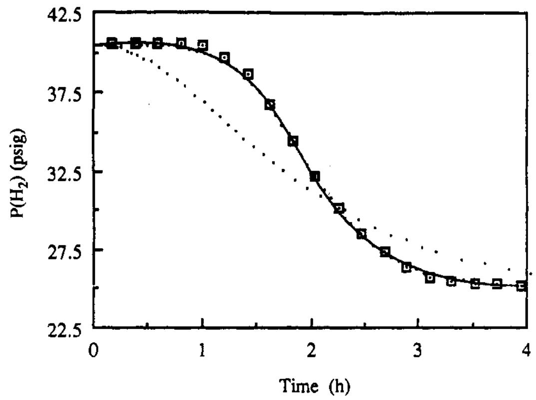

Figure 1. Plot of hydrogen loss vs time for 1.1×10^{-3} M **1** in cyclohexene (1.65 M)/acetone in comparison to curves generated by numerical integration curve-fitting[5] of the experimental data according to the stepwise sequence of reactions shown in Scheme I, eqs 1–4: experimental data (squares with center dots); curve computed by including eq 3 (solid line); curve computed by excluding eq 3 (dotted line), showing the necessity of the autocatalysis (step 3) for a close fit of the experimental data. Additional experimental details are available.[3]

evidence against *traditional types*[13] of colloids (and all other species) of *nonuniform reactivity*, for example those of *nonuniform size* or *surface area* (and thus variable number of exposed metal atoms).

We have also tried the well-known, but often problematic, Hg(0) test. Unfortunately, a control experiment reveals that under our normal conditions of catalysis (acetone, 1.65 M cyclohexene), **1** reacts with, and is precipitated by, Hg(0); this test is useless for the present example.

The results provided herein demonstrate that Ir to polyoxoanion bonding must be retained in the catalyst derived from ***1***. This has encouraged us to attempt to characterize polyoxoanion-supported catalytic intermediates, such as the species formed from **1** plus 3.0 equiv of H_2 showing a ^1H NMR peak at −14.5 ppm, which we *tentatively* formulate as $\{[(H)_2(\text{solvent})Ir\cdot P_2W_{15}Nb_3O_{62}]^{8-}\}_x$. Our goal from here is to fully define each stage of the catalytic cycle[14] and then to develop other polyoxoanion-supported catalytic reactions.

Acknowledgment. Support from NSF Grant CHE-831345 and from DOE Grant DE-FG06-089ER13998 is gratefully acknowledged.

Supplementary Material Available: Text presenting details of the catalytic hydrogenation studies (1 page). Ordering information is given on any current masthead page.

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[14] As has proven possible, for example, in classic studies of Wilkinson's catalyst: (a) Halpern, J.; Okamoto, T.; Zakharier, A. *J. Mol. Catal.* **1976**, *2*, 65. Halpern, J. *Inorg. Chim. Acta* **1981**, *50*, 11. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science: Mill Valley, CA, 1987; Chapter 10.

Chemistry of Zerovalent Tungsten Alkoxides. Synthesis, X-ray Structure, and Reactivity toward Carbon Dioxide

Zerovalent group 6 transition-metal alkoxide complexes have been established as intermediates in the catalytic hydrogenation of ketones and aldehydes to alcohols.[1] Because of the reversible nature of eq 1, it has not been possible to isolate and characterize

$$(CO)_5M{-}H^- + O{=}CRR' \rightleftharpoons (CO)_5M{-}OCHRR'^- \tag{1}$$

the metal alkoxides formed in the reaction due to their general instability toward β-hydride elimination.[2] However, the analogous group 6 pentacarbonyl aryloxide complexes have been synthesized and structurally defined and their reactivity investigated.[3]

In addition, monomeric group 6 metal carbonyl hydroxide, alkoxide, and aryloxide complexes are prone to condensation reactions subsequent to carbonyl loss to form clusters having bridging hydroxide, alkoxide, and aryloxide ligands.[3-8] The conversions illustrated in Scheme I have been established for hydroxides, aryloxides ($R = C_6H_5$, $C_6H_4CH_3$-*m*), and alkoxides ($R = CH_3$, CH_2CH_3). All the derivatives shown, except for the dimer in the box, have been previously observed, with several of these being isolated and fully characterized. The metal pentacarbonyl hydroxide, aryloxide, and alkoxide anions, in the absence of excess carbon monoxide, form the tetranuclear species $[W_4(CO)_{12}(\mu\text{-}OR)_4]^{4-}$, where the oxygen and tungsten atoms occupy the opposite tetrahedral sites of a distorted cubane skeleton, with no spectral evidence for the intermediacy of a dimer of the type $[W_2(CO)_8(\mu\text{-}OR)_2]^{2-}$. Only dimeric species of the sort $[W_2(CO)_6(\mu\text{-}OR)_3]^{3-}$ have been isolated, which are formed from either the monomer or the tetramer in the presence of excess hydroxide, aryloxide, or alkyloxide. There is precedence for carbonyl dimers of tungsten with two alkane- and arenethiolates, $[W_2(CO)_8(\mu\text{-}SR)_2]^{2-}$, which are produced following thermal CO loss from the monomeric anion $[W(CO)_5SR]^-$.[9]

In this communication, we report the synthesis, characterization, and the reactivity toward carbon dioxide of tungsten 2,2,2-trifluoroethoxide mononuclear and polynuclear carbonyl derivatives. Included in this report is the X-ray structure determination of a novel double-bridged μ_2-alkoxide dimer. As previously mentioned there is a problem with β-elimination inherent to transition-metal alkoxide chemistry which we avoided by the use of the alkoxide 2,2,2-trifluoroethoxide, which has electron-withdrawing substituents on the γ-carbon. In general, electron-withdrawing substituents on the alkoxide ligand stabilize the metal–alkoxide complex toward decomposition by β-hydrogen elimination.[10]

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(5) Darensbourg, D. J.; Sanchez, K. M.; Reibenspies, J. H. *Inorg. Chem.* **1988**, *27*, 3269.

(6) (a) McNeese, T. J.; Cohen, M. B.; Foxman, B. M. *Organometallics* **1984**, *3*, 552. (b) McNeese, T. J.; Mueller, T. E.; Wierda, D. A.; Darensbourg, D. J.; Delord, T. J. *Inorg. Chem.* **1985**, *24*, 3465.

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(8) Albano, V. G.; Ciana, G.; Manassero, M. *J. Organomet. Chem.* **1970**, *25*, C55.

(9) (a) Darensbourg, D. J.; Sanchez, K. M.; Reibenspies, J. *Inorg. Chem.* **1988**, *27*, 3636. (b) Zhuang, B.; McDonald, J. W.; Schultz, F. A.; Newton, W. E. *Organometallics* **1984**, *3*, 943. (c) Rosenheim, L. D.; Newton, W. E.; McDonald, J. W. *Inorg. Chem.* **1987**, *26*, 1695. (d) Zhuang, B.; McDonald, J. W.; Schultz, F. A.; Newton, W. E. *Inorg. Chim. Acta* **1985**, *99*, L29.

(10) (a) Yoshida, T.; Okano, T.; Otsuka, S. *J. Chem. Soc., Dalton Trans.* **1976**, 993. (b) Arnold, D. P.; Bennett, M. A. *Inorg. Chem.* **1984**, *23*, 2110. (c) Bryndza, H. E.; Calabrese, J. C.; Marsi, M.; Roe, D. C.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 4805.

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The metal alkoxide was synthesized by reaction of the alcohol with the tungsten pentacarbonyl methyl anion[11a] to produce the desired product and methane (eq 2).[11b] This route proved to be

$$W(CO)_5CH_3^- + HOCH_2CF_3 \rightarrow W(CO)_5OCH_2CF_3^- + CH_4 \quad (2)$$

a quantitative, clean, and convenient way to synthesize the metal alkoxide under mild conditions. The tungsten pentacarbonyl alkoxide was shown to interact with excess alcohol in solution. This was detected by a shift to higher frequencies in the carbonyl stretching region of the infrared spectrum. The infrared frequency shift is assumed to be the result of a hydrogen-bonding interaction, where the interaction of the lone pairs on the oxygen of the ligated alkoxide with the alcohol makes it a slightly less donating ligand.[12] Such hydrogen-bonding interactions have previously been shown to occur both in solution and in the solid state.[3,13] The metal alkoxide monomer reacted rapidly and reversibly with carbon dioxide at a pressure of one atmosphere to form the metal alkyl carbonate (eq 3). This was detected both by infrared spectroscopy

$$W(CO)_5OCH_2CF_3^- + {}^{13}CO_2 \rightleftharpoons W(CO)_5O^{13}C(O)OCH_2CF_3^- \quad (3)$$

in the ν(CO) region and by the characteristic resonance for the carbonate in the ^{13}C NMR spectrum.[14]

Though unable to grow crystals of [PPN][$W(CO)_5OCH_2CF_3$], we were successful in obtaining crystals suitable for X-ray structure determination of the dimer, $[PPN]_2[W_2(CO)_8(OCH_2CF_3)_2]$. This was the first time in our laboratories we have conclusively detected a double-alkoxo-bridged tungsten carbonyl species. This dimer lends support for the intermediate mentioned in the clustering mechanism for tungsten alkoxy carbonyls shown in Scheme I; however, this particular dimer's role in the clustering mechanism has not been fully established. [PPN][$W(CO)_5OCH_2CF_3$] apparently loses CO to form the dimer with no subsequent CO loss from the resultant complex, $[PPN]_2[W_2(CO)_8(OCH_2CF_3)_2]$, to form either the triple-bridged dimer or the tetramer being noted. The dimerization process was found to be inhibited by pressures of CO or the presence of excess alcohol in solution. That is, when a solution of the monomer is left to stir under a CO atmosphere or in the presence of excess alcohol for 2 days, no formation of the dimer is observed. Interaction of the ligated alkoxide with alcohol reduces the cis-labilizing ability of the alkoxide ligand in the $W(CO)_5OCH_2CF_3^-$ anion. This observation is consistent with the lack of facile CO loss in neutral derivatives such as W(CO)$_5$THF or W(CO)$_5$MeOH.

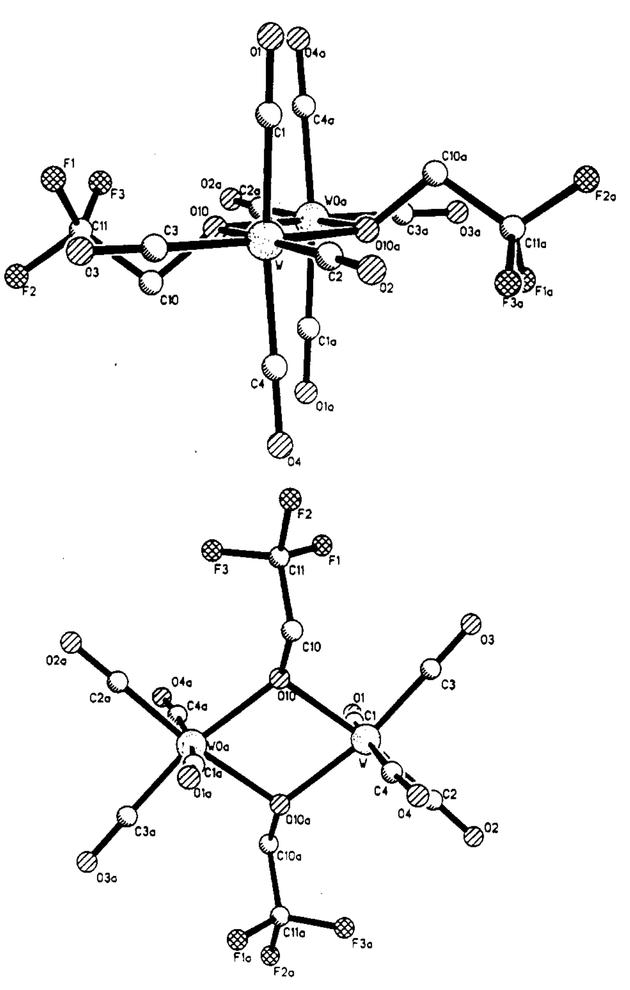

Figure 1. Perspective views of the $W_2(CO)_8(CH_2CF_3)_2^{2-}$ dianion with the atomic labeling scheme.

The compound $[PPN]_2[W_2(CO)_8(OCH_2CF_3)_2]$ has been characterized by single-crystal X-ray diffraction techniques.[15] Plots of the ball and stick model are shown in Figure 1. The "CH_2CF_3" groups were found to be disordered. The tungsten–oxygen distances are 2.17 (2) and 2.20 (2) Å. These distances are similar to the average W–O bond length in the triple-bridged

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(11) (a) Casey, C. P.; Polichnowski, S. W. *J. Am. Chem. Soc.* **1978**, *100*, 1565. (b) Synthesis of compounds were performed as follows. For [PPN][$W(CO)_5OCH_2CF_3$], [PPN][$W(CO)_5CH_3$] (30–100 mg, 0.034–0.11 mmol) was placed in a Schlenk tube containing a stir bar. Excess $HOCH_2CF_3$ was added via syringe along with 10 mL of THF. An orange solution formed, indicating quantitative conversion of the [PPN][$W(CO)_5CH_3$] to the desired alkoxide. The reaction was monitored by solution infrared spectroscopy in THF. The alkoxide was isolated as an oil by the addition of hexane to THF solution and washed with several 5-mL aliquots of hexane. IR (THF, cm^{-1}): 2059 (w), 1903 (s), 1839 (m). ^1H NMR (ppm): cation (($CD_3)_2CO$), 7.52–7.92 (($Ph_3P)_2N^+$, m); anion (($CD_3)_2CO$), 4.03 (CH_2, q). ^{13}C NMR (ppm): carbonyls (THF/($CD_3)_2CO$), 201.0 (4 CO), 203.3 (1 CO). For [PPN][$W_2(CO)_8(OCH_2CF_3)_2$], a THF solution of [PPN][$W(CO)_5OCH_2CF_3$] was stirred for 1 h and a small concentration of [PPN][$W_2(CO)_8(OCH_2CF_3)_2$] forms as detected by IR spectroscopy: Crystals were isolated by the layering of hexane over a THF solution of the alkoxide cooled to −78 °C and then placed in a freezer for 3 days. IR (KBr, cm^{-1}): 1993 (w), 1856 (s), 1816 (m), 1778 (s).

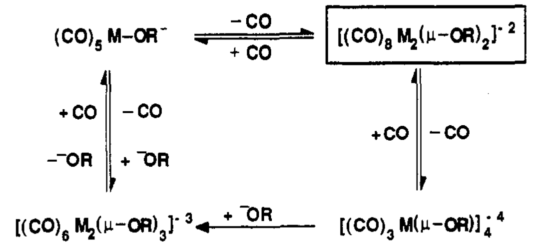
(12) The non-hydrogen-bonded alkoxide $W(CO)_5OCH_2CF_3^-$ exhibits ν(CO) infrared bands at 2059 (w), 1903 (s), 1839 (m) cm^{-1} and upon addition of excess alcohol bonding the carbonyls exhibit stretches at ν(CO) 2062 (w), 1911 (s), and 1849 (m) cm^{-1}.

(13) (a) Kegley, S. E.; Schaverien, C. J.; Freudenberger, J. H.; Bergman, R. G.; Nolan, S. P.; Hoff, C. D. *J. Am. Chem. Soc.* **1987**, *109*, 6563. (b) Braga, D.; Sabatino, P.; Di Bugno, C.; Leoni, P.; Pasquali, M. *J. Organomet. Chem.* **1987**, *334*, C46. (c) Kim, Y.-J.; Osakada, K.; Takenaka, A.; Yamamoto, A. *J. Am. Chem. Soc.* **1990**, *112*, 1096.

(14) Upon reaction with 1 atm of CO_2 in THF the ν(CO) three-band pattern typical for C_{4v} symmetry shifted to 2061 (w), 1912 (s), and 1847 (m) and exhibited a characteristic carbonate resonance in the ^{13}C NMR at 156.7 ppm when enriched $^{13}CO_2$ was used in the synthesis. ^{13}C NMR of the carbonyls in THF/($CD_3)_2CO$ (ppm): 204.0 (4 CO s), 209.4 (1 CO).

(15) Crystallographic data for $[PPN]_2[W_2(CO)_8(OCH_2CF_3)_2]$: Examination and data collection of an orange plate [0.11 × 0.21 × 0.38 mm] (formula = $C_{84}H_{66}N_2O_{10}F_6P_4W_2$; fw = 1869.0 amu) were performed on a Nicolet R3m/V X-ray diffractometer (oriented graphite monochromator; Mo Kα radiation; λ = 0.71073 Å) to give a triclinic, unit cell $P\bar{1}$, with a = 13.460 (11) Å, b = 12.318 (5) Å, c = 13.842 (10) Å, α = 82.73 (5)°, β = 59.11 (5)°, γ = 80.09 (5)°, V = 1938 (2) Å^3, D_x = 1.601 g cm^{-3}, μ = 3.183 mm^{-1}, Z = 1, and $F(000)$ = 926e. Data were collected for $4.0° \le 2\theta \le 50.0°$ [ω (Wyckoff scans), $-16 \le h \le +13$, $-14 \le k \le +14$, $-16 \le l \le 0$] at 186 (1) K. Lorentz and polarization corrections were applied to 6229 reflections. A semiempirical absorption correction was applied [thin plate approximation; face (001); T_{max} = 0.9888, T_{min} = 0.9132]. A total of 3559 unique observed reflections (R_{int} = 0.04), with $|I| \ge 3.0 \times \sigma|I|$, were used in further calculations. The structure was solved by direct methods (SHELXS, SHELXTL-PLUS program packages). The anion was found to sit about an inversion center. The complete cation was found in the asymmetric volume of the unit cell. Full-matrix least-squares isotropic refinement for C10, C10′, C11, C11′, F1, F1′, F2, F2′, F3, F3′, C1, O1, C2, O2, C3, O3, C4, O4, and O10 and anisotropic refinement for all remaining non-hydrogen atoms [SHELXLS, SHELXTL-PLUS program packages; quantity minimized $\Sigma w(F_o - F_c)^2$; $w = \sigma^2(F) + gF^2$, g = 0.0008] yielded R = 0.074, R_w = 0.092, and S = 2.202 at convergence [largest Δ/σ = 0.0062; mean Δ/σ = 0.0001; largest positive peak in the final Fourier difference map = 1.50 e Å^3; largest negative peak in the final fourier difference map = −2.20 e Å^3). Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 0.08 Å^2. Neutral-atom scattering factors taken from: Cromer, D. T.; Waber, J. T. *International Tables For X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974.

Scheme I



phenoxide dimer, $[Et_4N]_3[W_2(CO)_6(\mu\text{-}OPh)_3]$,[3] where the average W–O length is 2.222 (5) Å, and the W–O bond lengths of the triple-bridged hydroxy dimer $[K]_3[W_2(CO)_6(\mu\text{-}OH)_3]$, where the average W–O bond length is 2.16 (2) Å.[8] The W–CO distances range from 1.90 (3) to 1.95 (1) Å, with an average distance of 1.93 (3) Å. The geometry at each metal center is that of a distorted octahedron, where the W–O–W bond angle of the W_2O_2 core is 107.8 (5)°. This angle is significantly more obtuse than either the triple-bridged hydroxy or phenoxy dimers, 97 (1) and 96.7 (3)°, respectively. Furthermore, this angle is significantly more open than the W–S–W angle of the tungsten dimer, $[Et_4N]_2[W_2(CO)_8(\mu\text{-}SPh)_2]$, of 103.1°.[9a]

Acknowledgment. The financial support of this research by the National Science Foundation (Grant 88-17873) is greatly appreciated.

Supplementary Material Available: Tables of atomic coordinates and equivalent isotropic displacement parameters, bond distances and angles, anisotropic displacement parameters, and H atom coordinates and isotropic displacement parameters for $[PPN]_2[W_2(CO)_8(CH_2CF_3)_2]$ (6 pages). Ordering information is given on any current masthead page.

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Molecular Structure of $[(O)_2Re(bpy)(py)_2](ClO_4)$: An Unusual Example of a d^2 Metal Complex with a *cis*-Dioxo Ligand Configuration

Dioxo rhenium(V) species, especially with pyridyl-type ligands, have attracted significant interest recently—on account of both their electrochemical properties[1] and their photophysical and photochemical reactivity characteristics.[2,3] We have been examining these species from the point of view of multielectron-transfer kinetics (i.e. Re(V) ⇄ Re(III) and Re(V) ⇄ Re(II)), especially at electrochemical interfaces.[4] In the course of those studies we have had occasion to introduce relatively minor modifications to the ligand environment. One of these—the replacement of a pair of pyridine(py) ligands by 2,2′-bipyridine(bpy) in the prototypical complex, *trans*-$(O)_2Re(py)_4^+$—had profound chemical consequences. Formal potentials shifted by up to 600 mV, photophysical activity disappeared, and a rare display of three-electron redox chemistry emerged at high pH's. Furthermore, the kinetics of the multielectron electrochemical reduction were greatly accelerated. Finally, there were marked changes in NMR, Raman, UV-vis, and infrared spectra.[4]

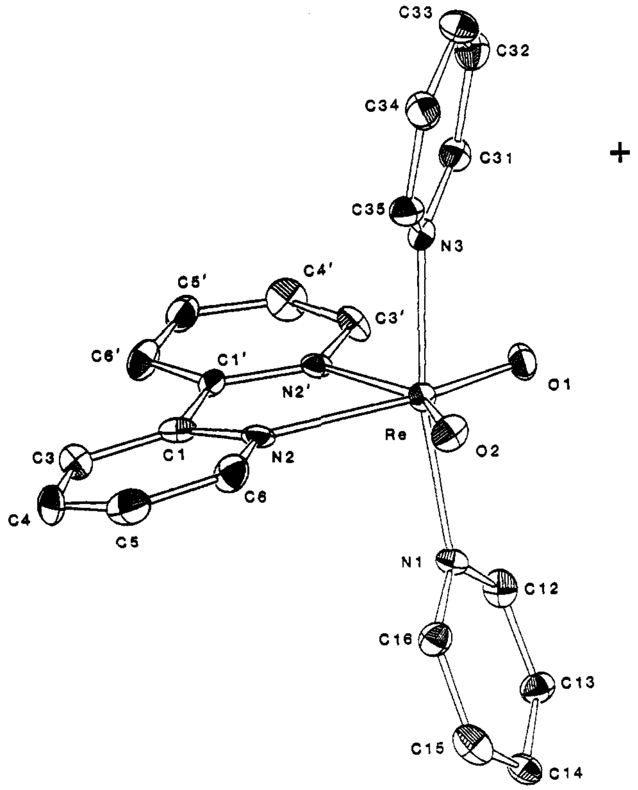

Figure 1. ORTEP drawing of *cis*-$(O)_2Re(bpy)(py)_2^+$.

On the basis of extensive circumstantial evidence we were forced to conclude that the changes were brought about by trans to cis isomerization upon bpy substitution. (The conclusion was particularly attractive, however, because it could account for the rather remarkable kinetic effects.) It was noted, nevertheless, that a rigorous structural assignment was impossible based upon either magnetic or vibrational spectroscopy—the reason being that both *cis*- and *trans*-$(O)_2Re(bpy)(py)_2^+$ would possess C_{2v} symmetry.[4,5] Furthermore, there were theoretical reasons to doubt the cis geometry.[6]

We now report, on the basis of X-ray crystal structure investigations,[7] that the product of bipyridyl substitution at *trans*-$(O)_2Re(py)_4^+$ is indeed *cis*-$(O)_2Re(bpy)(py)_2^+$. To our knowledge this is one of only two confirmed examples of a hexacoordinate d^2 metal complex with a *cis*-dioxo structure.[8,9] (It should be noted,

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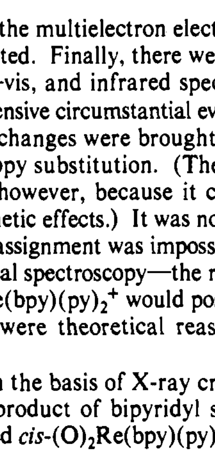
(1) Pipes, D. W.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 3256.

(2) (a) Winkler, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 1371. (b) Winkler, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **1985**, *24*, 346. (c) Thorp, H. H.; Van Houten, J.; Gray, H. B. *Inorg. Chem.* **1989**, *28*, 889. (d) Thorp, H. H.; Kumar, C. V.; Turro, N. J.; Gray, H. B. *J. Am. Chem. Soc.* **1989**, *111*, 4364.

(3) Newsham, M. D.; Giannelis, E. P.; Pinnavia, T. J.; Nocera, D. E. *J. Am. Chem. Soc.* **1988**, *110*, 3885.

(4) Ram, M. S.; Johnson, C. S.; Blackbourn, R. L.; Hupp, J. T. *Inorg. Chem.* **1990**, *29*, 238.

(5) NMR studies did, however, enable us to rule out an even lower symmetry cis structure:



(6) Mingos, D. M. P. *J. Organomet. Chem.* **1979**, *179*, C29.

(7) Crystal data: formula = $[ReO_2(py)_2(bpy)]ClO_4\cdot 0.33(pyH)ClO_4\cdot 0.33(CH_3)_2CO$, M = 711.25, rhombohedral, space group $R\bar{3}$ (No. 148), a = 24.627 (5) Å, c = 19.748 (5) Å, V = 10,372 (7) Å^3, Z = 18. The structure was solved by Patterson and Fourier techniques and refined to $R(F)$ and $R_w(F)$ of 0.052 and 0.070, respectively. A total of 2260 absorption-corrected reflections with $I > 3\sigma(I)$ were measured on an Enraf-Nonius CAD4 diffractometer up to $2\theta_{max}$ = 55° (Mo Kα radiation, λ = 0.71069 Å).

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