dmapy)]PF₆, (which is obtained directly from trans-(O)₄Re-(py)₃(dmapy)²) now indicate that trans,trans isomers are obtained.¹⁰

To summarize, cis-(O)₄Re(bpy-Y)₃(py-X)²⁺ and trans-(O)₄Re(py-X)₃(py-Y)² complexes featuring both electron-donating and electron-withdrawing substituents have been obtained in good yields via the synthetic intermediacy of (O)₄Re(py-Y)₂(1) 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.


(18) Jones, L. M. Unpublished results.