

Reactions of the Dirhenium(III) Carboxylate Complexes $\text{Re}_2(\text{O}_2\text{CR})_2\text{X}_4\text{L}_2$ ($\text{R} = \text{Me, Et}$; $\text{X} = \text{Cl, Br}$; $\text{L} = \text{H}_2\text{O, 4-Mepy}$) with 2-Hydroxypyridine (Hhp) and 2-Hydroxy-6-methylpyridine (Hmhp). Isolation and Structural Characterization of Complexes of the Types $\text{Re}_2(\text{hp})_2\text{X}_4\text{Hhp}$ and $\text{Re}_2(\text{mhp})_2\text{X}_4\text{Hmhp}$ and Hydrolysis of Nitriles ($\text{R}'\text{CN}$) To Give the Carboxylate-Bridged Species $\text{Re}_2(\mu\text{-O}_2\text{CR}')(\text{mhp})_2\text{X}_3$

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The reactions between $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{X}_4\text{L}_2$ ($\text{X} = \text{Cl, Br}$; $\text{L} = \text{H}_2\text{O, 4-methylpyridine}$) and 2-hydroxypyridine (Hhp) or 2-methyl-6-hydroxypyridine (Hmhp) in THF or acetone afford the diamagnetic dirhenium(III) complexes $\text{Re}_2(\text{hp})_2\text{Cl}_4\text{Hhp}\cdot\text{THF}$ and $\text{Re}_2(\text{mhp})_2\text{X}_4\text{Hmhp}\cdot\text{S}$ ($\text{X} = \text{Cl, Br}$; $\text{S} = \text{THF, (CH}_3)_2\text{CO}$) in yields of ca. 70%. The complex $\text{Re}_2(\text{mhp})_2\text{Cl}_4\text{Hmhp}\cdot(\text{CH}_3)_2\text{CO}$ has been characterized by X-ray crystallography. This complex crystallizes in the triclinic space group $P\bar{1}$ with the following unit cell dimensions: $a = 9.527$ (2) Å, $b = 16.975$ (3) Å, $c = 9.405$ (2) Å, $\alpha = 104.77$ (2)°, $\beta = 111.61$ (2)°, $\gamma = 75.14$ (2)°, $V = 1345$ (1) Å³, and $Z = 2$. The structure was refined to $R = 0.071$ ($R_w = 0.088$) for 2698 data with $F^2 > 3.0\sigma(F^2)$. The two mhp ligands are in a trans disposition to one another and are bound in a polar arrangement; i.e., they are oriented so as to give a Re_2L_8 species that contains $[\text{ReCl}_2\text{O}_2]$ and $[\text{ReCl}_2\text{N}_2]$ units. The Hmhp ligand is bound through its oxygen atom to the rhenium atom contained in the $[\text{ReCl}_2\text{O}_2]$ ligand set. The Re-Re quadruple-bond distance is 2.210 (1) Å. While $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4(\text{H}_2\text{O})_2$ reacts with Hhp in acetonitrile (or ethanol) to produce $\text{Re}_2(\text{hp})_2\text{Cl}_4$, the Hmhp ligand reacts with $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{X}_4(\text{H}_2\text{O})_2$ in nitriles $\text{R}'\text{CN}$ ($\text{R}' = \text{Me, Et}$) to give products, viz., $\text{Re}_2(\text{O}_2\text{CR}')(\text{mhp})_2\text{X}_3$, that result from the hydrolysis of $\text{R}'\text{CN}$. The propionate complex $\text{Re}_2(\text{O}_2\text{CC}_2\text{H}_5)_2(\text{mhp})_2\text{X}_3$, which was characterized by X-ray crystallography, crystallizes in the orthorhombic space group $P2_12_12_1$ with the following unit cell dimensions: $a = 8.831$ (1) Å, $b = 14.310$ (5) Å, $c = 15.563$ (5) Å, $V = 1971$ (2) Å³, and $Z = 4$. The molecule contains three monoanionic bridging ligands and a polar arrangement of the two trans mhp ligands so that there are $[\text{ReN}_2\text{OCl}]$ and $[\text{ReO}_3\text{Cl}]$ units. The third chloride ligand is bound to the less sterically encumbered rhenium atom, i.e. that which contains the three oxygen ligand atoms. The Re-Re quadruple-bond distance is 2.204 (1) Å.

Introduction

The stabilization of multiply bonded metal complexes by substituted pyridine ligands has been examined by a number of workers.^{1,2} Among the most commonly used ligands are 6-methyl-2-hydroxypyridine (Hmhp) and the less sterically demanding 2-hydroxypyridine (Hhp). In 1979, Cotton and Gage reported the synthesis and structural characterization of the complex dichlorotetrakis(2-hydroxypyridinato)dirhenium(III), $\text{Re}_2(\text{hp})_4\text{Cl}_2$.³ Later, we developed a high-yield synthetic procedure for the set of three halide complexes $\text{Re}_2(\text{hp})_4\text{X}_2$ ($\text{X} = \text{Cl, Br, I}$) and examined their redox chemistry, a study which led to the isolation of the paramagnetic monoanions $[\text{Re}_2(\text{hp})_4\text{X}_2]^-$.⁴

During the development of the high-yield synthetic route to $\text{Re}_2(\text{hp})_4\text{X}_2$, through the reactions of $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{X}_8$ with Hhp in refluxing 1-pentanol,⁴ we noted that soluble green intermediates were formed. At the time, these intermediates were not isolated in sufficient quantities or purity to permit their adequate characterization. However, during our more recent investigations into the unusual chemical reactivities of the quadruply bonded bis(carboxylate) complexes of the type $\text{Re}_2(\text{O}_2\text{CR})_2\text{X}_4\text{L}_2$ ($\text{R} = \text{Me, Et}$; $\text{X} = \text{Cl, Br}$; $\text{L} = \text{neutral donor}$),^{5,6} we have studied their reactions with Hhp and Hmhp in acetone and tetrahydrofuran and have now identified, we believe, these green "intermediates". They are the complexes $\text{Re}_2(\text{hp})_2\text{X}_4\text{Hhp}$ and $\text{Re}_2(\text{mhp})_2\text{X}_4\text{Hmhp}$ ($\text{X} = \text{Cl, Br}$). Related reactions performed in neat nitrile solvents ($\text{R}'\text{CN}$) have also been examined. While reactions of the complex $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4(\text{H}_2\text{O})_2$ with Hhp in acetonitrile produce only $\text{Re}_2(\text{hp})_4\text{Cl}_2$, the Hmhp ligand forms a surprising set of carboxylate-containing species. These are of stoichiometry Re_2 -

$(\text{O}_2\text{CR})(\text{mhp})_2\text{X}_3$ and contain a coordinated carboxylate group that corresponds to the hydrolyzed form of the nitrile solvent. The latter reactions proceed through the intermediacy of $\text{Re}_2(\text{mhp})_2\text{X}_4\text{Hmhp}$. The synthesis and characterization of these products are described herein.

Experimental Section

Starting Materials. The compounds $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{X}_8$ ⁷ ($\text{X} = \text{Cl, Br}$) were converted into $\text{Re}_2(\text{O}_2\text{CR})_2\text{X}_4\text{L}_2$ ($\text{R} = \text{Me, Et}$; $\text{X} = \text{Cl, Br}$; $\text{L} = \text{H}_2\text{O, 4-Mepy}$) according to the published procedures.^{6,8} All common solvents were used as received from commercial sources. The ligand 2-hydroxypyridine (Hhp) was purified by sublimation prior to use while 2-hydroxy-6-methylpyridine (Hmhp) was used without prior purification.

Reaction Procedures. All syntheses were performed under an atmosphere of dry nitrogen at the pressure provided by bubbling the outlet nitrogen through a column of mercury approximately 8 cm in depth. All solvents were deoxygenated prior to use.

A. Preparation of Complexes Containing Two 2-Hydroxypyridinato Ligands. (i) $\text{Re}_2(\text{hp})_2\text{Cl}_4\text{Hhp}\cdot\text{THF}$. A mixture of $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4\cdot(4\text{-Mepy})_2$ (0.20 g, 0.24 mmol) and Hhp (0.08 g, 0.84 mmol) was refluxed for 48 h in 15 mL of THF. The reaction mixture was cooled slowly to room temperature and filtered. The small green crystals were washed with fresh THF and dried; yield 0.16 g (77%). Anal. Calcd for $\text{C}_{19}\text{H}_{21}\text{Cl}_4\text{N}_5\text{O}_4\text{Re}_2$: C, 26.24; H, 2.43. Found: C, 26.77; H, 3.04. The presence of lattice THF was confirmed by ¹H NMR spectroscopy on a CD₃CN solution of the complex (multiplets at $\delta +3.63$ and $+1.74$).

The related starting material $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4(\text{H}_2\text{O})_2$ also yielded this same product. A mixture of $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4(\text{H}_2\text{O})_2$ (0.17 g, 0.26 mmol) and excess Hhp (0.19 g, 2.02 mmol) was reacted in refluxing THF with stirring for 17 h and the reaction mixture then allowed to cool without agitation. The green powder was washed sparingly with hexanes and dried; yield 0.16 g (72%).

When $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4(\text{H}_2\text{O})_2$ is reacted with Hhp with the use of ethanol or acetonitrile as the reaction solvent, then the complex $\text{Re}_2(\text{hp})_4\text{Cl}_2$ ^{3,4} is isolated in quite high yield. For example, a sample of $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4(\text{H}_2\text{O})_2$ (0.147 g, 0.22 mmol) was reacted with Hhp (0.156 g, 1.64 mmol) in 20 mL of refluxing EtOH for 24 h. The cooled reaction mixture was filtered and the red-brown solid washed with fresh solvent and dried; yield 0.128 g (71%). With CH₃CN as solvent, the

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complex $\text{Re}_2(\text{hp})_4\text{Cl}_2$ was isolated in 61% yield. The identification of this product was, in each instance, based upon its spectroscopic and electrochemical properties.⁴

On the basis of the foregoing observations, it was expected that the reaction of $\text{Re}_2(\text{hp})_2\text{Cl}_4\cdot\text{Hhp}\cdot\text{THF}$ in ethanol with further Hhp would give $\text{Re}_2(\text{hp})_4\text{Cl}_2$. A sample of $\text{Re}_2(\text{hp})_2\text{Cl}_4\cdot\text{Hhp}\cdot\text{THF}$ (0.10 g, 0.11 mmol) was admixed with Hhp (0.07 g, 0.74 mmol) and heated in 15 mL of EtOH for 24 h. The dark red-brown product was filtered from the cooled reaction mixture, washed with fresh solvent, and dried; yield 0.07 g (78%). Identification of the product as $\text{Re}_2(\text{hp})_4\text{Cl}_2$ was based upon a comparison of its IR spectrum and cyclic voltammogram to those of an authentic sample.⁴

(ii) $\text{Re}_2(\text{hp})_2\text{Br}_4\cdot\text{Hhp}\cdot\text{S}$. Reactions between $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{Br}_4\text{L}_2$ (L = H_2O , 4-Mepy) and Hhp in THF and acetone gave products that contained red-brown $\text{Re}_2(\text{hp})_4\text{Br}_2$ as a major contaminant (as monitored by cyclic voltammetry). Pure samples of the green title complex were not isolated.

(iii) $\text{Re}_2(\text{mhp})_2\text{Cl}_4\cdot\text{Hmhp}\cdot(\text{CH}_3)_2\text{CO}$. A mixture of $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4(\text{H}_2\text{O})_2$ (0.25 g, 0.37 mmol) and Hmhp (0.15 g, 1.4 mmol) was heated at reflux for ~24 h in 20 mL of acetone. The solution was cooled to room temperature, and the green needles were filtered from the pale green reaction solution. The solid was washed quickly with fresh acetone and dried; yield 0.25 g (75%). Anal. Calcd for $\text{C}_{21}\text{H}_{25}\text{Cl}_4\text{N}_3\text{O}_4\text{Re}_2$: C, 28.10; H, 2.81; Cl, 15.80. Found: C, 27.22; H, 2.65; Cl, 16.26. The presence of lattice acetone was inferred from IR spectroscopy (Nujol mull, $\nu(\text{C}=\text{O})$ 1700 cm^{-1}) and ^1H NMR spectroscopy (CDCl_3 , δ +2.16 s).

(iv) $\text{Re}_2(\text{mhp})_2\text{Cl}_4\cdot\text{Hmhp}\cdot\text{THF}$. A sample of $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4(\text{H}_2\text{O})_2$ (0.15 g, 0.23 mmol) was admixed with Hmhp (0.15 g, 1.4 mmol) and the mixture refluxed in 20 mL of THF for 12 h. The green reaction mixture was cooled and filtered and the solid washed with fresh diethyl ether. The green powder was dried; yield 0.15 g (72%). Anal. Calcd for $\text{C}_{22}\text{H}_{27}\text{Cl}_4\text{N}_3\text{O}_4\text{Re}_2$: C, 28.98; H, 2.99. Found: C, 28.40; H, 3.19. ^1H NMR spectroscopy (CDCl_3) confirmed the presence of lattice THF (δ +3.77 m and +1.77 m).

(v) $\text{Re}_2(\text{mhp})_2\text{Br}_4\cdot\text{Hmhp}\cdot(\text{CH}_3)_2\text{CO}$. A procedure similar to that in A(iii) involving the reaction of $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{Br}_4(\text{H}_2\text{O})_2$ (0.22 g, 0.26 mmol) with Hmhp (0.24 g, 2.2 mmol) in 15 mL of acetone for ~12 h gave the title complex as green needles; yield 0.18 g (64%). Anal. Calcd for $\text{C}_{21}\text{H}_{25}\text{Br}_4\text{N}_3\text{O}_4\text{Re}_2$: C, 23.45; H, 2.34. Found: C, 23.40; H, 2.27. IR and ^1H NMR spectroscopy (CDCl_3) confirmed the presence of acetone.

(vi) $\text{Re}_2(\text{mhp})_2\text{Br}_4\cdot\text{Hmhp}\cdot\text{THF}$. The reaction of $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{Br}_4(\text{H}_2\text{O})_2$ (0.16 g, 0.19 mmol) and Hmhp (0.18 g, 1.6 mmol) in 15 mL of THF for 14 h gave the title complex as green crystals, yield 0.14 g (67%). Anal. Calcd for $\text{C}_{22}\text{H}_{27}\text{Br}_4\text{N}_3\text{O}_4\text{Re}_2$: C, 24.25; H, 2.49. Found: C, 24.68; H, 2.73. ^1H NMR spectroscopy (CDCl_3) showed the presence of lattice THF.

B. Reactions of $\text{Re}_2(\text{mhp})_2\text{X}_4\cdot\text{Hmhp}$ (X = Cl, Br) with 4-Methylpyridine. (i) $\text{Re}_2(\text{mhp})_2\text{Cl}_4\cdot 4\text{-Mepy}$. A sample of $\text{Re}_2(\text{mhp})_2\text{Cl}_4\cdot\text{Hmhp}\cdot(\text{CH}_3)_2\text{CO}$ (0.024 g, 0.03 mmol) was mixed with 6 mL of acetone, and 0.5 mL of 4-methylpyridine was added with stirring. The resultant bright green suspension was stirred for 10 min and the volume of the reaction mixture reduced to ca. 3 mL. The insoluble product was isolated by centrifugation, washed successively with 2 mL each of acetone, THF, and hexanes, and dried in vacuo; yield 0.006 g (29%). Additional product was obtained upon evaporating the supernatant to dryness and extracting the residue with a small volume of CH_2Cl_2 . The addition of hexanes to the extract precipitated the product; yield 0.005 g (25%). The two crops of product were combined and recrystallized from CH_2Cl_2 /hexanes. Anal. Calcd for $\text{C}_{18}\text{H}_{19}\text{Cl}_4\text{N}_3\text{O}_2\text{Re}_2$: C, 26.25; H, 2.33. Found: C, 25.89; H, 2.47.

(ii) $\text{Re}_2(\text{mhp})_2\text{Br}_4\cdot 4\text{-Mepy}$. $\text{Re}_2(\text{mhp})_2\text{Br}_4\cdot\text{Hmhp}\cdot(\text{CH}_3)_2\text{CO}$ (0.034 g, 0.03 mmol) was stirred with 0.5 mL of 4-methylpyridine and 12 mL of acetone for 15 min. The product was isolated by using a procedure similar to that described for its chloride analogue; yield 0.029 g (92%). It was purified by recrystallization from CH_2Cl_2 /hexanes. Anal. Calcd for $\text{C}_{18}\text{H}_{19}\text{Br}_4\text{N}_3\text{O}_2\text{Re}_2$: C, 21.60; H, 1.91. Found: C, 20.79; H, 1.92.

C. Preparation of the Complexes $\text{Re}_2(\text{O}_2\text{CR}')(\text{mhp})_2\text{X}_3$ from the Reactions of $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{X}_4(\text{H}_2\text{O})_2$ (X = Cl, Br) with R'CN. (i) $\text{Re}_2(\text{O}_2\text{CCH}_3)_2(\text{mhp})_2\text{Cl}_3$. A sample of $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4(\text{H}_2\text{O})_2$ (0.27 g, 0.41 mmol) was reacted with Hmhp (0.19 g, 1.7 mmol) in 20 mL of refluxing CH_3CN for 12 days. The reaction mixture was filtered while it was hot, and the red/green crystals were washed with fresh CH_3CN and dried; yield 0.19 g (61%). Anal. Calcd for $\text{C}_{14}\text{H}_{15}\text{Cl}_3\text{N}_2\text{O}_4\text{Re}_2$: C, 22.30; H, 2.01. Found: C, 22.66; H, 2.21.

(ii) $\text{Re}_2(\text{O}_2\text{CC}_2\text{H}_5)_2(\text{mhp})_2\text{Cl}_3$. A mixture of $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4(\text{H}_2\text{O})_2$ (0.21 g, 0.31 mmol) and Hmhp (0.21 g, 1.9 mmol) was refluxed in 25 mL of $\text{C}_2\text{H}_5\text{CN}$ for 4 days. The hot reaction mixture was filtered, and the dark crystals were washed with fresh $\text{C}_2\text{H}_5\text{CN}$ and dried; yield 0.14

g (59%). Anal. Calcd for $\text{C}_{15}\text{H}_{17}\text{Cl}_3\text{N}_2\text{O}_4\text{Re}_2$: C, 23.46; H, 2.23. Found: C, 23.41; H, 2.34.

(iii) $\text{Re}_2(\text{O}_2\text{CC}_2\text{H}_5)_2(\text{mhp})_2\text{Br}_3$. A sample of $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{Br}_4(\text{H}_2\text{O})_2$ (0.21 g, 0.24 mmol) was refluxed with Hmhp (0.36 g, 3.3 mmol) in 20 mL of $\text{C}_2\text{H}_5\text{CN}$ for 10 days. The reaction mixture was filtered and the dark crystalline solid washed with fresh $\text{C}_2\text{H}_5\text{CN}$ and dried; yield 0.13 g (69%). Anal. Calcd for $\text{C}_{15}\text{H}_{17}\text{Br}_3\text{N}_2\text{O}_4\text{Re}_2$: C, 19.99; H, 1.90. Found: C, 20.74; H, 2.13.

D. Reaction of $\text{Re}_2(\text{O}_2\text{CC}_2\text{H}_5)_2\text{Cl}_4(\text{H}_2\text{O})_2$ with Acetonitrile. A sample of the sticky blue complex $\text{Re}_2(\text{O}_2\text{CC}_2\text{H}_5)_2\text{Cl}_4(\text{H}_2\text{O})_2$ (~0.18 g) was dissolved along with an excess of Hmhp (0.29 g, 2.7 mmol) in 20 mL of neat CH_3CN . The resulting solution was refluxed for 13 days. The solid was filtered from the hot solution, washed with fresh CH_3CN , and dried; yield 0.08 g. A cyclic voltammogram (recorded in 0.2 M TBAH/ CH_2Cl_2) and IR spectrum of the solid matched very closely those of $\text{Re}_2(\text{O}_2\text{CCH}_3)_2(\text{mhp})_2\text{Cl}_3$, but $\text{Re}_2(\text{O}_2\text{CC}_2\text{H}_5)_2(\text{mhp})_2\text{Cl}_3$ may be a minor contaminant. Workup of the filtrate gave a residue whose cyclic voltammogram (in 0.2 M TBAH/ CH_2Cl_2) indicated the presence of $\text{Re}_2(\text{mhp})_2\text{Cl}_4\cdot\text{Hmhp}$.

E. Reaction of $\text{Re}_2(\text{mhp})_2\text{Cl}_4\cdot\text{Hmhp}\cdot(\text{CH}_3)_2\text{CO}$ with Acetonitrile. A sample of $\text{Re}_2(\text{mhp})_2\text{Cl}_4\cdot\text{Hmhp}\cdot(\text{CH}_3)_2\text{CO}$ (0.12 g, 0.17 mmol) was refluxed for 5 days in 25 mL of undried reagent grade CH_3CN . The reaction mixture was filtered while it was hot, and the resulting crystals were washed with fresh CH_3CN and dried; yield 0.023 g (21%). Spectroscopic and electrochemical data for this product matched those for $\text{Re}_2(\text{O}_2\text{CCH}_3)_2(\text{mhp})_2\text{Cl}_3$ (see C(i)). An examination of the green residue from the reaction filtrate by cyclic voltammetry (in 0.2 M TBAH/ CH_2Cl_2) indicated the presence of both $\text{Re}_2(\text{O}_2\text{CCH}_3)_2(\text{mhp})_2\text{Cl}_3$ and unreacted $\text{Re}_2(\text{mhp})_2\text{Cl}_4\cdot\text{Hmhp}$ in approximately equal amounts.

F. Reactions of $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4(4\text{-Mepy})_2$ with Hmhp. (i) **In the Presence of $\text{HBF}_4(\text{aq})$.** A mixture of $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4(4\text{-Mepy})_2$ (0.12 g, 0.15 mmol) and Hmhp (0.14 g, 1.3 mmol) was refluxed for 11 days in 20 mL of CH_3CN to which 0.3 mL of aqueous HBF_4 (48%) had been added. The solid product was filtered from the hot reaction mixture, washed with fresh solvent, and dried; yield 0.042 g (37%). The electrochemical and spectroscopic properties of this product showed it to be pure $\text{Re}_2(\text{O}_2\text{CCH}_3)_2(\text{mhp})_2\text{Cl}_3$. An examination of the electrochemical properties of the residue from the reaction filtrate indicated the presence of some $\text{Re}_2(\text{mhp})_2\text{Cl}_4\cdot\text{Hmhp}$.

(ii) **In Neat Acetonitrile.** A mixture of $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4(4\text{-Mepy})_2$ (0.12 g, 0.15 mmol) and Hmhp (0.14 g, 1.3 mmol) was refluxed for 11 days in 20 mL of CH_3CN that had been dried by distillation from CaH_2 . The hot solution was filtered and the solid washed with fresh CH_3CN and dried; yield 0.03 g. The cyclic voltammogram and the IR spectrum of this product showed it to be $\text{Re}_2(\text{mhp})_2\text{Cl}_4\cdot\text{Hmhp}$. The residue obtained by workup of the reaction filtrate is primarily $\text{Re}_2(\text{mhp})_2\text{Cl}_4\cdot\text{Hmhp}$ as judged by its electrochemical properties.

X-ray Crystal Structure Analyses. Crystals of $\text{Re}_2(\text{mhp})_2\text{Cl}_4\cdot\text{Hmhp}\cdot(\text{CH}_3)_2\text{CO}$ (**1**) were synthesized by the reaction of $\text{Re}_2(\text{O}_2\text{CC}_2\text{H}_5)_2\text{Cl}_4(\text{H}_2\text{O})_2$ with Hmhp in refluxing acetone (procedure A(iii)) in the presence of a white birch boiling stick. Good-quality crystals of $\text{Re}_2(\text{O}_2\text{CC}_2\text{H}_5)_2(\text{mhp})_2\text{Cl}_3$ (**2**) were obtained directly from the reaction of $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4(\text{H}_2\text{O})_2$ and Hmhp in refluxing propionitrile (procedure C(ii)) in a similar fashion.

The structures of complexes **1** and **2** were determined by application of general procedures that are described more fully elsewhere.⁹ Crystal data and information relating to data collection and structure refinement are listed in Table I. The cell parameters are based on 25 reflections with $15.4 < \theta < 22.4^\circ$ for **1** and $13.9 < \theta < 19.4^\circ$ for **2**. Three standard reflections were measured every 5000 s of beam exposure during data collection and displayed no systematic variation in intensity in the case of the crystal of **2**. However, a wider than normal variation in the standards occurred during the data collection on the crystal of **1** due to fluctuations in the X-ray beam intensity and, accordingly, we used the decay correction program CHORT (part of the Enraf-Nonius SDP package) to correct for this. The overall decay in the intensity standards was 9% during the course of the data collection.

Calculations were performed on a PDP11/34 computer using the Enraf-Nonius structure determination package. For **1** and **2**, the atoms were located and refined from initial Patterson maps. In both instances an empirical absorption correction was applied,¹⁰ the linear absorption coefficients being 95.50 cm^{-1} (for **1**) and 128.77 cm^{-1} (for **2**). No correction for extinction was applied. The least-squares program minimized the function $w(|F_o| - |F_c|)^2$, where w is a weighting factor defined as $w = 1/\sigma^2(F_o)$. All atoms except hydrogen were refined anisotropically, and

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Table I. Crystallographic Data and Data Collection Parameters for $\text{Re}_2(\text{mhp})_2\text{Cl}_4\cdot\text{Hmhp}\cdot(\text{CH}_3)_2\text{CO}$ (**1**) and $\text{Re}_2(\text{O}_2\text{CC}_2\text{H}_5)(\text{mhp})_2\text{Cl}_3$ (**2**)^a

	1	2
formula	$\text{Re}_2\text{Cl}_4\text{O}_4\text{N}_3\text{C}_{21}\text{H}_{25}$	$\text{Re}_2\text{Cl}_3\text{O}_4\text{N}_2\text{C}_{15}\text{H}_{17}$
fw	897.66	768.07
space group	<i>P1</i>	<i>P2_12_12_1</i>
<i>a</i> , Å	9.527 (2)	8.831 (1)
<i>b</i> , Å	16.975 (3)	14.310 (5)
<i>c</i> , Å	9.405 (2)	15.563 (5)
α , deg	104.77 (2)	90
β , deg	111.61 (2)	90
γ , deg	75.14 (2)	90
<i>V</i> , Å ³	1345 (1)	1971 (2)
<i>Z</i>	2	4
<i>d</i> _{calcd.} , g cm ⁻³	2.216	2.588
cryst dimens, mm	0.41 × 0.12 × 0.04	0.70 × 0.60 × 0.47
temp, °C	22.0	22.0
radiation (wavelength, Å)	Mo K α (0.710 73 Å)	Mo K α (0.710 73 Å)
monochromator	graphite	graphite
linear abs coeff, cm ⁻¹	95.50	128.77
abs cor applied	empirical ^b	empirical ^b
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
scan method	θ - 2θ	θ - 2θ
<i>hkl</i> limits	0 to 10, -17 to 18, -10 to 9	0 to 11, 0 to 18, 0 to 20
2θ range, deg	4.00-45.00	4.00-55.00
scan width, deg	0.89 + 0.35 tan θ	0.80 + 0.35 tan θ
takeoff angle, deg	3.50	4.90
programs used	Enraf-Nonius SDP	Enraf-Nonius SDP
<i>F</i> ₀₀₀	422.0	1416.0
<i>p</i> factor used in weighting	0.070	0.070
no. of data collected	3500	2592
data with <i>I</i> > 3.0 σ (<i>I</i>)	2698	2349
no. of variables	305	235
largest shift/esd in final cycle	0.09	0.01
<i>R</i> ^c	0.071	0.045
<i>R</i> _w ^d	0.088	0.067
goodness of fit ^e	1.638	1.607

^a Numbers in parentheses following certain data are estimated standard deviations occurring in the least significant digit. ^b Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 158. ^c $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^d $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^{1/2}]^{1/2}$; $w = 1/\sigma^2(F_o)$. ^e Goodness of fit = $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{observns}} - N_{\text{params}})]^{1/2}$.

corrections for anomalous scattering were applied.¹¹ Positions for hydrogen atoms were calculated by assuming idealized geometry and a C-H bond distance of 0.95 Å. For methyl groups, one hydrogen was located in a difference Fourier map, its position was idealized, and the remaining positions were calculated. While the hydrogens were used in the calculation of *F*_o, they were not included in the least-squares refinement.

In the case of crystals of **1**, the presence of a molecule of lattice acetone, which had been inferred from IR and ¹H NMR spectroscopy, was confirmed by the crystal structure analysis. The final residuals were *R* = 0.071 and *R*_w = 0.088, the quality of fit was 1.638, and the final difference Fourier map displayed no peaks of chemical significance.

For the structure determination of **2**, the space group *P2₁2₁2₁* is enantiomorphic and refinement was performed on both possible orientations without the inclusion of any hydrogen atoms. The final residuals for the two enantiomorphs were as follows: *R* = 0.0459 and *R*_w = 0.069; *R* = 0.0534 and *R*_w = 0.0791. Refinement was completed on the enantiomorph with the lowest *R* factor (quality of fit 1.607). No molecules of lattice solvent were found, and the final difference Fourier map displayed no peaks of chemical significance.

Further details concerning the data set, the structure solution, and the structure refinement may be obtained from P.E.F. Tables II and III list the atomic positional parameters and their errors for **1** and **2**, while Tables IV and V list important intramolecular bond distances and angles.

Table II. Positional Parameters and Equivalent Isotropic Displacement Parameters (Å²) for Non-Hydrogen Atoms of **1** and Their Estimated Standard Deviations^a

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Re(1)	0.54258 (8)	0.27262 (5)	0.53296 (9)	2.77 (2)
Re(2)	0.66116 (8)	0.18445 (5)	0.37768 (9)	2.48 (2)
Cl(11)	0.6925 (7)	0.2271 (4)	0.7693 (6)	3.9 (1)
Cl(12)	0.3507 (6)	0.3496 (3)	0.3514 (7)	3.7 (1)
Cl(21)	0.8724 (6)	0.1035 (3)	0.5263 (6)	3.7 (1)
Cl(22)	0.5297 (6)	0.2080 (3)	0.1277 (6)	3.2 (1)
O(10)	0.401 (1)	0.1962 (8)	0.494 (2)	3.1 (3)
O(20)	0.674 (1)	0.3531 (8)	0.577 (1)	2.6 (3)
O(30)	0.415 (2)	0.3569 (9)	0.689 (2)	4.3 (4)
O(100)	0.836 (2)	0.648 (1)	0.085 (2)	4.7 (4)
N(11)	0.530 (2)	0.098 (1)	0.347 (2)	2.8 (4)
N(21)	0.800 (2)	0.269 (1)	0.412 (2)	2.9 (4)
N(31)	0.300 (2)	0.459 (1)	0.831 (2)	3.3 (4)
C(12)	0.408 (2)	0.124 (1)	0.415 (3)	3.8 (5)
C(13)	0.313 (3)	0.071 (1)	0.401 (3)	3.7 (6)
C(14)	0.322 (3)	-0.005 (1)	0.306 (2)	3.9 (6)
C(15)	0.435 (3)	-0.030 (1)	0.231 (3)	3.8 (6)
C(16)	0.535 (2)	0.021 (1)	0.249 (3)	3.7 (5)
C(17)	0.661 (3)	-0.003 (1)	0.186 (3)	4.2 (6)
C(22)	0.789 (2)	0.340 (1)	0.516 (3)	4.2 (6)
C(23)	0.877 (3)	0.398 (2)	0.551 (3)	4.5 (6)
C(24)	0.994 (2)	0.381 (1)	0.488 (3)	4.0 (5)
C(25)	1.008 (2)	0.311 (2)	0.385 (3)	4.6 (6)
C(26)	0.918 (2)	0.253 (1)	0.346 (2)	3.5 (5)
C(27)	0.921 (2)	0.176 (2)	0.222 (3)	6.5 (7)
C(32)	0.388 (3)	0.434 (1)	0.743 (2)	3.1 (5)
C(33)	0.454 (2)	0.495 (1)	0.724 (3)	3.8 (6)
C(34)	0.425 (3)	0.573 (1)	0.800 (3)	4.4 (6)
C(35)	0.333 (3)	0.595 (1)	0.897 (3)	4.4 (6)
C(36)	0.271 (2)	0.536 (1)	0.913 (3)	3.4 (5)
C(37)	0.166 (3)	0.551 (2)	1.006 (3)	5.4 (7)
C(101)	0.893 (3)	0.766 (2)	0.035 (3)	5.0 (6)
C(102)	0.837 (2)	0.721 (1)	0.119 (2)	3.4 (5)
C(103)	0.782 (3)	0.772 (2)	0.247 (3)	5.4 (7)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $4/3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

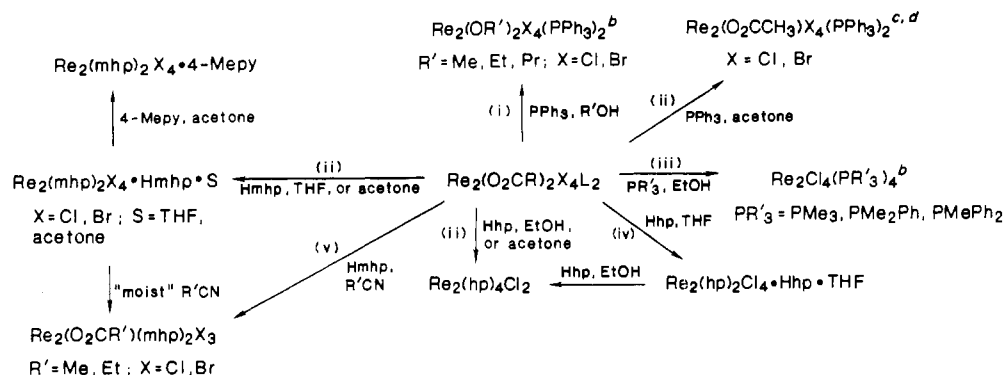
Table III. Positional Parameters and Equivalent Isotropic Displacement Parameters for Non-Hydrogen Atoms of **2** and Their Estimated Standard Deviations^a

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Re(1)	0.37466 (6)	0.98821 (4)	0.34591 (4)	1.68 (1)
Re(2)	0.58509 (6)	1.07055 (4)	0.33929 (4)	1.476 (9)
Cl(11)	0.1825 (5)	1.1014 (4)	0.3327 (3)	3.44 (9)
Cl(12)	0.1766 (5)	0.8660 (4)	0.3582 (3)	3.25 (9)
Cl(21)	0.5229 (5)	1.2254 (3)	0.3172 (3)	2.64 (8)
O(1)	0.517 (2)	0.876 (1)	0.3587 (9)	3.2 (3)
O(2)	0.723 (1)	0.9609 (7)	0.3525 (8)	2.0 (2)
O(10)	0.365 (1)	1.0003 (8)	0.4736 (7)	2.1 (2)
O(20)	0.371 (1)	0.9726 (9)	0.2175 (7)	2.4 (2)
N(11)	0.579 (2)	1.0922 (9)	0.4718 (8)	1.7 (2)
N(21)	0.595 (2)	1.053 (1)	0.2057 (8)	1.9 (2)
C(1)	0.662 (2)	0.877 (1)	0.3544 (9)	2.0 (3)
C(2)	0.767 (2)	0.795 (1)	0.358 (1)	2.7 (3)
C(3)	0.700 (4)	0.712 (2)	0.409 (2)	5.9 (7)
C(12)	0.684 (2)	1.145 (1)	0.517 (1)	2.5 (3)
C(13)	0.673 (3)	1.160 (1)	0.604 (1)	3.6 (4)
C(14)	0.553 (2)	1.118 (2)	0.648 (1)	3.6 (4)
C(15)	0.449 (2)	1.065 (2)	0.606 (1)	2.9 (4)
C(16)	0.464 (2)	1.053 (1)	0.516 (1)	1.8 (3)
C(17)	0.811 (2)	1.187 (2)	0.465 (1)	3.6 (4)
C(22)	0.711 (2)	1.089 (1)	0.157 (1)	2.4 (3)
C(23)	0.704 (2)	1.081 (2)	0.068 (1)	3.5 (4)
C(24)	0.580 (3)	1.038 (2)	0.031 (1)	3.3 (4)
C(25)	0.469 (2)	0.997 (2)	0.078 (1)	2.7 (3)
C(26)	0.477 (2)	1.004 (1)	0.169 (1)	2.1 (3)
C(27)	0.843 (2)	1.127 (1)	0.206 (1)	2.6 (3)

^a See footnote a of Table II.

(11) (a) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1. (b) For the scattering factors used in the structure solution see: Cromer, D. T.; Waber, J. T. *Ibid.*, Table 2.2B.

Thermal parameters (Tables S1 and S2), positional parameters for the hydrogen atoms (Tables S3 and S4), complete listings of bond distances (Tables S5 and S6) and bond angles (Tables S7 and S8), and torsional

Scheme I^a

^a Reaction key: (i) L = H₂O, DMF, DMSO and R = Me, Et; (ii) L = H₂O and R = Me; (iii) L = H₂O, py and R = Me; (iv) L = H₂O, 4-Mepy and R = Me; (v) L = H₂O and R = Me, Et. ^b From ref 6. ^c From ref 17. ^d This product is also formed when L = py, 4-Mepy and EtOH is used as the reaction solvent.

Table IV. Important Bond Distances (Å) and Angles (deg) for 1^a

Re(1)-Re(2)	2.2096 (9)	Re(2)-N(11)	2.07 (2)
Re(1)-Cl(11)	2.356 (5)	Re(2)-N(21)	2.08 (1)
Re(1)-Cl(12)	2.362 (5)	O(10)-C(12)	1.26 (2)
Re(1)-O(10)	1.98 (1)	O(20)-C(22)	1.36 (2)
Re(1)-O(20)	1.95 (1)	O(30)-C(32)	1.28 (2)
Re(1)-O(30)	2.25 (1)	C(102)-O(100)	1.20 (2)*
Re(2)-Cl(21)	2.320 (5)	C(102)-C(101)	1.52 (3)*
Re(2)-Cl(22)	2.304 (4)	C(102)-C(103)	1.47 (3)*
Re(2)-Re(1)-Cl(11)	99.3 (1)	O(20)-Re(1)-O(30)	91.0 (4)
Re(2)-Re(1)-Cl(12)	99.8 (1)	Re(1)-Re(2)-Cl(21)	108.7 (1)
Re(2)-Re(1)-O(10)	91.3 (3)	Re(1)-Re(2)-Cl(22)	108.0 (1)
Re(2)-Re(1)-O(20)	92.1 (3)	Re(1)-Re(2)-N(11)	90.6 (3)
Re(2)-Re(1)-O(30)	176.9 (3)	Re(1)-Re(2)-N(21)	90.1 (3)
Cl(11)-Re(1)-Cl(12)	160.9 (2)	Cl(21)-Re(2)-Cl(22)	143.3 (2)
Cl(11)-Re(1)-O(10)	89.9 (4)	Cl(21)-Re(2)-N(11)	89.2 (4)
Cl(11)-Re(1)-O(20)	90.3 (4)	Cl(21)-Re(2)-N(21)	88.9 (4)
Cl(11)-Re(1)-O(30)	80.3 (4)	Cl(22)-Re(2)-N(11)	90.8 (4)
Cl(12)-Re(1)-O(10)	89.8 (4)	Cl(22)-Re(2)-N(21)	90.5 (4)
Cl(12)-Re(1)-O(20)	88.9 (4)	N(11)-Re(2)-N(21)	178.1 (6)
Cl(12)-Re(1)-O(30)	80.7 (4)	Re(1)-O(10)-C(12)	126 (1)
O(10)-Re(1)-O(20)	176.6 (4)	Re(1)-O(20)-C(22)	123 (1)
O(10)-Re(1)-O(30)	85.6 (4)	Re(1)-O(30)-C(32)	137 (1)

^a Numbers in parentheses are estimated standard deviations in the least significant digits. Starred distances are for the acetone of crystallization.

angles (Tables S9 and S10) for **1** and **2** are available as supplementary material.

Physical Measurements. Infrared spectra were recorded as Nujol mulls with an IBM Instruments IR/32 Fourier transform (4800–400 cm⁻¹) spectrometer. Electronic absorption spectra were recorded on IBM Instruments 9420 UV-visible, Hewlett-Packard HP8451A, and Cary 17D spectrophotometers. Electrochemical measurements were carried out by using a Bioanalytical Systems, Inc., Model CV-1A instrument on dichloromethane solutions that contained 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. $E_{1/2}$ values, determined as $(E_{pa} + E_{pc})/2$, were referenced to the silver/silver chloride (Ag/AgCl) electrode at room temperature and are uncorrected for junction potentials. Under our experimental conditions the ferrocenium/ferrocene couple is $E_{1/2} = +0.47$ V vs Ag/AgCl. ¹H NMR spectra were recorded on a Varian XL-200 spectrometer. Resonances were referenced internally to the residual protons in the incompletely deuterated solvent.

Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

Results and Discussion

(a) Synthesis and Characterization of Complexes That Contain Two 2-Hydroxypyridinato-Type Ligands. The preparation of the complexes $\text{Re}_2(\text{hp})_4\text{X}_2$ from the reactions between (*n*-Bu₄N)₂Re₂X₈ (X = Cl, Br) and 2-hydroxy-pyridine (Hhp) in 1-pentanol proceeds through a green, highly soluble intermediate that we were unable to isolate pure. However, a cyclic voltammogram of a 0.2 M TBAH/CH₂Cl₂ solution of this product displayed a single reversible reduction process at $E_{1/2} = -0.45$ V

Table V. Important Bond Distances (Å) and Angles (deg) for 2^a

Re(1)-Re(2)	2.2041 (6)	Re(2)-O(2)	2.000 (9)
Re(1)-Cl(11)	2.357 (4)	Re(2)-N(11)	2.09 (1)
Re(1)-Cl(12)	2.483 (4)	Re(2)-N(21)	2.10 (1)
Re(1)-O(1)	2.05 (1)	O(1)-C(1)	1.28 (2)
Re(1)-O(10)	1.996 (9)	O(2)-C(1)	1.33 (2)
Re(1)-O(20)	2.011 (9)	O(10)-C(16)	1.33 (2)
Re(2)-Cl(21)	2.313 (4)	O(20)-C(26)	1.28 (2)
Re(2)-Re(1)-Cl(11)	103.5 (1)	Re(1)-Re(2)-Cl(21)	108.7 (1)
Re(2)-Re(1)-Cl(12)	167.3 (1)	Re(1)-Re(2)-O(2)	95.0 (3)
Re(2)-Re(1)-O(1)	84.7 (3)	Re(1)-Re(2)-N(11)	90.7 (3)
Re(2)-Re(1)-O(10)	92.0 (3)	Re(1)-Re(2)-N(21)	90.8 (3)
Re(2)-Re(1)-O(20)	91.5 (3)	Cl(21)-Re(2)-O(2)	156.2 (3)
Cl(11)-Re(1)-Cl(12)	89.2 (2)	Cl(21)-Re(2)-N(11)	89.9 (3)
Cl(11)-Re(1)-O(1)	171.7 (3)	Cl(21)-Re(2)-N(21)	88.8 (3)
Cl(11)-Re(1)-O(10)	89.9 (3)	O(2)-Re(2)-N(11)	91.8 (4)
Cl(11)-Re(1)-O(20)	88.8 (3)	O(2)-Re(2)-N(21)	89.0 (4)
Cl(12)-Re(1)-O(1)	82.6 (3)	N(11)-Re(2)-N(21)	178.2 (5)
Cl(12)-Re(1)-O(10)	87.5 (3)	Re(1)-O(1)-C(1)	127 (1)
Cl(12)-Re(1)-O(20)	89.2 (3)	Re(2)-O(2)-C(1)	118.1 (8)
O(1)-Re(1)-O(10)	89.8 (5)	Re(1)-O(10)-C(16)	121.3 (8)
O(1)-Re(1)-O(20)	91.1 (5)	Re(1)-O(20)-C(26)	122.3 (9)
O(10)-Re(1)-O(20)	176.4 (4)		

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

vs. Ag/AgCl. Since this electrochemical behavior was reminiscent of that exhibited by bis(carboxylate) complexes of the type $\text{Re}_2(\text{O}_2\text{CR})_2\text{X}_4\text{L}_2$ (X = Cl, Br),⁶ we surmised that the green intermediates might be complexes of the type $\text{Re}_2(\text{hp})_2\text{X}_4$. Accordingly, we carried out the reaction of $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4(\text{H}_2\text{O})_2$ with Hhp in THF from which we isolated a product whose microanalytical data and ¹H NMR spectrum (recorded in CD₃CN) were consistent with the stoichiometry $\text{Re}_2(\text{hp})_2\text{Cl}_4 \cdot \text{Hhp} \cdot \text{THF}$. Upon reaction of this product with an excess of Hhp in hot ethanol, the red-brown complex $\text{Re}_2(\text{hp})_4\text{Cl}_2$ ⁴ was formed in high yield (see Scheme I).

In an analogous fashion, the reactions of $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{X}_4 \cdot (\text{H}_2\text{O})_2$ (X = Cl, Br) with the ligand 6-methyl-2-hydroxypyridine (Hmhp) in refluxing THF or acetone give green complexes of stoichiometry $\text{Re}_2(\text{mhp})_2\text{X}_4 \cdot \text{Hmhp} \cdot \text{S}$ (Scheme I; S = THF, (CH₃)₂CO). The presence of uncoordinated lattice solvent has been demonstrated by IR and ¹H NMR spectroscopy (see Experimental Section) and the identical properties of the THF- and acetone-containing products. These complexes bear a close structural and electronic relationship to $\text{Re}_2(\text{hp})_2\text{Cl}_4 \cdot \text{Hhp} \cdot \text{THF}$, as the similarity of their electronic absorption spectra and electrochemical redox properties attests (see Table VI). There are also rather close resemblances between the properties of these complexes and those of $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{X}_4\text{L}_2$.^{6,12}

(12) Shtemenko, A. V.; Golovaneva, I. F.; Kotelnikova, A. S.; Misailova, T. *V. Russ. J. Inorg. Chem. (Engl. Transl.)* **1980**, *25*, 704.

Table VI. Electrochemical and Electronic Absorption Spectral Data for Complexes of the Types $\text{Re}_2(\text{hp})_2\text{X}_4\text{-Hhmp}$, $\text{Re}_2(\text{mhp})_2\text{X}_4\text{-Hmhp}$, and $\text{Re}_2(\text{O}_2\text{CR})(\text{mhp})_2\text{X}_3$ (X = Cl, Br)

complex	electronic abs spectrum, nm ^a	voltammetric half-wave potentials, V ^b		
		$E_{1/2}(\text{ox})^c$	$E_{1/2}(\text{red})^d$	$E_{p,c}^e$
$\text{Re}_2(\text{hp})_2\text{Cl}_4\text{-Hhmp}^f$	712 (700), 442 (1800), 370 (2000)	~+1.4	-0.47	~-1.8
$\text{Re}_2(\text{mhp})_2\text{Cl}_4\text{-Hmhp}^f$	~860 (~100), 700 (1000), 432 (4400)	~+1.5	-0.46	~-1.85
$\text{Re}_2(\text{mhp})_2\text{Br}_4\text{-Hmhp}^f$	712 (1500), 448 (5300)	~+1.5	-0.32	~-1.55
$\text{Re}_2(\text{mhp})_2\text{Cl}_4\text{-4-Mepy}$	706 (600), 430 (2700)	~+1.6	-0.49	~-1.8
$\text{Re}_2(\text{mhp})_2\text{Br}_4\text{-4-Mepy}$	715 (1000), 443 (4600)	~+1.5?	-0.38	~-1.5
$\text{Re}_2(\text{O}_2\text{CCH}_3)(\text{mhp})_2\text{Cl}_3$	596 (650), 422 (5700)		-0.62	
$\text{Re}_2(\text{O}_2\text{CC}_2\text{H}_5)(\text{mhp})_2\text{Cl}_3$	594 (650), 420 (5700)		-0.62	
$\text{Re}_2(\text{O}_2\text{CC}_2\text{H}_5)(\text{mhp})_2\text{Br}_3$	610 (770), 430 (6300)		-0.52	

^a Measured in CH_2Cl_2 ; ϵ_{max} values in parentheses. ^b Vs Ag/AgCl; recorded on solutions in 0.2 M TBAH/ CH_2Cl_2 by using a Pt-bead electrode. Data were obtained at $v = 200$ mV/s. ^c This process is fairly close to the solvent limit and is not generally well defined. ^d Under our experimental conditions, the ΔE_p values (i.e. $E_{p,a} - E_{p,c}$) were in the range 90–120 mV. ^e Properties independent of whether acetone or THF is present as the solvent of crystallization.

The 200-MHz ^1H NMR spectrum of the free Hmhp ligand (recorded in CDCl_3) displays a singlet at $\delta +2.32$ due to the methyl protons. The pattern in the phenyl region consists of two doublets centered at $\delta +6.37$ and $+6.02$, each of which is due to one of the inequivalent 3,5-protons on the nitrogen ring split by coupling to the 4-proton. A doublet of doublets at $\delta +7.32$ is associated with that 4-proton. A broad resonance near $\delta +13.5$ corresponds to the unique "hydroxyl" proton. The ^1H NMR spectrum of the acetone solvate $\text{Re}_2(\text{mhp})_2\text{Cl}_4\text{-Hmhp}\cdot(\text{CH}_3)_2\text{CO}$ is representative of the spectra of this group of complexes as a whole. The principal differences are the resonances due to the lattice acetone or THF molecules (see Experimental Section). Three singlets between $\delta +2.0$ and $+2.8$ are present. The singlet at $\delta +2.16$ is associated with free acetone, while singlets at $\delta +2.39$ and $+2.60$ have an area ratio of 1:2 and are assignable to the methyl protons present in one unique Hmhp and two equivalent mhp ligands. The presence of three pyridyl moieties, one of which is unique, is supported by the pattern in the phenyl region. Two doublets at $\delta +6.67$ and $+6.36$ correspond to the 3,5-protons of the Hmhp ligand. A doublet of twice the area of either of these two doublets appears at $\delta +7.01$. This is associated with one set of 3,5-protons on the two equivalent mhp ligands. A complex multiplet centered at δ ca. $+7.5$ was of an intensity consistent with it arising from the overlap of the additional 3,5-proton doublet and the resonances of the 4-protons of all three mhp-type ligands.

Although we did not locate the "hydroxyl" proton of the Hmhp ligand in the ^1H NMR spectra of these complexes, the presence of such a ligand can be inferred from the observation that it can be easily displaced by 4-methylpyridine to give the complexes $\text{Re}_2(\text{mhp})_2\text{X}_4\text{-4-Mepy}$ (Scheme I), whose properties (Table VI) clearly conform very closely to those of their Hmhp-containing analogues. The ^1H NMR spectrum of the 4-Mepy complex $\text{Re}_2(\text{mhp})_2\text{Cl}_4\text{-4-Mepy}$ provides confirmation of the assignments made for the resonances due to the mhp and Hmhp ligands. The Hmhp resonances at $\delta +2.39$ (s), $+6.67$ (d), and $+6.36$ (d) are replaced by new resonances due to the 4-Mepy ligand at $\delta +2.32$ (s), $+7.14$ (d), and $+8.45$ (d); all show the correct integrations relative to those of the two remaining mhp ligands.

(b) **X-ray Crystal Structure of $\text{Re}_2(\text{mhp})_2\text{Cl}_4\text{-Hmhp}\cdot(\text{CH}_3)_2\text{CO}$ (1).** The structure of this complex is based upon that of an eclipsed M_2L_8 geometry.^{1,2} The ORTEP representation (Figure 1) shows that the two mhp ligands are in a *trans* disposition to one another and are bound in a polar arrangement;² i.e., they are oriented in the same direction so as to give a dimetal unit that contains $[\text{ReCl}_2\text{O}_2]$ and $[\text{ReCl}_2\text{N}_2]$ units. The Hmhp ligand is bound through its oxygen atom to the rhenium atom that is coordinated by the oxygen atoms of the two mhp ligands. This situation is at first sight similar to that seen in the structurally characterized complexes $\text{Ru}_2(\text{hp})_4\text{Cl}\cdot\text{Hhmp}^{13}$ and $\text{Rh}_2(\text{mhp})_4\text{-Hmhp}^{14}$. However, we cannot say for certain whether the Hmhp ligand in 1 has its

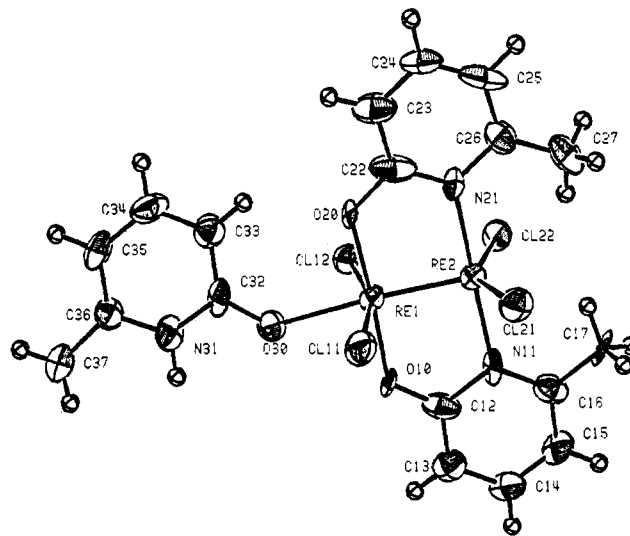
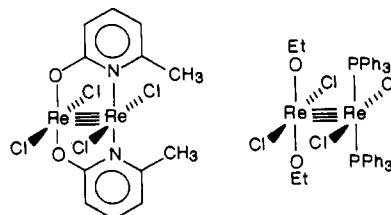


Figure 1. ORTEP view of the structure of the molecule $\text{Re}_2(\text{mhp})_2\text{Cl}_4\cdot\text{Hmhp}$ in its acetone solvate. The thermal ellipsoids are drawn at the 50% probability level.

unique ionizable hydrogen bound to oxygen or to nitrogen. The latter possibility is perhaps the more likely of the two, but there is no intramolecular $\text{N-H}\cdots\text{O}(\text{mhp})$ hydrogen bond involving the oxygen atom of one of the mhp ligands to confirm such a supposition. This feature is seen in the structures of $\text{Ru}_2(\text{hp})_4\text{Cl}\cdot\text{Hhmp}^{13}$ and $\text{Rh}_2(\text{mhp})_4\text{-Hmhp}^{14}$. Indeed, unlike the situation in these last two molecules,^{13,14} the axially bound Hmhp ligand in 1 is rotated about its C–O bond (C(32)–O(30)) in such a fashion so as to minimize any such hydrogen-bonding interaction.

The Re–Re distance of 2.210 (1) Å is in accord with 1 being a quadruply bonded dirhenium(III) complex. It resembles closely the Re–Re distance in $\text{Re}_2(\text{hp})_4\text{Cl}_2^3$ and in a variety of dirhenium(III) carboxylates of the general type $\text{Re}_2(\text{O}_2\text{CR})_2\text{X}_4$.^{1,2}

The other structural parameters for 1 are normal (see Table IV) and, with one notable exception, do not merit further discussion at this time. This exception concerns the Re–Cl distances, which are significantly longer for the Re atom that also has the two Re–O bonds than for the Re atom that is bound to the two pyridyl nitrogen atoms, i.e. ~ 2.36 versus ~ 2.32 Å. A similar difference is seen in the structure of the quadruply bonded mixed-valent dirhenium(IV,II) alkoxide complex $(\text{EtO})_2\text{Cl}_2\text{Re-ReCl}_2(\text{PPh}_3)_2$.^{5,6} Both complexes bear a close formal relationship to one another



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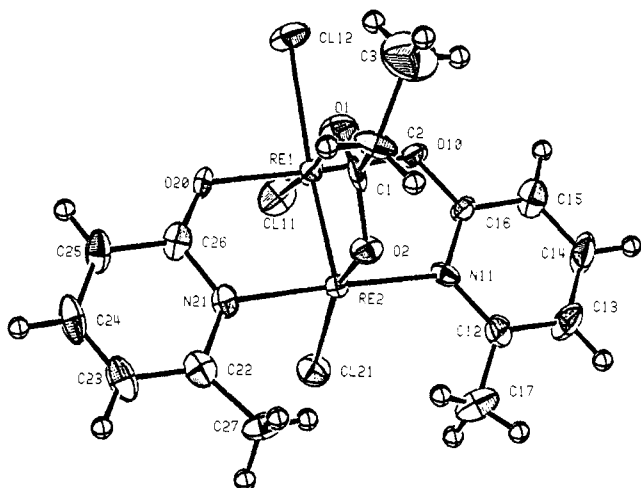


Figure 2. ORTEP view of $\text{Re}_2(\text{O}_2\text{CC}_2\text{H}_5)(\text{mhp})_2\text{Cl}_3$. The thermal ellipsoids are drawn at the 50% probability level.

with the pyridyl moieties in **1** replacing the two PPh_3 ligands. However, the ability of the bridging mhp ligands to delocalize charge ensures an electronic structure for **1**, and other compounds of this type, that more closely mimics that which is expected for symmetrical quadruply bonded $\text{Re}(\text{III})\text{--Re}(\text{III})$ complexes,^{1,2} at least insofar as the electrochemical and electronic absorption spectral properties of these compounds are concerned. These properties are quite different from those of the mixed-valent $\text{Re}(\text{IV})\text{--Re}(\text{II})$ alkoxide compounds $(\text{RO})_2\text{X}_2\text{ReReX}_2(\text{PPh}_3)_2$.^{5,6}

(c) Synthesis and Characterization of the Complexes $\text{Re}_2(\text{O}_2\text{CR})(\text{mhp})_2\text{X}_3$. The reactions between $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{X}_4\text{L}_2$ and Hhp or Hmhp, which in THF and acetone afford $\text{Re}_2(\text{hp})_2\text{X}_4\text{Hhp}\cdot\text{S}$ or $\text{Re}_2(\text{mhp})_2\text{X}_4\text{Hmhp}\cdot\text{S}$ ($\text{X} = \text{Cl}, \text{Br}; \text{S} = \text{THF}, (\text{CH}_3)_2\text{CO}$), are different in nitrile solvents (see Scheme I). Thus, the reaction of $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4(\text{H}_2\text{O})_2$ with Hhp in refluxing acetonitrile gives the red-brown complex $\text{Re}_2(\text{hp})_4\text{Cl}_2$ via the intermediacy of $\text{Re}_2(\text{hp})_2\text{Cl}_4\cdot\text{Hhp}$. When Hmhp is used in place of Hhp in the reaction with $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{X}_4(\text{H}_2\text{O})_2$ ($\text{X} = \text{Cl}, \text{Br}$) in acetonitrile, then extended reaction times (several days) are necessary to produce an isolable product. Dark red/green crystals were isolated that were of stoichiometry $\text{Re}_2(\text{O}_2\text{CCH}_3)(\text{mhp})_2\text{X}_3$. The electrochemical and electronic absorption spectral properties of these complexes are presented in Table VI. Cyclic voltammograms of solutions of each of these complexes in 0.2 M TBAH/ CH_2Cl_2 revealed a reversible-looking couple, corresponding to a one-electron reduction of the bulk complex, at potentials similar to those measured for other Re_2^{6+} core complexes such as $\text{Re}_2(\text{hp})_4\text{X}_2$,⁴ $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{X}_4\text{L}_2$,⁶ and $\text{Re}_2(\text{mhp})_2\text{X}_4\text{Hmhp}$ (Table VI). The ^1H NMR spectrum of $\text{Re}_2(\text{O}_2\text{CCH}_3)(\text{mhp})_2\text{Cl}_3$ (measured in CD_2Cl_2) is fully in accord with this formulation, with pyridyl ring resonances at $\delta +7.6$ (d) and $+7.0$ (t), in an intensity ratio of 2:1, and methyl singlets at $\delta +2.88$ (acetate) and $+2.37$ (mhp) of intensity 1:2.

Related reactions between $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{X}_4(\text{H}_2\text{O})_2$ ($\text{X} = \text{Cl}, \text{Br}$) and Hmhp in refluxing propionitrile again afforded red/green crystals that turned out to be those of the related propionate complexes $\text{Re}_2(\text{O}_2\text{CC}_2\text{H}_5)(\text{mhp})_2\text{X}_3$ ($\text{X} = \text{Cl}, \text{Br}$). Their electrochemical and spectroscopic properties (Table VI) are very similar to those of their acetate analogues. The ^1H NMR spectra of both propionate derivatives (recorded in CD_2Cl_2) are essentially the same. In the case of $\text{X} = \text{Cl}$, a singlet at $\delta +2.42$ is due to the methyl groups of the mhp ligands, while a triplet at $\delta +1.17$ and quartet at $\delta +3.17$ arise from the propionate ligand. The pyridyl rings give resonances at $\delta +7.63$ (d, intensity 2) and $+7.01$ (t, intensity 1). The identity of this particular complex was confirmed by an X-ray structure analysis (vide infra).

On the basis of the foregoing observations concerning the propionate derivatives, it is clear that the carboxylate ligand arises

from the hydrolysis of the nitrile solvent. Hydrolysis of nitriles is known to proceed via both acid and base catalysis.¹⁵

The water for these hydrolysis reactions must come primarily from the coordinated water in the starting complexes $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{X}_4(\text{H}_2\text{O})_2$. Thus, in the reaction between the 4-methylpyridine adduct $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4(4\text{-Mepy})_2$ and Hmhp in dry acetonitrile, the product is $\text{Re}_2(\text{mhp})_2\text{Cl}_4\cdot\text{Hmhp}$ and not $\text{Re}_2(\text{O}_2\text{CCH}_3)(\text{mhp})_2\text{Cl}_3$. However, when the intermediate $\text{Re}_2(\text{mhp})_2\text{Cl}_4\cdot\text{Hmhp}$ is reacted with reagent grade acetonitrile, which had not been subject to any special drying, then the reaction proceeds slowly to give $\text{Re}_2(\text{O}_2\text{CCH}_3)(\text{mhp})_2\text{Cl}_3$. This latter product was also formed when $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4(4\text{-Mepy})_2$ was reacted with Hmhp in acetonitrile to which a small amount of aqueous HBF_4 had been added; the latter reagent is a source of water and serves to labilize the acetate ligands through protonation.

As mentioned above, with propionitrile as the solvent the propionate derivatives $\text{Re}_2(\text{O}_2\text{CC}_2\text{H}_5)(\text{mhp})_2\text{X}_3$ are formed. Likewise, the acetate complex $\text{Re}_2(\text{O}_2\text{CCH}_3)(\text{mhp})_2\text{Cl}_3$ is formed when $\text{Re}_2(\text{O}_2\text{CC}_2\text{H}_5)_2\text{Cl}_4(\text{H}_2\text{O})_2$ is reacted with Hmhp in acetonitrile, thereby showing that carboxylate exchange is a feature of these reactions, although the details of the mechanism remain to be determined.

(d) X-ray Crystal Structure of $\text{Re}_2(\text{O}_2\text{CC}_2\text{H}_5)(\text{mhp})_2\text{Cl}_3$ (2**).**

The most striking feature of the title complex is the presence of a propionate bridge (Figure 2), even though **2** is synthesized from a bis(μ -acetate) starting material, viz., $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4(\text{H}_2\text{O})_2$. **2** contains three monoanionic bridging ligands and has a Re–Re distance (2.204 (1) Å) that conforms, as expected, to that for a quadruple bond.¹ While **2** is structurally related to tris(carboxylato) complexes of dirhenium(III), e.g. $\text{Re}_2(\text{O}_2\text{CCMe}_3)_3\text{Cl}_3$,¹⁶ there are of course some differences because of the less symmetrical nature of **2**. Important structural parameters are listed in Table V. Complex **2**, like **1**, has a polar arrangement² of the two mhp ligands, and as a consequence, the Re–O and Re–Cl distances involving the chloride-deficient rhenium atom (Re(2)) are shorter than the comparable distances to Re(1). The unsymmetrical nature of the propionate bridge is further reflected by a corresponding disparity in the two C–O distances. The Re–Cl distance that is trans to, and essentially collinear with, the Re–Re bond is longer than the equatorial Re–Cl distances (by between 0.12 and 0.17 Å). Also, the Re(1)–Cl(12) distance is much shorter than the comparable distance in $\text{Re}_2(\text{O}_2\text{CCMe}_3)_3\text{Cl}_3$ ¹⁶ (by ca. 0.15 Å), signifying the disparity in charge distributions between these two molecules.

(e) Concluding Remarks. The reactions of the complexes $\text{Re}_2(\text{O}_2\text{CR})_2\text{X}_4(\text{H}_2\text{O})_2$ and similar adducts with Hhp and Hmhp provide important examples of the synthetic utility of these bis(carboxylate) complexes. Key aspects of the reaction chemistry we have explored in the present report, and certain reactions described previously,^{6,17} are summarized in Scheme I. The complexes $\text{Re}_2(\text{hp})_2\text{X}_4\cdot\text{Hhp}$ and $\text{Re}_2(\text{mhp})_2\text{X}_4\cdot\text{Hmhp}$ are intermediates on the way to $\text{Re}_2(\text{hp})_4\text{X}_2$ and $\text{Re}_2(\text{O}_2\text{CR})(\text{mhp})_2\text{X}_3$, respectively. The different reaction course in the case of the mhp-containing system is presumably a consequence of the instability of the sterically congested complex $\text{Re}_2(\text{mhp})_4\text{X}_2$.

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Supplementary Material Available: Thermal parameters (Tables S1 and S2), positional parameters for the hydrogen atoms (Tables S3 and S4), complete listings of bond distances (Tables S5 and S6) and bond angles (Tables S7 and S8), and torsional angles (Tables S9 and S10) (12 pages); tables of observed and calculated structure factors for **1** and **2** (22 pages). Ordering information is given on any current masthead page.

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