cordance with the earlier suggestions of an electrophilic species derived from peroxodicopper(II) in tyrosinase[13a] and the recently described Fe(III) mediated electrophilic activation of hydrogen peroxide toward oxygenation of organic substrates.[13b] No unique assignment of oxidation states is possible for the time between O-O bond rupture and oxygenation. No free oxygen atom is expected to form in view of the 100% selectivity of the reaction, and coordination of O to $2Cu^{2+}$ would be equivalent to O^{2-} coordinating to $2Cu^{3+}$ or even to one Cu^{4+} as CuO^{2+}. Whether splitting off OH^- and oxygenation of the aromatic ring are in fact two sequential steps or one synchronous reaction may remain experimentally ambiguous due to the high reactivity of all species involved.

Experiments presently in progress[26] will shed further light on the relation of the H_2O_2 induced reaction presented in this paper with the analogous reaction, **2** → **3**, starting from Cu(I) and O_2.

Acknowledgment. We thank the Swiss National Science Foundation (Grant no. 2.851-0.85) and the National Institutes of Health (Grant no. GM28962) for financial support of this research. We also thank Amjad Farooq and Brett Cohen for the preparation of L-H and L-D and their nitrate complexes.

Isomerization in Metal-Metal Bonded M_2L_{10} Systems Involving Cis and Trans Sets of Bis(diphenylphosphino)methane Ligands

Ann R. Cutler, Daniel R. Derringer, Phillip E. Fanwick, and Richard A. Walton*

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. *Received November 9, 1987*

Abstract: The reactions of the dirhenium(III) complexes $Re_2(O_2CR)_4X_2$ (R = CH_3, C_2H_5, C_6H_5; X = Cl, Br), $Re_2(O_2CR)_2X_4L_2$ (R = CH_3, C_2H_5; X = Cl, Br; L = H_2O, 4-methylpyridine, DMF, DMSO), and $(n\text{-}Bu_4N)_2Re_2X_8$ (X = Cl, Br) with $Ph_2PCH_2PPh_2$ (abbreviated dppm) or, in the case of $(n\text{-}Bu_4N)_2Re_2X_8$, $Ph_2CH_2PPh_2$/acetate mixtures affords the reduced complexes $Re_2(O_2CR)X_4(dppm)_2$ and *cis*- and *trans*-$Re_2(O_2CR)_2X_2(dppm)_2$ depending upon the choice of reaction conditions. The thermolysis of $Re_2(O_2CR)X_4(dppm)_2$ provides a high yield synthetic route to $Re_2X_4(dppm)_2$ (X = Cl, Br), a procedure that can be adapted to produce $Re_2I_4(dppm)_2$ directly from $Re_2(O_2CCH_3)_2I_4{\cdot}nH_2O$. The cis and trans isomers of the triply bonded dirhenium(II) compounds $Re_2(O_2CR)_2X_2(dppm)_2$ can be oxidized to paramagnetic *cis*-$[Re_2(O_2CR)_2X_2(dppm)_2]PF_6$ and *trans*-$[Re_2(O_2CR)_2X_2(dppm)_2]PF_6$ by $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ and $(C_7H_7)PF_6$, respectively. The structures of representative members of these groups of new complexes have been established by X-ray crystallography, viz., $Re_2(O_2CCH_3)Cl_4(dppm)_2{\cdot}2(CH_3)_2CO$ (**1**), *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$ (**2**), and *trans*-$[Re_2(O_2CCH_3)_2Cl_2(dppm)_2]PF_6{\cdot}CH_2Cl_2$ (**3**). Complex **1** crystallizes in the monoclinic space group $P2_1/c$ with the following unit cell dimensions: a = 12.720 (2) Å, b = 35.593 (5) Å, c = 9.405 (2) Å, β = 104.36 (1)°, V = 5610 (3) Å^3, and Z = 4. The structure was refined to R = 0.036 and R_w = 0.055 for 5822 data with $F^2 > 3.0\sigma(F^2)$. The structure contains symmetrically bridging acetate and dppm ligands and is based upon an eclipsed M_2L_{10} geometry, with two axial and two equatorial Re-Cl bonds. The Re-Re distance is 2.300 (1) Å, which is in accord with the presence of a Re-Re bond of order 3.5. The unit cell dimensions for complexes **2** and **3**, which crystallize in the monoclinic space groups $P2_1/c$ and $C2/c$, respectively, are as follows: for **2**, a = 14.634 (6) Å, b = 15.190 (5) Å, c = 24.281 (6) Å, β = 107.24 (3)°, V = 5155 (6) Å^3, and Z = 4; for **3**, a = 22.853 (5) Å, b = 18.712 (3) Å, c = 14.236 (4) Å, β = 107.48 (2)°, V = 5807 (4) Å^3, and Z = 4. The structure of **2** was refined to R = 0.045 and R_w = 0.061 for 4468 data with $F^2 > 3.0\sigma(F^2)$, whereas for **3** the refinement gave R = 0.034 and R_w = 0.049 for 2936 data with $F^2 > 3.0\sigma(F^2)$. Both complexes contain pairs of bridging acetate and dppm ligands and axial Re-Cl bonds. In **2** the pairs of acetate (and dppm) ligands are cis to one another, while they assume a trans disposition in **3**. The Re-Re distance is 2.315 (1) Å in **2** and 2.275 (1) Å in **3**.

Complexes that contain pairs of metal atoms spanned by two bridging bidentate phosphine ligands of the type $R_2PCH_2PR_2$ constitute an important and extensive class of molecules that range from those that contain no metal-metal interactions to those in which the metal-metal bond order may be 1, 2, 3, or 4.[1-3] From the extensive body of data that has accumulated we are not aware of any reports that describe the isolation and characterization of isomers in which the $R_2PCH_2PR_2$ ligands span a metal-metal bond and are in cis and trans arrangements to one another. Upon examining the reactions of the dirhenium(III) carboxylates $Re_2(O_2CR)_4X_2$ and $Re_2(O_2CR)_2X_4L_2$ (R = alkyl or aryl; X = Cl or Br; L = monodentate neutral donor)[4,5] toward the ligand $Ph_2PCH_2PPh_2$ (abbreviated dppm) we have discovered the existence of pairs of cis and trans isomers of stoichiometry $Re_2(O_2CR)_2X_2(dppm)_2$. We now report the synthesis, properties, and structural characterization of this novel class of triply bonded dirhenium(II) complexes.

Experimental Section

Starting Materials. The compounds $(n\text{-}Bu_4N)_2Re_2X_8$ (X = Cl, Br, or I) were synthesized as described in the literature.[6-9] In the case of X = Cl or Br, these salts were converted into the bis-carboxylate complexes $Re_2(O_2CR)_2X_4L_2$ (R = CH_3 or C_2H_5; L = H_2O, 4-Mepy, DMF, or DMSO) with use of the published procedures.[10] The iodide complex

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$Re_2(O_2CCH_3)_2I_4 \cdot nH_2O$ was prepared by the use of a related procedure. A sample of $(n\text{-}Bu_4N)_2Re_2I_8$ (1.38 g, 0.74 mmol) was added to 20 mL of acetic anhydride which contained 0.6 mL of 48% HBF_4(aq). The resulting dark green solution was stirred under an atmosphere of N_2(g) of 14 h and then evaporated to give a gummy green-black residue (ca. 1.6 g). Attempts to isolate a solid residue failed. Identification of this product as $Re_2(O_2CCH_3)_2I_4 \cdot nH_2O$ is based upon similarities between its reactivity and that of $Re_2(O_2CCH_3)_2X_4(H_2O)_2$ (X =Cl or Br). The tetrakis-carboxylato derivatives $Re_2(O_2CR)_4X_2$ (R = CH_3, C_2H_5, or C_6H_5; X = Cl or Br) were prepared by using the established literature procedures.[11] The phosphine ligands bis(diphenylphosphino)methane (abbreviated dppm) and 1,2-bis(diphenylphosphino)ethane (abbreviated dppe) were purchased from Strem Chemical Co. and used without further purification.

Reaction Procedures. Syntheses were performed in an atmosphere of dry nitrogen under the pressure provided by passing the outlet nitrogen through a column of mercury approximately 8 cm in depth or with the use of a mineral oil bubbler. All solvents were deoxygenated prior to use and reactions were usually carried out in the presence of a pine boiling stick.

A. Reactions of $Re_2(O_2CR)_4X_2$ (R = CH_3, C_2H_5, or C_6H_5; X = Cl or Br) with $Ph_2PCH_2PPh_2$. (a) Synthesis of *cis*-$Re_2(O_2CR)_2X_2(dppm)_2$, (i) *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$. A mixture of $Re_2(O_2CCH_3)_4Cl_2$ (0.100 g, 0.147 mmol) and dppm (0.339 g, 0.883 mmol) was refluxed in methanol (20 mL) for 2 days. The red-purple crystalline product was separated from the green mother liquor by filtration and washed with toluene, ethanol, and diethyl ether and dried under vacuum; yield 0.123 g (63%). Anal. Calcd for $C_{54}H_{50}Cl_2O_4P_4Re_2$: C, 48.76; H, 3.79. Found: C, 48.58; H, 4.26.

For the following four compounds a procedure similar to that described in A(a)(i) was used, with a $Re_2(O_2CR)_4X_2$:dppm stoichiometric ratio of ca. 1:6. The reaction solvent, reaction time, and product yield are given in parentheses.

(ii) ***cis*-$Re_2(O_2CC_2H_5)_2Cl_2(dppm)_2$** (ethanol, 2 days, 75%). Anal. Calcd for $C_{56}H_{54}Cl_2O_4P_4Re_2$: C, 49.52; H, 4.01. Found: C, 49.32; H, 4.08.

(iii) ***cis*-$Re_2(O_2CC_6H_5)_2Cl_2(dppm)_2$** (ethanol, 5.5 days, 66%). Anal. Calcd for $C_{64}H_{54}Cl_2O_4P_4Re_2$: C, 52.86; H, 3.74. Found: C, 51.86; H, 3.69.

(iv) ***cis*-$Re_2(O_2CCH_3)_2Br_2(dppm)_2$** (methanol, 5.5 days, 70%). Anal. Calcd for $C_{54}H_{50}Br_2O_4P_4Re_2$: C, 45.70; H, 3.55. Found: C, 46.09; H, 3.97.

(v) ***cis*-$Re_2(O_2CC_2H_5)_2Br_2(dppm)_2$** (ethanol, 20 h, 43%). Anal. Calcd for $C_{56}H_{54}Br_2O_4P_4Re_2$: C, 46.48; H, 3.76. Found: C, 46.81; H, 4.16.

(vi) ***cis*-$Re_2(O_2CC_6H_5)_2Br_2(dppm)_2$.** A suspension of $Re_2(O_2CC_6H_5)_4Br_2$ (0.100 g, 0.098 mmol) and dppm (0.227 g, 0.590 mmol) was refluxed in ethanol (20 mL) for 6 days. The product was isolated in a fashion analogous to the one described in A(a)(i); yield 0.113 g. However, characterization of the product revealed that it was a mixture of the cis and trans isomers. Our attempts to prepare the cis isomer exclusively have been unsuccessful. Other systems were found to give such cis/trans mixtures under the appropriate conditions (see A(b)).

(b) Attempted Synthesis of *trans*-$Re_2(O_2CR)_2X_2(dppm)_2$ That Led to Cis/Trans Mixtures. When the reactions described in A(a)(i)–A(a)(v) were carried out with the use of lower $Re_2(O_2CR)_4X_2$:dppm stoichiometric ratios (1:<4) and shorter reaction times it was found that mixtures of *cis*- and *trans*-$Re_2(O_2CR)_2X_2(dppm)_2$ were produced. Characterization of these products was based upon a study of their spectroscopic and electrochemical properties (see Results and Discussion). The most convenient means of separating these components is through their oxidation to the corresponding paramagnetic monocations $[Re_2(O_2CR)_2X_2(dppm)_2]^+$ (see D(a)). Representative reactions are as follows.

The reaction between $Re_2(O_2CCH_3)_4Cl_2$ (0.100 g, 0.147 mmol) and dppm (0.226 g, 0.589 mmol) in 5 mL of refluxing methanol for 2 days afforded 0.130 g of an insoluble product that was shown (by cyclic voltammetry) to be an approximately 30:70 mixture of *cis*- and *trans*-$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$. Workup of the product was similar to that described in A(a)(i).

A similar reaction between $Re_2(O_2CC_6H_5)_4Cl_2$ (0.100 g, 0.108 mmol) and dppm (0.104 g, 0.269 mmol) in ethanol (20 mL) for 16 h gave 0.070 g of a 40:60 mixture of *cis*- and *trans*-$Re_2(O_2CC_6H_5)_2Cl_2(dppm)_2$.

The reaction of $Re_2(O_2CCH_3)_4Br_2$ (0.100 g, 0.130 mmol) with dppm (0.200 g, 0.521 mmol) in 5 mL of methanol for 24 h gave 0.113 g of a 10:90 mixture of *cis*- and *trans*-$Re_2(O_2CCH_3)_2Br_2(dppm)_2$.

Many other reactions were tried, including those between dppm and $Re_2(O_2CC_2H_5)_4Cl_2$, $Re_2(O_2CC_2H_5)_4Br_2$, or $Re_2(O_2CC_6H_5)_4Br_2$, but in no instance were we able to isolate pure *trans*-$Re_2(O_2CR)_2X_2(dppm)_2$ by this procedure. A mixture of cis and trans isomers was always prepared under these conditions although the relative proportions of each were not usually very reproducible.

(c) The Synthesis of *trans*-$[Re_2(O_2CC_6H_5)_2Br_2(dppm)_2]Y$ (Y = Br or PF_6). A suspension of $Re_2(O_2CC_6H_5)_4Br_2$ (0.122 g, 0.120 mmol) and dppm (0.106 g, 0.276 mmol) was stirred in refluxing methanol (20 mL) for 1 h. The yellow powder that formed was filtered off and washed with toluene, methanol, and diethyl ether and then dried under vacuum. The compound was recrystallized from dichloromethane/diethyl ether; yield 0.090 g (47%). Anal. Calcd for $C_{64}H_{54}Br_3O_4P_4Re_2$: C, 47.36; H, 3.35. Found: C, 46.81; H, 3.89.

A mixture containing $Re_2(O_2CC_6H_5)_4Br_2$ (0.090 g, 0.089 mmol), dppm (0.100 g, 0.260 mmol), and KPF_6 (0.500 g, 2.72 mmol) in methanol (20 mL) was stirred at reflux for 1 h. The yellow precipitate of *trans*-$[Re_2(O_2CC_6H_5)_2Br_2(dppm)_2]PF_6$ that formed was filtered off and washed with toluene, methanol, and diethyl ether and then dried in vacuo; yield 0.065 g (43%). Anal. Calcd for $C_{64}H_{54}Br_2F_6O_4P_5Re_2$: C, 45.53; H, 3.22. Found: C, 45.81; H, 3.11.

B. Reactions of $Re_2(O_2CR)_2X_4L_2$ (R = CH_3 or C_2H_5; X = Cl, Br, or I; L = H_2O, 4-Mepy, DMF, or DMSO) with $Ph_2PCH_2PPh_2$. (a) Synthesis of $Re_2(O_2CCH_3)Cl_4(dppm)_2$. A mixture of $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ (0.61 g, 0.91 mmol) and dppm (0.71 g, 1.85 mmol) was refluxed in 35 mL of ethanol. At the onset of reflux, bright yellow crystals were observed in the solution. After a period of 2 h, the cooled reaction mixture was filtered, and the yellow solid was washed with fresh ethanol and dried in vacuo; yield 0.99 g (76%). Anal. Calcd for $C_{56}H_{59}Cl_4O_4P_4Re_2$ (i.e., $Re_2(O_2CCH_3)Cl_4(dppm)_2 \cdot 2C_2H_5OH$): C, 46.89; H, 4.15. Found: C, 46.22; H, 4.22. The presence of lattice ethanol was confirmed by ^1H NMR spectroscopy (δ +1.17 (triplet, CH_3) and δ +3.59 (quartet, CH_2)) and IR spectroscopy (ν(OH) at $\simeq$3500 m-w cm^{-1}).

Three other adducts, $Re_2(O_2CCH_3)_2Cl_4L_2$ (L = Mepy, DMF, or DMSO), reacted with dppm under similar conditions to form this same product in 48, 75, and 80% yield, respectively.

The corresponding acetone solvate $Re_2(O_2CCH_3)Cl_4(dppm)_2 \cdot 2(CH_3)_2CO$ was prepared in an analogous fashion. A sample of $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ (0.21 g, 0.31 mmol) was admixed with dppm (0.23 g, 0.60 mmol) and the mixture heated under reflux in 15 mL of acetone for 18 h. The cooled reaction mixture was filtered and the red crystals washed with fresh acetone and dried in vacuo; yield 0.13 g (30%). Anal. Calcd for $C_{58}H_{59}Cl_4O_4P_4Re_2$: C, 47.77; H, 4.08; Cl, 9.73. Found: C, 47.22; H, 3.98; Cl, 9.48. The presence of lattice acetone was confirmed by IR spectroscopy (ν(CO) at 1698 s cm^{-1}).

When this reaction was carried out for extended periods of time (3 days or more) no evidence was found for other products.

(b) Synthesis of $Re_2(O_2CCH_3)Br_4(dppm)_2$. A sample of $Re_2(O_2CCH_3)_2Br_4(H_2O)_2$ (0.36 g, 0.43 mmol) was refluxed with dppm (0.37 g, 0.96 mmol) in 30 mL of ethanol for 2 h. The cooled reaction mixture was filtered, and the orange solid was washed with fresh ethanol and dried in vacuo; yield 0.48 g (69%). Anal. Calcd for $C_{56}H_{59}Br_4O_4P_4Re_2$ (i.e., $Re_2(O_2CCH_3)Br_4(dppm)_2 \cdot 2C_2H_5OH$): C, 41.72; H, 3.69. Found: C, 41.40; H, 3.04. The presence of lattice ethanol was confirmed by IR spectroscopy (ν(OH) at $\simeq$3400 m-w cm^{-1}).

With the use of related procedures, the starting materials $Re_2(O_2CCH_3)_2Br_4L_2$ (L = 4-Mepy, DMF, or DMSO) were reacted with dppm in refluxing ethanol to form $Re_2(O_2CCH_3)Br_4(dppm)_2 \cdot 2C_2H_5OH$ in 48, 66, and 60% yield, respectively.

The bis-acetone solvate was formed as dark red crystals when $Re_2(O_2CCH_3)_2Br_4(H_2O)_2$ was reacted with dppm in refluxing acetone for 18 h; yield 86%. Anal. Calcd for $C_{55}H_{53}Br_4O_3P_4Re_2$: C, 41.87; H, 3.39. Found: C, 41.61; H, 3.96. An IR spectrum confirmed the presence of lattice acetone (ν(CO) at 1698 s cm^{-1}).

(c) Synthesis of $Re_2(O_2CC_2H_5)Cl_4(dppm)_2$. A mixture of $Re_2(O_2CC_2H_5)_2Cl_4(4\text{-}Mepy)_2$ (0.10 g, 0.11 mmol) and dppm (0.090 g, 0.23 mmol) was refluxed in 15 mL of ethanol for 30 min. The cooled solution was filtered and the yellow solid washed with fresh ethanol. The solid was pumped in vacuo but remained somewhat sticky. All spectroscopic and electrochemical evidence was in accord with the formulation of the solid as $Re_2(O_2CC_2H_5)Cl_4(dppm)_2 \cdot nC_2H_5OH$.

(d) Synthesis of $Re_2Cl_4(dppm)_2$. A mixture of $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ (0.25 g, 0.37 mmol) and dppm (0.36 g, 0.94 mmol) was refluxed in 25 mL of ethanol. The yellow solid $Re_2(O_2CCH_3)Cl_4(dppm)_2 \cdot 2C_2H_5OH$ formed initially, but after 15 h only a purple crystalline solid was present. This was filtered off, washed with fresh ethanol, and dried in vacuo; yield 0.36 g (76%). The identity of this material was confirmed by comparison of its spectroscopic and electrochemical properties with those of an authentic sample.[12,13]

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The other bis-acetate complexes, $Re_2(O_2CCH_3)_2Cl_4L_2$ (L = 4-Mepy, DMF, or DMSO), reacted under similar conditions with dppm to produce $Re_2Cl_4(dppm)_2$ in yields of 70, 70, and 41%, respectively.

When the complexes $Re_2(O_2CCH_3)Cl_4(dppm)_2\cdot 2S$, where S = C_2H_5OH or $(CH_3)_2CO$ (see B(a)), were heated in methanol for 24 h, the purple complex $Re_2Cl_4(dppm)_2$ was the dominant product (as monitored by cyclic voltammetry).

(e) **Synthesis of $Re_2Br_4(dppm)_2$.** A mixture of $Re_2(O_2CCH_3)_2Br_4(H_2O)_2$ (0.17 g, 0.20 mmol) and dppm (0.22 g, 0.57 mmol) was refluxed in 20 mL of ethanol for 18 h. (The orange complex $Re_2(O_2CCH_3)Br_4(dppm)_2$ was clearly present at the early stages of reaction.) The resulting purple crystals were filtered from the cooled reaction mixture, washed with fresh ethanol, and dried in vacuo; yield 0.20 g (78%). Anal. Calcd for $C_{50}H_{44}Br_4P_4Re_2$: C, 41.11; H, 3.04. Found: C, 41.35; H, 3.18.

The other adducts $Re_2(O_2CCH_3)_2Br_4L_2$ (L = 4-Mepy, DMF, or DMSO) afforded $Re_2Br_4(dppm)_2$ in yields of 60, 77, and 62%, respectively, when used in place of $Re_2(O_2CCH_3)_2Br_4(H_2O)_2$. Also, the complex which is formed during short periods of reflux, viz., $Re_2(O_2CCH_3)Br_4(dppm)_2\cdot 2C_2H_5OH$, when heated in refluxing ethanol for 12 h formed $Re_2Br_4(dppm)_2$ in 78% yield. A similar transformation occurred upon heating the acetone solvate $Re_2(O_2CCH_3)Br_4(dppm)_2\cdot 2(CH_3)_2CO$ (see B(b)) in methanol for 24 h (as monitored by cyclic voltammetry).

(f) **Synthesis of $Re_2I_4(dppm)_2$.** A batch of $Re_2(O_2CCH_3)_2I_4\cdot nH_2O$ (0.55 g, 0.26 mmol) was mixed with dppm (0.57 g, 1.5 mmol) and the mixture refluxed in ethanol for 50 h. The reaction mixture was cooled and then filtered. The resulting crop of small green crystals was washed with several portions of fresh ethanol and dried in vacuo; yield 0.35 g. Anal. Calcd for $C_{50}H_{44}I_4P_4Re_2$: C, 36.42; H, 2.69. Found: C, 35.53; H, 2.88.

(g) **Synthesis of *cis*-$Re_2(O_2CR)_2X_2(dppm)_2$.** (i) ***cis*-$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$.** The reaction of $Re_2(O_2CCH_3)_2Cl_4(4\text{-}Mepy)_2$ (0.13 g, 0.16 mmol) and dppm (0.31 g, 0.81 mmol) in 15 mL of refluxing methanol produced, after 3 days, a mixture of small yellow crystals and an orange powder. The mixture was filtered hot to reduce precipitation of unreacted ligand, and the solid was washed with fresh acetone. The acetone dissolved the small quantity of yellow crystals of $Re_2(O_2CCH_3)Cl_4(dppm)_2$ (identified by cyclic voltammetry). The remaining orange powder, $Re_2(O_2CCH_3)_2Cl_2(dppm)_2$, was dried in vacuo; yield 0.04 g (23%). The formulation of this product was based upon its spectroscopic and electrochemical properties as compared to those of a sample prepared by an alternate procedure (see A(a)(i)).

When the preceding reaction was carried out in the presence of a large excess of added ammonium acetate (lithium acetate can also be used), then the reaction proceeded more rapidly to give *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$ (~30% yield of red crystals after 7 h) without the initial precipitation of the yellow intermediate $Re_2(O_2CCH_3)Cl_4(dppm)_2$.

(ii) ***cis*-$Re_2(O_2CCH_3)_2Br_2(dppm)_2$.** A reaction similar to that described in B(g)(i) produced red crystalline *cis*-$Re_2(O_2CCH_3)_2Br_2(dppm)_2$, uncontaminated by $Re_2(O_2CCH_3)Br_4(dppm)_2$, when $Re_2(O_2CCH_3)_2Br_4(4\text{-}Mepy)_2$ was used as the starting material with a reaction time of 30 h; yield 35%. Anal. Calcd for $C_{54}H_{50}Br_2O_4P_4Re_2$: C, 45.70; H, 3.55. Found: C, 46.10; H, 3.89

The addition of an excess of ammonium acetate to the preceding reaction mixture increased the yield of *cis*-$Re_2(O_2CCH_3)_2Br_2(dppm)_2$ (53%) with a shorter reaction time. There was no evidence for the initial precipitation of $Re_2(O_2CCH_3)Br_4(dppm)_2$ under these reaction conditions.

The reactions of other adducts of the bis-acetate complexes, $Re_2(O_2CCH_3)_2X_4L_2$ (X = Cl or Br; L = H_2O, DMF, or DMSO), with dppm in refluxing methanol usually gave mixtures of products (viz., $Re_2(O_2CCH_3)X_4(dppm)_2$, $Re_2X_4(dppm)_2$, and/or *cis*-$Re_2(O_2CCH_3)_2X_2(dppm)_2$). Separation of the components was not attempted.

(iii) ***cis*-$Re_2(O_2CC_2H_5)_2Cl_2(dppm)_2$.** A sample of this orange complex was prepared from $Re_2(O_2CC_2H_5)_2Cl_4(4\text{-}Mepy)_2$ with the use of a procedure similar to B(g)(i) and a reaction time of 4 days; yield 44%. Its identity was based upon electrochemical and infrared spectral measurements.

(iv) ***cis*-$Re_2(O_2CC_2H_5)_2Br_2(dppm)_2$.** With $Re_2(O_2CC_2H_5)_2Br_4(4\text{-}Mepy)_2$ as the starting material and a reaction time of 2 days, the title complex was isolated as red crystals following procedure B(g)(i); yield 48%. The product was identified on the basis of its spectroscopic and electrochemical properties.

C. Reactions of $Re_2(O_2CCH_3)_2X_4(H_2O)_2$ (X = Cl, Br, or I) with $Ph_2PCH_2CH_2PPh_2$. (a) **Synthesis of β-$Re_2Cl_4(dppe)_2$.** A mixture of $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ (0.08 g, 0.12 mmol) and dppe (0.11 g, 0.28 mmol) was refluxed in 15 mL of ethanol for 12 h. The cooled reaction mixture was filtered and the green solid washed several times with fresh ethanol and then dried in vacuo; yield 0.07 g. Cyclic voltammetric measurements on a solution of the green powder dissolved in 0.1 M TBAH–CH_2Cl_2 indicated that the material was a sample of β-$Re_2Cl_4(dppe)_2$[14] contaminated with minor amounts of the monomeric cleavage product $[Re(dppe)_2Cl_2]Cl$. The latter complex is characterized by redox processes at $E_{1/2}(ox) = +1.53$ V, $E_{p,a} = +1.23$ V, $E_{1/2}(red) = -0.24$ V, and $E_{p,c} = -1.43$ V vs Ag/AgCl, with the process at $E_{p,a} = +1.23$ V being due to Cl^-. The electrochemical properties of the latter species resemble closely those reported previously for other mononuclear rhenium(III) complexes of this type.[15] Subsequent washing of the solid with a large volume of methanol afforded pure insoluble β-$Re_2Cl_4(dppe)_2$.

A similar reaction when carried out in refluxing acetone afforded a crop of green crystalline β-$Re_2Cl_4(dppe)_2\cdot(CH_3)_2CO$; yield 14%. Inclusion of acetone in the lattice was indicated by IR spectroscopy (ν(CO) at 1705 s cm^{-1}) and confirmed by ^{1}H NMR spectroscopy (singlet at δ +2.07) on a CD_2Cl_2 solution of this product. The identity of this material was further confirmed by comparison of its spectroscopic and electrochemical characteristics to those of an authentic sample.[12,14]

In an analogous fashion, the complex $Re_2(O_2CCH_3)_2Cl_4(4\text{-}Mepy)_2$ was reacted with dppe in refluxing acetone to form β-$Re_2Cl_4(dppe)_2\cdot(CH_3)_2CO$ in 48% yield.

(b) **Synthesis of β-$Re_2Br_4(dppe)_2$.** Procedures similar to those described in section C(a) produced β-$Re_2Br_4(dppe)_2$ and its acetone solvate in yields of 55% and 23%, respectively, when ethanol and acetone were used as the reaction solvents. The substitution of the 4-Mepy adduct for the aquo adduct, $Re_2(O_2CCH_3)_2Br_4(H_2O)_2$, with acetone as the reaction solvent, produced β-$Re_2Br_4(dppe)_2\cdot(CH_3)_2CO$ in a much higher yield (71%). The identity of these products was based upon their electrochemical and spectroscopic properties.[12,14]

(c) **Synthesis of β-$Re_2I_4(dppe)_2$.** A portion of the black gummy starting material $Re_2(O_2CCH_3)_2I_4\cdot nH_2O$ (0.64 g, 0.30 mmol; calculated on the assumption of a 100% conversion of $(n\text{-}Bu_4N)_2Re_2I_8$ to $Re_2(O_2CCH_3)_2I_4\cdot nH_2O$) was admixed with dppe (0.58 g, 1.5 mmol) and ethanol (20 mL) was added via a syringe. The solution was refluxed for 50 h and the reaction mixture was cooled to room temperature and then filtered. The insoluble red solid was washed several times with fresh ethanol and dried in vacuo; yield 0.49 g. A cyclic voltammogram of a solution of the product in 0.1 M TBAH–CH_2Cl_2 and an IR spectrum of a Nujol mull indicated that this material was a mixture of β-$Re_2I_4(dppe)_2$ and the cleavage product $[Re(dppe)_2I_2]I$. Identification of the latter material was made on the basis of the similarity of its electrochemistry to that of its chloro analogue with $E_{1/2}(ox) = +1.30$ V, $E_{p,a} = +0.58$ V, $E_{p,a} = +0.32$ V, $E_{1/2}(red) = -0.18$ V, and $E_{p,c} = -1.19$ vs Ag/AgCl. The processes at $E_{p,a} = +0.58$ and $+0.32$ V are due to I^-. The two components of this mixture were separated by column chromatography on silica with CH_2Cl_2 as eluent, and the identity of β-$Re_2I_4(dppe)_2$ was established through a comparison of its properties with those possessed by authentic samples.[12,16]

D. Reactions of *cis*- and *trans*-$Re_2(O_2CR)_2X_2(dppm)_2$. (a) **Synthesis of $[Re_2(O_2CR)_2Cl_2(dppm)_2]PF_6$.** (i) ***cis*-$[Re_2(O_2CCH_3)_2Cl_2(dppm)_2]PF_6$.** Batches of *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$ (0.100 g, 0.075 mmol) and $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ (0.032 g, 0.097 mmol) were combined with 10 mL of dichloromethane and the mixture was stirred at room temperature for 15 min. The resulting solution was filtered into ca. 50 mL of diethyl ether to precipitate the green title compound. Microcrystals of this product were obtained upon its recrystallization from acetone/diethyl ether; yield 0.060 g (54%). Anal. Calcd for $C_{54}H_{50}Cl_2F_6O_4P_5Re_2$: C, 43.97; H, 3.42. Found: C, 44.09; H, 3.62.

(ii) ***cis*-$[Re_2(O_2CC_2H_5)_2Cl_2(dppm)_2]PF_6$.** This complex was prepared with the use of a procedure similar to that described in D(a)(i); yield 72%. Anal. Calcd for $C_{56}H_{54}Cl_2F_6O_4P_5Re_2$: C, 44.74; H, 3.62. Found: C, 44.30; H, 4.02.

(iii) ***trans*-$[Re_2(O_2CCH_3)_2Cl_2(dppm)_2]PF_6$.** A mixture of the cis and trans isomers of $Re_2(O_2CCH_3)_2Cl_2(dppm)_2$ (0.164 g; see A(b)) was combined with $(C_7H_7)PF_6$ (0.040 g) in dichloromethane (10 mL) and the mixture was stirred at room temperature for 30 min. The resulting solution was filtered into ca. 75 mL of diethyl ether to precipitate the yellow product. The title compound was obtained in pure form by recrystallization from dichloromethane/diethyl ether followed by acetone/diethyl ether; yield 0.013 g. Anal. Calcd for $C_{54}H_{50}Cl_2F_6O_4P_5Re_2$: C, 43.97; H, 3.42. Found: C, 44.47; H, 3.83.

(iv) ***trans*-$[Re_2(O_2CCH_3)_2Br_2(dppm)_2]PF_6$.** A cis/trans mixture of $Re_2(O_2CCH_3)_2Br_2(dppm)_2$ (0.110 g) was converted into *trans*-$[Re_2$-

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$(O_2CCH_3)_2Br_2(dppm)_2]PF_6$ by a procedure similar to D(a)(iii); yield 0.086 g. Anal. Calcd for $C_{54}H_{50}Br_2F_6O_4P_5Re_2$: C, 41.47; H, 3.22. Found: C, 41.37; H, 3.46.

(v) *trans*-[$Re_2(O_2CC_2H_5)_2Br_2(dppm)_2$]$PF_6$. A cis/trans mixture of $Re_2(O_2CC_2H_5)_2Br_2(dppm)_2$ (0.047 g) was oxidized to give *trans*-[$Re_2(O_2CC_2H_5)_2Br_2(dppm)_2$]$PF_6$ with use of the procedure outlined in D-(a)(iii); yield 0.025 g. Anal. Calcd for $C_{56}H_{54}Br_2F_6O_4P_5Re_2$: C, 42.25; H, 3.42. Found: C, 41.98; H, 3.78.

(b) Thermolysis of *cis*- and *trans*-[$Re_2(O_2CR)_2X_2(dppm)_2$]$^{n+}$ (*n* = 1 or 0). Various reactions were carried out in which the neutral and cationic cis and trans isomers were heated in deoxygenated ethanol for periods ranging from several hours to several days. In all instances the neutral cis isomers were produced. These appear to be the thermodynamically more stable form. Representative examples are as follows.

(i) *cis*-$Re_2(O_2CC_2H_5)_2Cl_2(dppm)_2$ (0.100 g) was unchanged upon heating a suspension of it in ethanol (20 mL) for 1 week; yield 0.080 g (80%).

(ii) *trans*-[$Re_2(O_2CCH_3)_2Br_2(dppm)_2$]$PF_6$ (0.030 g) was heated in refluxing ethanol (5 mL) for 1 day to afford a quantity of insoluble *cis*-$Re_2(O_2CCH_3)_2Br_2(dppm)_2$; yield 0.010 g (37%).

(iii) *cis*-[$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$]$PF_6$ (0.040 g) was heated in ethanol (5 mL) for 20 h to afford a moderate yield of *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$; yield 0.017 g (47%).

The identity of the products was based upon their electrochemical and spectroscopic properties.

(c) Carboxylate Exchange Reactions with Trichloroacetic Acid. (i) ***cis*-$Re_2(O_2CCCl_3)_2Cl_2(dppm)_2$.** A mixture of *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$ (0.052 g, 0.039 mmol) and CCl_3CO_2H (0.015 g, 0.090 mmol) was heated in refluxing methanol (10 mL) for 18 h. The red-brown microcrystalline product was separated from the reaction mixture by filtration, washed with ethanol and diethyl ether, and then dried in vacuo; yield 0.030 g (50%). Anal. Calcd for $C_{54}H_{44}Cl_8O_4P_4Re_2$: C, 42.20; H, 2.89. Found: C, 42.92; H, 3.51.

This same complex was also prepared from *cis*-$Re_2(O_2CC_2H_5)_2Cl_2(dppm)_2$ by an analogous procedure; yield 34%.

(ii) ***cis*-$Re_2(O_2CCCl_3)_2Br_2(dppm)_2$.** This orange product was prepared from *cis*-$Re_2(O_2CCH_3)_2Br_2(dppm)_2$ by the use of a procedure analogous to that in D(c)(i); yield 58%. Anal. Calcd for $C_{54}H_{44}Br_2Cl_6O_4P_4Re_2$: C, 39.89; H, 2.73. Found: C, 40.11; H, 2.80.

(d) Synthesis of $Re_2Cl_4(dppm)_2$ from *cis*-$Re_2(O_2CC_2H_5)_2Cl_2(dppm)_2$. A small volume of Me_3SiCl (2 mL) was added to a suspension of *cis*-$Re_2(O_2CC_2H_5)_2Cl_2(dppm)_2$ (0.050 g, 0.036 mmol) in tetrahydrofuran (10 mL). The reaction mixture was warmed and stirred for 8 h and then cooled to room temperature, and the solution was reduced in volume and treated with an excess of diethyl ether. This caused precipitation of the purple title compound. The product was filtered off, washed with ethanol and diethyl ether, and then dried in vacuo; yield 0.035 g (74%).

E. Reactions of $Re_2(O_2CCH_3)X_4(dppm)_2$ with Lithium Acetate. (i) **Synthesis of *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$.** A sample of $Re_2(O_2CCH_3)Cl_4(dppm)_2{\cdot}2(CH_3)_2CO$ (0.13 g, 0.09 mmol) was heated with lithium acetate (0.87 g, 13.2 mmol) in 15 mL of MeOH for 18 h. The cooled reaction mixture was filtered and the bright red cuboidal crystals washed with fresh methanol and dried in vacuo; yield 0.06 g (50%). The cyclic voltammogram and IR spectrum of this product confirmed its identity.

(ii) **Synthesis of *cis*-$Re_2(O_2CCH_3)_2Br_2(dppm)_2$.** This bromo analogue was prepared from the reaction between lithium acetate and $Re_2(O_2CCH_3)Br_4(dppm)_2{\cdot}2(CH_3)_2CO$ by a procedure analogous to that in E(i); yield 44%.

F. Reactions of (n-$Bu_4N)_2Re_2X_8$ (X = Cl or Br). (i) Synthesis of $Re_2(O_2CCH_3)Cl_4(dppm)_2$. A quantity of ($n$-$Bu_4N)_2Re_2Cl_8$ (0.100 g, 0.088 mmol) was combined with an excess of dppm (0.150 g, 0.390 mmol) and 3 mL of an acetic acid/acetic anhydride mixture (5:3) in ethanol (20 mL) and the mixture heated to reflux. The reaction was stopped after 1 h, the reaction mixture cooled to room temperature, and the yellow insoluble product filtered off, washed with ethanol and diethyl ether, and then dried in vacuo; yield 0.100 g (85%).

(ii) **Synthesis of $Re_2(O_2CCH_3)Br_4(dppm)_2$.** A reaction similar to that in F(i) was used to prepare the yellow title complex from (n-$Bu_4N)_2Re_2Br_8$; yield 79%.

(iii) **Synthesis of $Re_2(O_2CC_2H_5)Cl_4(dppm)_2$.** A procedure similar to that in F(i) was used; yield 59%.

(iv) **Synthesis of $Re_2(O_2CC_2H_5)Br_4(dppm)_2$.** A procedure similar to that in F(i) was used; yield 64%.

(v) **Synthesis of *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$.** A suspension of ($n$-$Bu_4N)_2Re_2Cl_8$ (0.100 g, 0.088 mmol), dppm (0.150 g, 0.390 mmol), and lithium acetate (0.870 g, 13.2 mmol) in methanol (15 mL) was refluxed for 18 h. The resulting mixture was then cooled to room temperature and the insoluble title complex filtered off and washed with toluene, methanol, and diethyl ether and then dried in vacuo; yield 0.030 g (26%).

(vi) **Synthesis of $Re_2Cl_4(dppm)_2$.** A mixture of reagents, (n-$Bu_4N)_2Re_2Cl_8$ (0.400 g, 0.351 mmol), sodium acetate (0.0647 g, 0.789 mmol), and dppm (0.303 g, 0.789 mmol) was refluxed in ethanol (20 mL) for 48 h. A yellow-green precipitate of $Re_2(O_2CCH_3)Cl_4(dppm)_2$ forms initially but then reacts further to give the title complex. This compound was filtered off, washed with ethanol and diethyl ether, and dried in vacuo; yield 0.38 g (85%).

G. Reactions of $Re_2X_4(dppm)_2$ with Lithium Acetate. (i) Synthesis of *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$. A sample of $Re_2Cl_4(dppm)_2$ (0.10 g, 0.08 mmol) was reacted with lithium acetate (0.70 g, 10.6 mmol) in 10 mL of refluxing methanol. Within the first few hours the solution turned red in color and red crystals were seen to be depositing. After 12 h, the cooled reaction mixture was filtered, and the solid was washed with fresh methanol and dried in vacuo; yield 0.07 g (66%). The material was identified as *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$ on the basis of its IR spectrum and electrochemical properties.

(ii) *cis*-$Re_2(O_2CCH_3)_2Br_2(dppm)_2$. This complex was prepared from $Re_2Br_4(dppm)_2$ by the use of a procedure similar to that in G(i); yield 56%.

X-ray Crystal Structure Analyses. Suitable single crystals of $Re_2(O_2CCH_3)Cl_4(dppm)_2{\cdot}2(CH_3)_2CO$ (**1**) and *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$ (**2**) were harvested directly from the appropriate reaction mixtures (B(a) and A(a), respectively). Good quality crystals of *trans*-[$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$]$PF_6$ (**3**) were grown by slow diffusion of deoxygenated diethyl ether into a dilute solution of this compound in deoxygenated dichloromethane. In the subsequent structural analysis of **3**, the crystals were found to be those of the dichloromethane solvate *trans*-[$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$]$PF_6{\cdot}CH_2Cl_2$.

The structures of complexes **1**, **2**, and **3** were determined by application of general procedures which are described more fully elsewhere.[17] 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 $17.9 < \theta < 22.1°$ for **1**, $11.3 < \theta < 12.6°$ for **2**, and $11.7 < \theta < 14.2°$ for **3**. Three standard reflections were measured every 5000 s of beam exposure during data collection and displayed no systematic variations in intensity for any of the crystals.

Calculations were performed on a PDP11/34 computer with the Enraf-Nonius structure determination package. For **1**, **2**, and **3**, the atoms were located and refined from initial Patterson maps. In all instances an empirical absorption correction was applied,[18,19] the linear absorption coefficients being 46.95 cm^{-1} (for **1**), 50.27 cm^{-1} (for **2**), and 46.06 cm^{-1} (for **3**). 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 $w = 1/\sigma^2(F_o)$. Hydrogens were not included in the least-squares refinement. For complex **1** the Re and Cl atoms, C and O atoms of acetate, and P and methylene C atoms of dppm were refined anisotropically; all other C and O atoms were refined isotropically. All atoms were refined anisotropically for **2** and **3**. Corrections for anomalous scattering were applied in all instances.[20]

For the structure determination of **1** the presence of lattice acetone, which had been inferred from IR spectroscopy on the crystals, was confirmed by the crystal structure analysis. Two crystallographically independent molecules of acetone per formula unit were present at general positions. These refined satisfactorily. While no lattice solvent was present in the crystals of **2**, we found evidence for dichloromethane of crystalline in the case of **3**. This solvent molecule was present on a special position which exhibited 2-fold symmetry. Refinement based on the assumption of one molecule of CH_2Cl_2 per formula unit gave large thermal parameters for the C and Cl atoms, doubtless reflecting a less than full occupancy of these lattice sites. Since this had no adverse affect on the remainder of the structure, we chose not to pursue refinement of this solvent molecule using partial occupancy. In **3** the dirhenium unit has crystallographically imposed $\bar{1}$ symmetry.

Further details concerning the data set, the structure solution, and the structure refinement may be obtained from Dr. P. E. Fanwick. Table II lists the positional parameters and their errors for non-phenyl group and non-solvent molecule atoms, for **1**, **2**, and **3**, while Tables III and IV list important intramolecular bond distances and angles. Tables that contain listings of positional parameters and their errors for the phenyl carbon atoms of **1**, **2**, and **3**, the lattice solvent molecule atoms of **1** and

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[17] Fanwick, P. E.; Harwood, W. S.; Walton, R. A. *Inorg. Chim. Acta* **1986**, *122*, 7.

[18] Flack, H. D. *Acta Crystalogr., Sect. A: Found Crystallogr.* **1977**, *A33*, 890.

[19] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found Crystallogr.* **1986**, *A39*, 158.

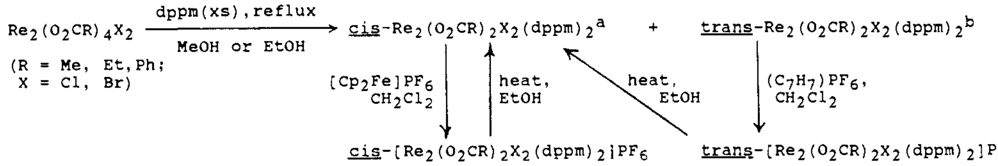
[20] (a) Cromer, D. T. *International Tables for X-ray Crystallography*; Knoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1. (b) For the scattering factors used in the structure solution see: Cromer, D. T.; Waber, J. T. *Ibid.*, Table 2.2B.

Table I. Crystallographic Data and Data Collection for $Re_2(O_2CCH_3)Cl_4(dppm)_2 \cdot 2(CH_3)_2CO$ (**1**), *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$ (**2**), and *trans*-$[Re_2(O_2CCH_3)_2Cl_2(dppm)_2]PF_6 \cdot CH_2Cl_2$ (**3**)[a]

	1	**2**	**3**
formula	$Re_2Cl_4P_4O_4C_{58}H_{59}$	$Re_2Cl_2P_4O_4C_{54}H_{50}$	$Re_2Cl_4P_5F_6O_4C_{55}H_{52}$
fw	1458.22	1330.20	1560.10
space gp	$P2_1/c$	$P2_1/c$	$C2/c$
a, Å	12.720 (2)	14.634 (6)	22.853 (5)
b, Å	35.593 (5)	15.190 (5)	18.712 (3)
c, Å	12.858 (3)	24.281 (6)	14.236 (4)
β, deg	104.36 (1)	107.24 (3)	107.48 (2)
V, Å^3	5610 (3)	5155 (6)	5807 (4)
Z	4	4	4
d_{calcd}, g cm^{-3}	1.717	1.714	1.784
crystal dimens, mm	0.19 × 0.39 × 0.35	0.29 × 0.22 × 0.11	0.35 × 0.19 × 0.12
temp, °C	22.0	22.0	22.0
radiation (wavelength, Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
monochromater	graphite	graphite	graphite
linear abs coeff, cm^{-1}	46.95	50.27	46.06
abs corr applied	empirical[b]	empirical[b]	empirical[c]
crystal radius, cm	0.041	0.020	
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4
scan method	θ–2θ	θ–2θ	θ–2θ
h, *k*, *l* limits	−13 to 13, 0 to 38, 0 to 13	−15 to 15, 0 to 21, 0 to 26	0 to 24, 0 to 20, −15 to 14
2θ range, deg	4.00–45.00	4.00–45.00	4.00–45.00
scan width, deg	0.72 + 0.35 tan (θ)	0.90 + 0.35 tan (θ)	0.80 + 0.35 tan (θ)
takeoff angle, deg	4.80	4.90	4.90
programs used	Enraf-Nonius SDP	Enraf-Nonius SDP	Enraf-Nonius SDP
F_{000}	2868.0	2600.0	3044.0
p factor used in weighting	0.070	0.070	0.070
no. of data collcd	7507	7029	3931
data with $I > 3.0\sigma(I)$	5822	4468	2936
no. of variables	369	595	344
largest shift/esd in final cycle	0.06	0.08	0.43
R^d	0.036	0.045	0.034
$R_w{}^e$	0.055	0.061	0.049
goodness of fit[f]	1.321	1.004	1.058

[a] Number in parentheses following certain data are estimated standard deviations occurring in the least significant digit. [b] Flack, H. D. *Acta Crystallogr., Sect., A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1977**, *A33*, 890. [c] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found Crystallogr.* **1983**, *A39*, 158. [d] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [e] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F_o)$. [f] Goodness of fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

Scheme I



[a] The formation of the cis isomer is favored by long reaction times (several days) and $Re_2(O_2CR)_4X_2$:dppm stoichiometric ratios of ~1:6. [b] The formation of the trans isomer is favored by shorter reaction times (1 day or less) and stoichiometric ratios of 1:≲4.

3, and the PF_6^- atoms of **3** (Tables S1, S2, and S3), thermal parameters (Tables S4, S5, and S6), and complete listings of bond distances (Tables S7, S8, and S9) and bond angles (Tables S10, S11, and S12) are available as supplementary material, as well as figures (Figure S1 and S2) which show the full atomic numbering schemes for **2** and **3**.

Physical Measurements. Infrared spectra were recorded as Nujol or fluorocarbon mulls with IBM Instruments IR/32 and 9198 FTIR spectrometers in the regions 4800–400 and 400–200 cm^{-1}, respectively. Electronic absorption spectra were recorded on IBM Instruments 9420 *UV*-visible, Hewlett Packard HP8451A, Cary 17D, or Perkin-Elmer 330 UV/VIS/NIR spectrophotometers. Electrochemical measurements were carried out by the use of a Bioanalytical Systems Inc. Model CV-1A instrument on dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, 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 at $E_{1/2}$ = +0.47 V vs Ag/AgCl. ^1H NMR spectra were recorded on Varian XL-200 and Nicolet 470 spectrometers. Resonances were referenced internally to the residual protons in the incompletely deuteriated solvent. $^{31}P\{^1H\}$ NMR spectra were obtained on a Varian XL-200 spectrometer. An internal deuterium lock and an external reference, 85% H_3PO_4, were used. Conductivity measurements were performed on acetone solutions of the samples at a concentration of ca. 1.0×10^{-3} M. Measurements were made with an Industrial Instruments Inc. Model RC-16B2 conductivity bridge. A magnetic moment was recorded on a CH_2Cl_2 solution of the complex $Re_2(O_2CCH_3)Br_4(dppm)_2$ by using the Evans method. X-band ESR spectra of dichloromethane solutions were recorded at ca. −160 °C with the use of a Varian E-109 spectrometer.

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

Results and Discussion

(a) Synthetic Details. (i) Reactions of $Re_2(O_2CR)_4X_2$. The reactions between dirhenium(III) caboxylates of type $Re_2(O_2CR)_4X_2$ and an excess of the bidentate phosphine ligand bis(diphenylphosphino)methane (abbreviated dppm) in refluxing methanol or, more usually, in ethanol lead to pure *cis*-$Re_2(O_2CR)_2X_2(dppm)_2$ or mixtures of the cis and trans isomers. The key details are summarized in Scheme I. The formation of the cis isomer is favored by long reaction times (several days) and $Re_2(O_2CR)_4X_2$:dppm stoichiometric ratios of ca. 1:6. Shorter reaction times (1 day or less) and stoichiometric ratios of ca. 1:4 afford a mixture of isomers, but in no instance were we able to control these reactions so as to give exclusively the pure *trans*-$Re_2(O_2CR)_2X_2(dppm)_2$. A strategy for separating the isomers was developed which was based upon their differing electrochemical redox properties (vide infra). Each show two reversible one-electron oxidations, the first process being accessed chemically

Table II. Positional Parameters and Equivalent Isotropic Displacement Parameters ($Å^2$) for Essential Atoms of **1**, **2**, and **3** and Their Estimated Standard Deviations

atom	*x*	*y*	*z*	*B*, $Å^2$
(i) $Re_2(O_2CCH_3)Cl_4(dppm)_2 \cdot 2(CH_3CO)$ (**1**)				
Re(1)	0.31727 (3)	0.08932 (1)	0.26523 (3)	2.473 (7)
Re(2)	0.21437 (3)	0.13750 (1)	0.17307 (3)	2.441 (7)
Cl(11)	0.2980 (2)	0.04222 (6)	0.1331 (2)	3.54 (5)
Cl(12)	0.4477 (2)	0.04783 (6)	0.4068 (2)	3.47 (5)
Cl(21)	0.1360(2)	0.10878 (6)	0.0068 (2)	3.56 (5)
Cl(22)	0.1158 (2)	0.20248 (6)	0.1092 (2)	3.21 (5)
P(11)	0.4856 (2)	0.10404 (6)	0.2108 (2)	2.70 (5)
P(12)	0.1739 (2)	0.05463 (6)	0.3231 (2)	2.95 (5)
P(21)	0.3487 (2)	0.16370 (6)	0.0833 (2)	2.62 (5)
P(22)	0.0419 (2)	0.11997 (7)	0.2165 (2)	2.99 (5)
O(11)	0.3511 (4)	0.1240 (1)	0.4009 (4)	2.7 (1)
O(21)	0.2631 (5)	0.1713 (2)	0.3080 (4)	3.0 (1)
C(1)	0.4437 (7)	0.1260 (2)	0.0776 (7)	3.1 (2)
C(2)	0.0450 (7)	0.0683 (2)	0.2325 (7)	3.2 (2)
C(3)	0.3207 (7)	0.1568 (2)	0.3951 (6)	2.9 (2)
C(4)	0.3506 (9)	0.1822 (3)	0.4940 (7)	4.5 (2)
(ii) *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$ (**2**)				
Re(1)	0.30197 (3)	0.28920 (3)	0.20411 (2)	2.22 (1)
Re(2)	0.19200 (3)	0.21281 (3)	0.23738 (2)	2.21 (1)
Cl(1)	0.4061 (2)	0.4034 (2)	0.1737 (2)	3.90 (8)
Cl(2)	0.0675 (2)	0.1614 (2)	0.2838 (1)	3.27 (7)
P(1)	0.4338 (2)	0.1898 (2)	0.2429 (1)	2.43 (7)
P(2)	0.2769 (2)	0.0765 (2)	0.2632 (1)	2.35 (7)
P(3)	0.2603 (2)	0.2328 (2)	0.1082 (1)	2.41 (7)
P(4)	0.0972 (2)	0.1608 (2)	0.1452 (1)	2.54 (7)
O(1)	0.2042 (6)	0.3958 (5)	0.1827 (4)	2.8 (2)
O(2)	0.1114 (6)	0.3317 (6)	0.2281 (4)	3.0 (2)
O(3)	0.3412 (6)	0.3592 (5)	0.2834 (4)	2.6 (2)
O(4)	0.2555 (6)	0.2680 (6)	0.3206 (3)	2.9 (2)
C(1)	0.3864 (8)	0.0771 (8)	0.2417 (6)	2.6 (3)
C(2)	0.1762 (8)	0.1425 (9)	0.1005 (5)	2.8 (3)
C(3)	0.1313 (9)	0.3971 (8)	0.2011 (6)	2.8 (3)
C(4)	0.067 (1)	0.477 (1)	0.1888 (8)	4.7 (4)
C(5)	0.3142 (9)	0.3344 (8)	0.3259 (6)	2.9 (3)
C(6)	0.349 (1)	0.379 (1)	0.3822 (7)	4.5 (4)
(iii) *trans*-$[Re_2(O_2CCH_3)_2Cl_2(dppm)_2]PF_6 \cdot CH_2Cl_2$ (**3**)				
Re	0.22626 (1)	0.28194 (2)	0.04600 (2)	2.516 (7)
Cl	0.1790 (1)	0.3476 (1)	0.1608 (1)	3.74 (5)
P(1)	0.2904 (1)	0.2305 (1)	0.2036 (2)	3.00 (5)
P(2)	0.1405 (1)	0.3409 (1)	−0.0794 (2)	2.99 (5)
O(10)	0.2877 (2)	0.3648 (3)	0.0528 (4)	3.0 (1)
O(11)	0.1657 (2)	0.1993 (3)	0.0348 (4)	3.0 (1)
C(1)	0.3663 (4)	0.2041 (5)	0.1967 (7)	4.0 (2)
C(12)	0.3273 (4)	0.3584 (5)	0.0059 (6)	3.1 (2)
C(13)	0.3633 (5)	0.4233 (5)	−0.0038 (7)	4.4 (2)

[a] Data for phenyl carbon atoms of **1**, **2**, and **3**, the lattice solvent molecule atoms of **1** and **3**, and the PF_6^- atoms of **3** are available as supplementary material. Anisotropically refined atoms are given in the form of 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. Some Important Bond Distances (Å) for **1**, **2**, and **3**[a]

atom 1	atom 2	distance	atom 1	atom 2	distance
(i) $Re_2(O_2CCH_3)Cl_4(dppm)_2 \cdot 2(CH_3)_2CO$ (**1**)					
Re(1)	Re(2)	2.2998 (4)	Re(2)	P(22)	2.475 (2)
Re(1)	Cl(11)	2.356 (2)	Re(2)	O(21)	2.075 (5)
Re(1)	Cl(12)	2.598 (2)	P(11)	C(1)	1.837 (7)
Re(1)	P(11)	2.469 (2)	P(21)	C(1)	1.820 (8)
Re(1)	P(12)	2.465 (2)	P(12)	C(2)	1.827 (8)
Re(1)	O(11)	2.093 (5)	P(22)	C(2)	1.851 (8)
Re(2)	Cl(21)	2.356 (2)	O(11)	C(3)	1.227 (9)
Re(2)	Cl(22)	2.662 (2)	O(21)	C(3)	1.284 (9)
Re(2)	P(21)	2.469 (2)	C(3)	C(4)	1.53 (1)
(ii) *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$ (**2**)					
Re(1)	Re(2)	2.3151 (7)	P(1)	C(1)	1.84 (1)
Re(1)	Cl(1)	2.558 (4)	P(2)	C(1)	1.83 (1)
Re(1)	P(1)	2.410 (3)	P(3)	C(2)	1.81 (1)
Re(1)	P(3)	2.384 (3)	P(4)	C(2)	1.83 (1)
Re(1)	O(1)	2.121 (8)	O(1)	C(3)	1.27 (2)
Re(1)	O(3)	2.125 (8)	O(2)	C(3)	1.27 (2)
Re(2)	Cl(2)	2.534 (4)	O(3)	C(5)	1.27 (2)
Re(2)	P(2)	2.400 (3)	O(4)	C(5)	1.31 (2)
Re(2)	P(4)	2.392 (3)	C(3)	C(4)	1.51 (2)
Re(2)	O(2)	2.133 (9)	C(5)	C(6)	1.47 (2)
Re(2)	O(4)	2.130 (8)			
(iii) *trans*-$[Re_2(O_2CCH_3)_2Cl_2(dppm)_2]PF_6 \cdot CH_2Cl_2$ (**3**)					
Re	Re	2.2748 (6)	P(2)	C(1)	1.83 (1)
Re	Cl	2.532 (2)	P(2)	C(211)	1.838 (9)
Re	P(1)	2.477 (2)	P(2)	C(221)	1.817 (9)
Re	P(2)	2.478 (2)	O(10)	C(12)	1.28 (1)
Re	O(10)	2.075 (6)	O(11)	C(12)	1.26 (1)
Re	O(11)	2.050 (6)	C(12)	C(13)	1.50 (1)
P(1)	C(1)	1.83 (1)			

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

by different oxidants, viz., $(C_7H_7)PF_6$ in the case of the trans isomers and $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ in the case of the cis. Subsequent studies, involving the heating of cis/trans mixtures of $Re_2(O_2CR)_2X_2(dppm)_2$, *trans*-$[Re_2(O_2CR)_2X_2(dppm)_2]PF_6$, and *cis*-$[Re_2(O_2CR)_2X_2(dppm)_2]PF_6$ in ethanol, indicated that *cis*-$Re_2(O_2CR)_2X_2(dppm)_2$ is the most thermodynamically stable member of the four *cis*- and *trans*-$[Re_2(O_2CR)_2X_2(dppm)_2]^{0,+}$ species.

In the case of the bis-benzoate complexes, we found large relative proportions of the trans isomers to be present in the mixtures (generally >50%), signifying that the trans isomers were, in these instances, quite stable. In accord with this observation we were able, in the case of the reaction between $Re_2(O_2CC_6H_5)_4Br_2$ and dppm in methanol, to isolate paramagnetic *trans*-$[Re_2(O_2CC_6H_5)_2Br_2(dppm)_2]Br$ (47% yield) when short reaction times (ca. 1 h) were used. If KPF_6 was present in this reaction the salt *trans*-$[Re_2(O_2CC_6H_5)_2Br_2(dppm)_2]PF_6$ was isolated. This result suggests that the mixed-valent Re_2^{5+} species *trans*-$[Re_2(O_2CR)_2X_2(dppm)_2]X$ may be intermediates in the course of all these reactions. The thermolysis of *trans*-$[Re_2(O_2CC_6H_5)_2Br_2(dppm)_2]X$ (X = Br or PF_6), as a suspension in ethanol, showed that *cis*-$Re_2(O_2CC_6H_5)_2Br_2(dppm)_2$ was formed, as monitored by cyclic voltammetry, but that this isomerization to the thermodynamically stable cis form was not complete even after 4 days.

(ii) Reactions of *cis*-$Re_2(O_2CR)_2X_4L_2$. As an alternative route to complexes of the type $Re_2(O_2CR)_2X_2(dppm)_2$ we have examined the reactions of dppm with the title complexes. These species possess a cis disposition of carboxylate groups and axially bound ligands L (H_2O, 4-Mepy, DMSO, or DMSO).[4,5,10] When ethanol solutions of $Re_2(O_2CR)_2X_4L_2$ (R = CH_3 or C_2H_5; X = Cl or Br; L = H_2O, 4-Mepy, DMF, or DMSO) and dppm (1:2 stoichiometry) are heated for ca. 2 h the paramagnetic, yellow-orange, crystalline ethanol solvates $Re_2(O_2CR)X_4(dppm)_2 \cdot 2C_2H_5OH$ are formed in yields that generally exceed 50%. When acetone is used as the reaction solvent, the corresponding bis-acetone solvates can be isolated. These complexes serve as intermediates on the way to $Re_2X_4(dppm)_2$ (X = Cl or Br) as shown by the formation of the latter complexes (i) by the thermolysis of $Re_2(O_2CR)X_4(dppm)_2 \cdot 2S$ (S = C_2H_5OH or $(CH_3)_2CO$) in methanol or ethanol and (ii) by the reaction of $Re_2(O_2CR)_2X_4L_2$ with dppm (1:3 stoichiometric proportions) in refluxing ethanol for the prolonged periods (5 h or more). When $Re_2(O_2CCH_3)_2I_4 \cdot nH_2O$ was reacted with dppm in ethanol the only product we identified was $Re_2I_4(dppm)_2$. We did not isolate $Re_2(O_2CCH_3)I_4(dppm)_2$. This chemistry is summarized in Scheme II.

Although the preparative yield of $Re_2Cl_4(dppm)_2$ is quite high (ca. 80%), an excellent alternative procedure already exists for the synthesis of this compound.[13] On the other hand, this synthetic procedure is the best yet available for $Re_2Br_4(dppm)_2$[12] and provides for the first time a route to the previously unreported iodide analogue $Re_2I_4(dppm)_2$. The chemistry of the latter complex will be the subject of a future report.

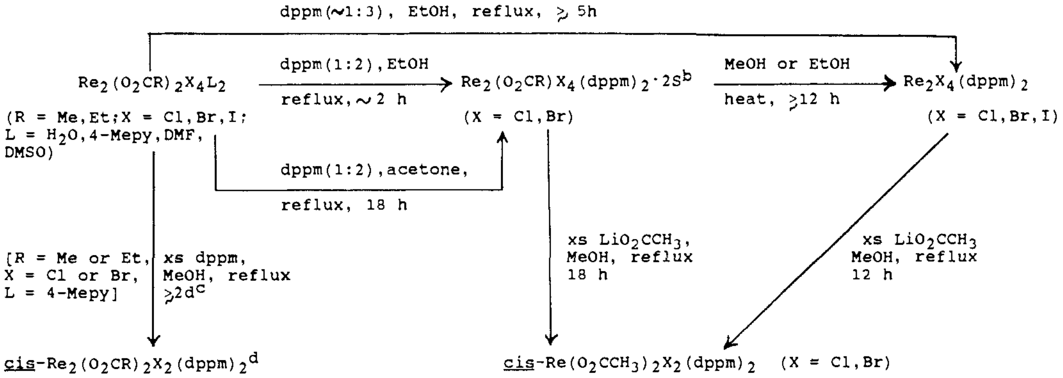
As we show in Scheme II, the complexes $Re_2(O_2CR)X_4(dppm)_2$ and $Re_2X_4(dppm)_2$ (X = Cl or Br) react with an excess of lithium acetate to afford *cis*-$Re_2(O_2CCH_3)_2X_2(dppm)_2$; the former reaction involves the net reduction of a Re_2^{5+} core to Re_2^{4+}. The

Table IV. Some Important Bond Angles (deg) for **1**, **2**, and **3**[a]

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
			(i) $Re_2(O_2CCH_3)Cl_4(dppm)_2\cdot 2(CH_3)_2CO$ (**1**)				
Re(2)	Re(1)	Cl(11)	102.40 (5)	Re(1)	Re(2)	Cl(21)	101.70 (5)
Re(2)	Re(1)	Cl(12)	165.43 (5)	Re(1)	Re(2)	Cl(22)	166.23 (4)
Re(2)	Re(1)	P(11)	96.81 (5)	Re(1)	Re(2)	P(21)	98.69 (5)
Re(2)	Re(1)	P(12)	99.20 (5)	Re(1)	Re(2)	P(22)	96.82 (5)
Re(2)	Re(1)	O(11)	87.8 (1)	Re(1)	Re(2)	O(21)	89.3 (1)
Cl(11)	Re(1)	Cl(12)	92.02 (7)	Cl(21)	Re(2)	Cl(22)	92.06 (7)
Cl(11)	Re(1)	P(11)	83.62 (7)	Cl(21)	Re(2)	P(21)	85.74 (7)
Cl(11)	Re(1)	P(12)	84.79 (7)	Cl(21)	Re(2)	P(22)	84.06 (7)
Cl(11)	Re(1)	O(11)	169.7 (1)	Cl(21)	Re(2)	O(21)	168.9 (1)
Cl(12)	Re(1)	P(11)	82.60 (7)	Cl(22)	Re(2)	P(21)	81.66 (6)
Cl(12)	Re(1)	P(12)	83.99 (7)	Cl(22)	Re(2)	P(22)	84.99 (7)
Cl(12)	Re(1)	O(11)	77.8 (1)	Cl(22)	Re(2)	O(21)	77.0 (1)
P(11)	Re(1)	P(12)	161.92 (7)	P(21)	Re(2)	P(22)	162.87 (7)
P(11)	Re(1)	O(11)	95.6 (1)	P(21)	Re(2)	O(21)	94.3 (1)
P(12)	Re(1)	O(11)	93.4 (1)	P(22)	Re(2)	O(21)	93.1 (1)
			(ii) *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$ (**2**)				
Re(2)	Re(1)	Cl(1)	167.35 (9)	Re(1)	Re(2)	Cl(2)	167.36 (8)
Re(2)	Re(1)	P(1)	96.21 (9)	Re(1)	Re(2)	P(2)	99.45 (9)
Re(2)	Re(1)	P(3)	99.07 (9)	Re(1)	Re(2)	P(4)	96.28 (9)
Re(2)	Re(1)	O(1)	88.9 (3)	Re(1)	Re(2)	O(2)	87.6 (3)
Re(2)	Re(1)	O(3)	87.9 (3)	Re(1)	Re(2)	O(4)	88.9 (3)
Cl(1)	Re(1)	P(1)	93.5 (1)	Cl(2)	Re(2)	P(2)	90.1 (1)
Cl(1)	Re(1)	P(3)	87.9 (1)	Cl(2)	Re(2)	P(4)	91.2 (1)
Cl(1)	Re(1)	O(1)	80.1 (3)	Cl(2)	Re(2)	O(2)	81.9 (3)
Cl(1)	Re(1)	O(3)	84.1 (3)	Cl(2)	Re(2)	O(4)	82.4 (3)
P(1)	Re(1)	P(3)	95.8 (1)	P(2)	Re(2)	P(4)	94.1 (1)
P(1)	Re(1)	O(1)	167.8 (2)	P(2)	Re(2)	O(2)	170.2 (3)
P(1)	Re(1)	O(3)	89.4 (2)	P(2)	Re(2)	O(4)	92.6 (2)
P(3)	Re(1)	O(1)	94.4 (2)	P(4)	Re(2)	O(2)	91.8 (2)
P(3)	Re(1)	O(3)	170.8 (2)	P(4)	Re(2)	O(4)	170.8 (3)
O(1)	Re(1)	O(3)	79.7 (3)	O(2)	Re(2)	O(4)	80.7 (3)
			(iii) *trans*-$[Re_2(O_2CCH_3)_2Cl_2(dppm)_2]PF_6\cdot CH_2Cl_2$ (**3**)				
Re	Re	Cl	175.24 (6)	P(1)	Re	O(11)	88.8 (2)
Re	Re	P(1)	93.56 (6)	P(2)	Re	O(10)	94.5 (2)
Re	Re	P(2)	103.28 (6)	P(2)	Re	O(11)	84.9 (2)
Re	Re	O(10)	89.2 (2)	O(10)	Re	O(11)	178.1 (2)
Re	Re	O(11)	89.2 (2)	Cl	Re	O(11)	90.4 (2)
Cl	Re	P(1)	81.68 (8)	P(1)	Re	P(2)	161.89 (8)
Cl	Re	P(2)	81.41 (8)	P(1)	Re	O(10)	92.3 (2)
Cl	Re	O(10)	91.2 (2)				

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

Scheme II[a]



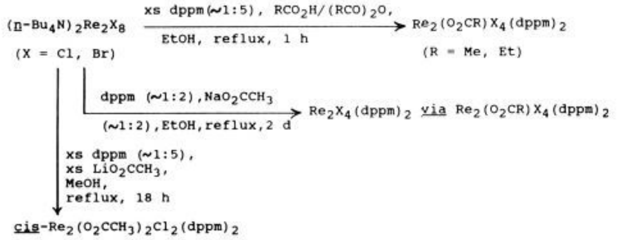
[a] Numbers in parentheses refer to the stoichiometric ratios of reagents (i.e., dirhenium complex:dppm). [b] S = EtOH or $(CH_3)_2CO$. [c] In the presence of excess LiO_2CCH_3 or NaO_2CCH_3 these reactions proceed much more rapidly (~7 h) to give exclusively *cis*-$Re_2(O_2CR)_2X_2(dppm)_2$. [d] A small amount of $Re_2(O_2CR)X_4(dppm)_2$ was also isolated in the case of R = Me and X = Cl.

complexes *cis*-$Re_2(O_2CR)_2X_2(dppm)_2$ can also be produced directly from $Re_2(O_2CR)_2X_4L_2$ (R = CH_3 or C_2H_5; X = Cl or Br; L = 4-Mepy) by the use of an excess of dppm and with methanol as solvent. While the mechanistic details of these redox reactions are unknown, the products produced when complexes of the type $Re_2(O_2CR)_2X_4L_2$ are used as starting materials clearly depend upon the solvent, the reaction stoichiometry, and the reaction time.

A study of the analogous reactions between $Re_2(O_2CCH_3)_2X_4L_2$ (X = Cl, Br, or I; L = H_2O or 4-Mepy) and 1,2-bis(diphenylphosphino)ethane (abbreviated dppe) in ethanol or acetone shows the formation of the previously characterized complexes β-$Re_2X_4(dppe)_2$.[12,14,16] Some mononuclear cleavage product $[Re(dppe)_2X_2]X$ is also produced in the case of X = Cl and I when the aquo adducts are used and the reaction solvent is ethanol. During the course of these reactions we found no evidence for the formation of intermediates such as $Re_2(O_2CR)X_4(dppe)_2$.

(iii) Reactions of $(n\text{-}Bu_4N)_2Re_2X_8$. These reactions, which are summarized in Scheme III, show that, *in the absence of an excess of acetate ion*, $Re_2(O_2CR)X_4(dppm)_2$ is an intermediate in the formation of $Re_2X_4(dppm)_2$ and does not *directly* convert to

Scheme III[a]



[a] Numbers in parentheses refer to the stoichiometric ratios of reagents (i.e., dirhenium complex:dppm).

cis-$Re_2(O_2CR)_2X_2(dppm)_2$. This conclusion is also consistent with the results shown in Scheme II, namely, that when $Re_2(O_2CR)X_4(dppm)_2$ is formed and then reacts further it does so to afford $Re_2X_4(dppm)_2$. Note that even in the reactions of $Re_2(O_2CCH_3)X_4(dppm)_2$ with excess lithium acetate in methanol to give *cis*-$Re_2(O_2CCH_3)_2X_2(dppm)_2$ (see Scheme II), the mechanism very likely involves the prior formation of $Re_2X_4(dppm)_2$ since the latter compounds are known to react rapidly and in high yield with acetate.

The reactions of $(n\text{-}Bu_4N)_2Re_2Cl_8$ with an excess of dppm and lithium acetate in methanol (Scheme III) may well involve the intermediacy of a species such as $Re_2(O_2CCH_3)_2Cl_4L_2$ (L = CH_3OH), and in this event would resemble the reactions of $Re_2(O_2CR)_2X_4L_2$ (R = CH_3 or C_2H_5; X = Cl or Br; L = 4-Mepy) with an excess of dppm in methanol (Scheme II). Once again these reactions may then proceed via $Re_2(O_2CR)X_4(dppm)_2$ and $Re_2X_4(dppm)_2$, the latter complex then being substituted by acetate to give the cis isomer of $Re_2(O_2CR)_2X_2(dppm)_2$. Evidence in support of such a mechanism is (i) the isolation of a small quantity of $Re_2(O_2CCH_3)Cl_4(dppm)_2$ in the reaction of $Re_2(O_2CCH_3)_2Cl_4(4\text{-Mepy})_2$ with dppm in methanol (Scheme II) and (ii) the much more rapid formation of *cis*-$Re_2(O_2CR)_2X_2(dppm)_2$ when an excess of acetate is added to the reaction mixtures which contain $Re_2(O_2CR)_2X_4(4\text{-Mepy})_2$ (R = CH_3 or C_2H_5; X = Cl or Br) and dppm in methanol (Scheme II).

A final point of note is that when $(n\text{-}Bu_4N)_2Re_2X_8$ (X = Cl or Br) is reacted with an excess of dppm in ethanol in the presence of carboxylic acid/anhydride mixtures, the appropriate Re_2^{5+} complex $Re_2(O_2CR)X_4(dppm)_2$ is formed rapidly and in high yield (Scheme III). Even with prolonged reaction times these reactions proceeded no further. Apparently, these acidic conditions hinder any further redox chemistry that could lead to the Re_2^{4+} species $Re_2X_4(dppm)_2$ or *cis*-$Re_2(O_2CR)_2X_2(dppm)_2$, behavior which differs from that observed when sodium or lithium acetate are present.

(b) X-ray Structural Results. Crystal structure determinations have been carried out on $Re_2(O_2CCH_3)Cl_4(dppm)_2\cdot 2(CH_3)_2CO$ (**1**), *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$ (**2**), and *trans*-$[Re_2(O_2CCH_3)_2Cl_2(dppm)_2]PF_6\cdot CH_2Cl_2$ (**3**), compounds which are representatives of the new classes of molecules that have been isolated in the present work. Important bond distances and angles for these three complexes are listed in Tables III and IV.

Complex **1**, which is a derivative of the Re_2^{5+} core, contains a single carboxylate bridge (Figure 1) and shows a resemblance to the previously characterized triphenylphosphine derivative $Re_2(\mu\text{-}O_2CCH_3)Cl_4(PPh_3)_2$.[21] However, the presence of two bridging dppm ligands in **1**, i.e., a four phosphine donor set, leads to two of the chloride ligands being axially bound, a not uncommon situation with complexes that possess the Re_2^{5+} and Re_2^{4+} cores.[4,5] The Re–Re bond of **1** is longer than that in $Re_2(\mu\text{-}O_2CCH_3)Cl_4(PPh_3)_2$ (2.300 (1) Å versus 2.217 (1) Å), a reflection of the weakening effect of the axially bound chlorides in **1**. As expected, the equatorial Re–Cl bonds (2.36 Å) are much shorter than are the axial Re–Cl interactions (2.63 Å).[22] The Re–P bond distances and the various angular distortions in this molecule appear to be normal. These structural results imply the essential similarity of the two metal centers, in accord with **1** being a symmetric mixed-valent species.

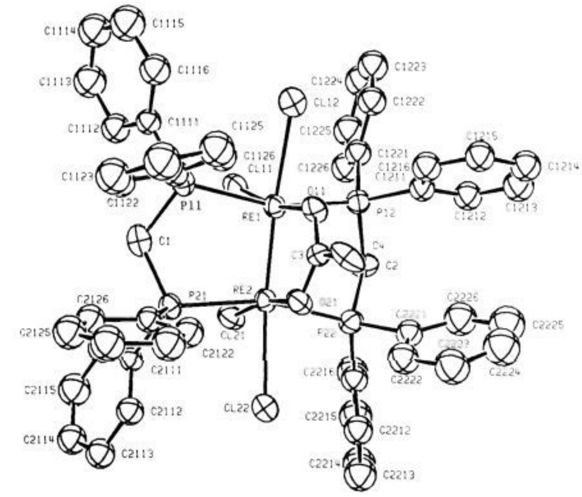


Figure 1. ORTEP view of $Re_2(O_2CCH_3)Cl_4(dppm)_2$ (**1**) in its bis-acetone solvate. Thermal ellipsoids are drawn at the 50% probability level.

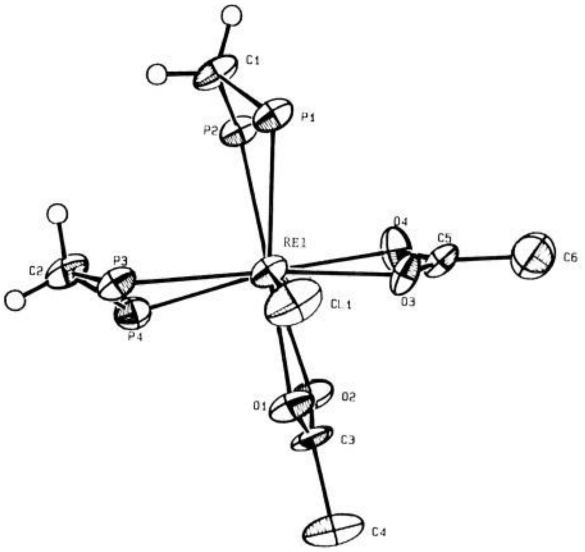


Figure 2. An ORTEP representation of *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$ (**2**) as viewed down the Re–Re axis. One rhenium (Re(2)) atom is obscured by the other. Phenyl rings have been omitted and atoms are given as their 50% probability ellipsoids.

Although we did not obtain suitable single crystals of the neutral complex, *trans*-$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$, we did so in the case of its one-electron oxidized congener *trans*-$[Re_2(O_2CCH_3)_2Cl_2(dppm)_2]PF_6$ (**3**), and so were able to confirm unambiguously the existence of cis and trans isomers. Bond distances and angles for **3** and *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$ (**2**) are given in Tables III and IV, and ORTEP representations of **2** and **3** are shown in Figures 2 and 3. These two figures (with the phenyl rings omitted) show the compounds as viewed down the Re–Re axes so that the rotational geometries can easily be seen.

Compound **2** is essentially isostructural with its singly bonded dirhodium(II) analogue $Rh_2(O_2CCH_3)_2Cl_2(dppm)_2\cdot 2CH_3CN$, a complex that has recently been prepared and structurally characterized.[23] The molecules of **2** reside on general positions in the unit cell. The twisting exhibited by the bridging acetato and dppm ligands is very similar in both molecules, with the average

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Table V. Electrochemical and Electronic Absorption Spectral Data for $Re_2(O_2CR)X_4(dppm)_2$ ($R = CH_3$ or C_2H_5; $X = Cl$ or Br)

complex	elect abs spectrum, nm[a]	Voltammetric half-wave potentials, V[b] $E_{1/2}(ox)$[c]	$E_{p,c}$
$Re_2(O_2CCH_3)Cl_4(dppm)_2$[d]	1260 (1500), 726 (150), 480 sh, 422 (1750)	+0.52 (100)	−0.60[e]
$Re_2(O_2CCH_3)Br_4(dppm)_2$[d]	1270 (1600), 760 (150), 458 (1650)	+0.55 (110)	−0.52[e]
$Re_2(O_2CC_2H_5)Cl_4(dppm)_2$	1270 (~1400), 740, ~480 sh, 424	+0.49 (110)	−0.58

[a] Measured in CH_2Cl_2; ϵ_{max} values in parentheses. [b] Versus Ag/AgCl. Recorded on solutions in 0.1 M $TBAH/CH_2Cl_2$ by the use of a Pt-bead electrode; data obtained at $\nu = 200$ mV s^{-1}. Under our experimental conditions $E_{1/2}$ for the ferrocenium/ferrocene couple was +0.47 V vs Ag/AgCl. [c] Numbers in parentheses are ΔE_p values (i.e., $E_{p,a} - E_{p,c}$). [d] The bis-acetone and bis-ethanol solvates displayed identical spectroscopic and electrochemical properties. [e] A product wave is seen at $E_{p,a} \simeq +0.3$ V on the second scan following this reduction.

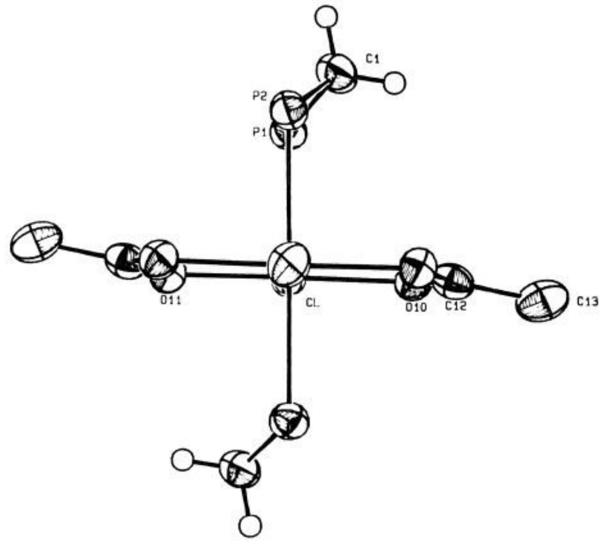

Figure 3. An ORTEP representation of the *trans*-$[Re_2(O_2CCH_3)_2Cl_2(dppm)_2]^+$ cation in its PF_6^- salt (**3**) as viewed down the Re–Re axis. One of the terminal Cl atoms obscures the rhenium atoms. Phenyl rings have been omitted and atoms are given as their 50% probability ellipsoids.

torsion angle (χ) being 11.5° in the case of **2** and 18° in the dirhodium compound.

The molecules of **3** reside on special positions and have crystallographically imposed $\bar{1}$ symmetry (i.e., $\chi = 0°$) with the methylene bridgehead carbons of the dppm ligands being disposed on opposite sides of the Re_2P_4 plane, in contrast to the situation in **2** where they are folded toward one another.

The Re–Re distance is shorter in **3** than **2** (2.275 (1) Å versus 2.315 (1) Å), in accord with the higher Re–Re bond order (3.5 versus 3) in the former complex. The Re–Cl, Re–P, and Re–O bond distances and the associated bond angles in both molecules are normal and need not be discussed further.

(c) Spectroscopic and Electrochemical Properties. The characterization of the paramagnetic compounds $Re_2(O_2CR)X_4(dppm)_2$ is based primarily upon their electrochemical and spectroscopic properties (Table V). Cyclic voltammetric (CV) measurements on solutions of these complexes in 0.1 M TBAH–CH_2Cl_2 show a reversible couple at ca. +0.5 V vs Ag/AgCl, which corresponds to a one-electron oxidation of the bulk complex, and an irreversible reduction at $E_{p,c} \simeq -0.55$ V. For the couples at $E_{1/2} \simeq +0.5$ V, constant $i_p/\nu^{1/2}$ ratios for sweep rates (ν) between 50 and 400 mV/s and $i_{p,c}/i_{p,a}$ ratios near unity are consistent with electron-transfer processes that approach reversibility. The chemical oxidation of $Re_2(O_2CCH_3)Cl_4(dppm)_2 \cdot 2EtOH$ was attempted with the use of the one-electron oxidizing agent $NOPF_6$. However, this reaction failed to yield a pure product.

CVs of dirhenium complexes that display a single oxidation and a single reduction are a common property for complexes of the Re_2^{5+} core.[4,21] Such species are expected to be paramagnetic. A magnetic moment determination by the Evans method on a sample of $Re_2(O_2CCH_3)Br_4(dppm)_2 \cdot 2(CH_3)_2CO$ dissolved in CH_2Cl_2 gave $\mu_{eff} = 1.6\ (\pm 0.1)\ \mu_B$. This value is consistent with the presence of one unpaired electron per dirhenium unit. Dichloromethane solutions of $Re_2(O_2CCH_3)X_4(dppm)_2$ ($X = Cl$ or Br) display complex ESR signals at low temperature (−160 °C).[24] In the case of the chloride complex, the signal spans the range from approximately 1.5 to 6 kG and is centered at $g \simeq 2.16$. Although resolvable coupling of 425 G is present on the higher field edge of the signal (probably due to Re hyperfine), the overall splitting pattern is not readily interpretable without recourse to computer simulation. The ESR signal reflects the resonance of a single unpaired electron residing in a molecular orbital delocalized about two quadrupolar rhenium nuclei ($I = {}^5/_2$).[4] A similar pattern is observed for the complex $Re_2(O_2CCH_3)Br_4(dppm)_2$.[24]

Table VI. Electrochemical Data for *cis*-$Re_2(O_2CR)_2X_2(dppm)_2$ and *trans*-$[Re_2(O_2CR)_2X_2(dppm)_2]PF_6$ ($R = CH_3$, C_2H_5, C_6H_5, or CCl_3; $X = Cl$ or Br)

complex	voltammetric half-wave potentials, V[a] $E_{1/2}(ox)(\mathbf{2})$[b]	$E_{1/2}(ox)(\mathbf{1})$[b]
cis-$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$	+1.34 (110)	+0.28 (100)
cis-$Re_2(O_2CC_2H_5)_2Cl_2(dppm)_2$	+1.38 (120)	+0.30 (140)
cis-$Re_2(O_2CC_6H_5)_2Cl_2(dppm)_2$	+1.34 (120)	+0.29 (120)
cis-$Re_2(O_2CCCl_3)_2Cl_2(dppm)_2$		+0.60 (100)
cis-$Re_2(O_2CCH_3)_2Br_2(dppm)_2$	+1.41 (110)	+0.35 (100)
cis-$Re_2(O_2CC_2H_5)_2Br_2(dppm)_2$	+1.41 (130)	+0.35 (110)
cis-$Re_2(O_2CC_6H_5)_2Br_2(dppm)_2$	+1.37 (100)	+0.36 (100)
cis-$Re_2(O_2CCCl_3)_2Br_2(dppm)_2$		+0.67 (110)
trans-$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$	+0.93 (110)	−0.27 (110)
trans-$Re_2(O_2CC_2H_5)_2Cl_2(dppm)_2$	+0.93 (100)	−0.29 (100)
trans-$Re_2(O_2CC_6H_5)_2Cl_2(dppm)_2$	+1.00 (110)	−0.25 (110)
trans-$Re_2(O_2CCH_3)_2Br_2(dppm)_2$	+0.97 (170)	−0.21 (150)
trans-$Re_2(O_2CC_6H_5)_2Br_2(dppm)_2$	+1.00 (100)	−0.22 (100)
cis-$[Re_2(O_2CCH_3)_2Cl_2(dppm)_2]PF_6$	+1.34 (120)	+0.28 (100)[c]
cis-$[Re_2(O_2CC_2H_5)_2Cl_2(dppm)_2]PF_6$	+1.38 (130)	+0.31 (110)[c]
trans-$[Re_2(O_2CCH_3)_2Cl_2(dppm)_2]PF_6$	+0.92 (110)	−0.28 (120)[c]
trans-$[Re_2(O_2CCH_3)_2Br_2(dppm)_2]PF_6$	+0.97 (110)	−0.21 (130)[c]
trans-$[Re_2(O_2CC_2H_5)_2Br_2(dppm)_2]PF_6$	+1.02 (110)	−0.20 (110)[c]
trans-$[Re_2(O_2CC_6H_5)_2Br_2(dppm)_2]Br$	+0.95 (110)[d]	−0.26 (110)[c]
trans-$[Re_2(O_2CC_6H_5)_2Br_2(dppm)_2]PF_6$	+1.00 (100)	−0.22 (100)[c]

[a] Versus Ag/AgCl. Recorded on solutions in 0.1 M $TBAH/CH_2Cl_2$ by the use of a Pt-bead electrode. Data obtained at $\nu = 200$ mV s^{-1}. Under our experimental conditions $E_{1/2}$ for the ferrocenium/ferrocene couple was +0.47 V vs Ag/AgCl. [b] Numbers in parentheses are ΔE_p values (i.e., $E_{p,a} - E_{p,c}$). [c] $E_{1/2}$(red). [d] $E_{p,a} = +0.72$ V for the outer sphere bromide ion.

The major features of the electronic absorption spectra of the complexes $Re_2(O_2CR)X_4(dppm)_2$ are listed in Table V. Of note is the rather intense, broad absorption near 1250 nm, a feature that is assignable to the $\delta \rightarrow \delta^*$ transition of a Re_2^{5+} core complex that contains the $\sigma^2\pi^4\delta^2\delta^{*1}$ ground-state electronic configuration.[4,25] A band of similar position and intensity was observed for the related triphenylphosphine complex $Re_2(O_2CCH_3)Cl_4(PPh_3)_2$.[21]

Of the complexes of stoichiometry $[Re_2(O_2CR)_2X_2(dppm)_2]^{n+}$ ($n = 0$ or 1) that we isolated, only the samples that contained the neutral *trans*-$Re_2(O_2CR)_2X_2(dppm)_2$ species were of insufficient purity to be fully characterized. Electrochemical data for these compounds are listed in Table VI. Electrochemical data for *trans*-$Re_2(O_2CR)_2X_2(dppm)_2$ are included since the voltammetric half-wave potentials of these complexes were easily discernible in mixtures of the cis and trans isomers. This table also contains

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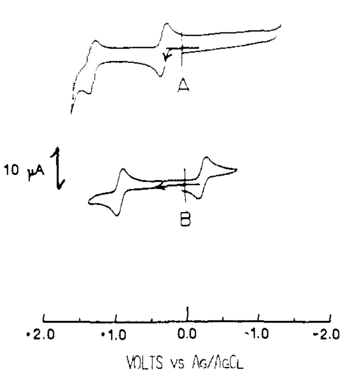

Figure 4. Single scan cyclic voltammograms of (A) *cis*-$\mathrm{Re_2(O_2CCH_3)_2Cl_2(dppm)_2}$ and (B) *trans*-$\mathrm{[Re_2(O_2CCH_3)_2Cl_2(dppm)_2]PF_6}$ recorded at ν = 200 mV s^{-1} with the use of a Pt-bead electrode.

data for the trichloroacetato derivatives *cis*-$\mathrm{Re_2(O_2CCCl_3)_2X_2(dppm)_2}$ (X = Cl or Br) that were prepared from *cis*-$\mathrm{Re_2(O_2CCH_3)_2X_2(dppm)_2}$ by carboxylate exchange reactions.

The electrochemical properties of the neutral complexes *cis*- and *trans*-$\mathrm{Re_2(O_2CR)_2X_2(dppm)_2}$ resemble quite closely related data for $\mathrm{Re_2Cl_4(dppm)_2}$[13] and other complexes of dirhenium(II)[25] in that they display two reversible one-electron oxidations. Since the cis and trans isomers contain a triply bonded $\sigma^2\pi^4\delta^2\delta^{*2}$ electronic configuration, these reversible processes correspond to oxidations to the $\sigma^2\pi^4\delta^2\delta^{*1}$ (monocation) and $\sigma^2\pi^4\delta^2$ (dication) configurations. For the monocations, the first process is now a reduction. Conductivity measurements on solutions of *cis*- and *trans*-$\mathrm{[Re_2(O_2CCH_3)_2X_2(dppm)_2]PF_6}$ in acetone ($\sim 1 \times 10^{-3}$ M) confirm them to be 1:1 electrolytes (Λ_m = 125–142 Ω^{-1} cm^2 mol^{-1}). The most useful diagnostic difference between the cis and trans isomers is seen in the shifts in the potentials of the two reversible one-electron processes that characterize their cyclic voltammograms (Table VI and Figure 4). Each of these processes is shifted by about 0.6 V to more negative potentials in the CVs of the trans isomers. The only exceptions are the CVs of the trichloroacetate derivatives *cis*-$\mathrm{Re_2(O_2CCCl_3)_2X_2(dppm)_2}$, where the electron-withdrawing effect of the $\mathrm{CCl_3}$ substituent causes a shift in $E_{1/2}$(ox)(1) to $\sim$+0.6 V vs Ag/AgCl. There is also a corresponding shift in $E_{1/2}$(ox)(2) so that it is now located sufficiently close to the solvent limit so as to preclude its accurate measurement. This difference in $E_{1/2}$(ox)(1) values (Table VI) can be utilized in using different chemical oxidants to generate the corresponding monocations of the cis and trans isomers. Tropylium hexafluorophosphate selectively oxidizes the trans isomer, thereby permitting the separation of this isomer in a mixture of isomers (see Experimental Section). Ferrocenium hexafluorophosphate can be used to oxidize the cis isomer to its monocation.

The most important difference between the electronic absorption spectra of the neutral and cationic species (Table S13)[26] is the presence of the characteristic $\delta \rightarrow \delta^*$ transition at $\sim$1000 nm (ϵ $\sim$ 1200) in the spectra of the paramagnetic cations, species that possess a $\sigma^2\pi^4\delta^2\delta^{*1}$ electronic configuration.[4,25]

IR spectral measurements down to 200 cm^{-1} revealed the presence of ν(Re–Cl) modes close to the spectral limit. Thus, the Nujol mull spectra of *cis*-$\mathrm{Re_2(O_2CCH_3)_2Cl_2(dppm)_2}$, *cis*-$\mathrm{Re_2(O_2CC_2H_5)_2Cl_2(dppm)_2}$, and *trans*-$\mathrm{[Re_2(O_2CCH_3)_2Cl_2(dppm)_2]PF_6}$ displayed ν(Re–Cl) as a strong band at 212, 208, and 227 cm^{-1}, respectively. These values reflect the relative weakness of these rather long axial Re–Cl bonds and are diagnostic of this type of system.[27]

As expected, the paramagnetic cis and trans cations do not exhibit well-defined NMR spectra but they are ESR active. X-Band ESR spectra of *cis*-$\mathrm{[Re_2(O_2CR)_2Cl_2(dppm)_2]PF_6}$ (R = $\mathrm{CH_3}$ and $\mathrm{C_2H_5}$), *trans*-$\mathrm{[Re_2(O_2CCH_3)_2Cl_2(dppm)_2]PF_6}$, and *trans*-$\mathrm{[Re_2(O_2CC_6H_5)_2Br_2(dppm)_2]Br}$ were recorded on $\mathrm{CH_2Cl_2}$ glasses at −160 °C. These spectra are not only very similar to one another, with a complex pattern centered at $g \simeq 2.16$, but they also resemble very closely the spectra of $\mathrm{Re_2(O_2CCH_3)X_4(dppm)_2}$ (X = Cl or Br).[24] Both the cis and trans isomers exhibit Re hyperfine structure in these spectra that is well resolved at the higher field limits ($A^{\mathrm{Re}} \simeq 425$ G). The most obvious spectral difference is the slightly smaller spectral width for the pattern of the cis cations compared to the trans (3900 G versus 4350 G).

The ^{31}P{^{1}H} NMR spectra of $\mathrm{CD_2Cl_2/CH_2Cl_2}$ solutions of these complexes are very simple. The spectra of *cis*-$\mathrm{Re_2(O_2CCH_3)_2X_2(dppm)_2}$ show singlets at δ −10.2 (X = Cl) and δ −12.6 (X = Br), whereas a mixture of cis and trans isomers of $\mathrm{Re_2(O_2CCH_3)_2Cl_2(dppm)_2}$ displays singlets at δ −10.2 (cis) and δ +2.26 (trans). The spectrum of *cis*-$\mathrm{Re_2(O_2CCCl_3)_2Cl_2(dppm)_2}$ is also characterized by a singlet (at δ −9.07).

Because of their superior solubility properties the propionate derivatives *cis*-$\mathrm{Re_2(O_2CC_2H_5)_2X_2(dppm)_2}$ gave the best ^{1}H NMR spectra (470 MHz). In accord with the results of the crystal structure determination on *cis*-$\mathrm{Re_2(O_2CCH_3)_2Cl_2(dppm)_2}$ (see Figure S1) we observed two sets of phenyl resonances, implying that the inequivalences seen in the solid state are preserved in solution; for X = Cl we have δ +7.64 (m) and δ +7.43 (m) for the o-H's, δ +7.31 (t) and δ +7.08 (t) for the p-H's, and δ +7.17 (t) and δ +6.98 (t) for the m-H's. The remainder of the spectrum of *cis*-$\mathrm{Re_2(O_2CC_2H_5)_2Cl_2(dppm)_2}$ showed propionate resonances at δ +2.78 (quartet, $-\mathrm{CH_2}-$) and δ +1.12 (triplet, $-\mathrm{CH_3}$) and dppm bridgehead $-\mathrm{CH_AH_M}-$ proton resonances centered at δ_A +6.44 and δ_M + 4.97. While these two latter resonances closely resemble quartets, they are in reality doublets-of-triplets due to geminal coupling between $\mathrm{H_A}$ and $\mathrm{H_M}$ and further coupling between these protons and two equivalent P nuclei ($I = {}^1/_2$) with $J(\mathrm{H_A{-}H_M}) \simeq 13$ Hz, $J(\mathrm{H_A{-}P}) \simeq 10$ Hz, and $J(\mathrm{H_M{-}P}) \simeq 13$ Hz. This spectrum, which is representative of this class of compounds as a whole, is unusual because of the very large chemical shift difference between $\mathrm{H_A}$ and $\mathrm{H_M}$. The relatively large values for $J(\mathrm{H_AP})$ and $J(\mathrm{H_MP})$ appear to be a characteristic fingerprint for a cis set of dppm ligands. Another complex that contains a bridging dppm ligand with no other phosphine ligands trans to it is $\mathrm{Re_2Cl_4(dppm)(PMe_3)_2}$, for which J(H–P) is 10.4 Hz.[28] Such values contrast with J(H–P) values of 4–5 Hz which characterize dirhenium(II) and dimolybdenum(II) complexes that have bridging dppm ligands trans to one another. Examples include $\mathrm{[Re_2Cl_3(dppm)_2(CO)_2(NCR)]PF_6}$,[29] $\mathrm{Re_2Cl_4(dppm)_2(CO)(CNR)}$,[30] $\mathrm{Re_2X_4(dppm)_2}$,[13] and $\mathrm{Mo_2X_4(dppm)_2}$ (X = Cl, Br, I).[31] These smaller values are a manifestation of the occurrence of virtual coupling between the bridgehead methylene protons and four phosphorus nuclei.

(d) Concluding Remarks. This study is especially noteworthy in that we have been able to isolate isomeric forms of multiply bonded dirhenium complexes in which there are cis or trans arrangements of $\mathrm{Ph_2PCH_2PPh_2}$ (dppm) ligands. These are the first examples of the preparation and characterization of such isomers. Although the cis isomer of the singly bonded dirhodium(II) complex $\mathrm{Rh_2(O_2CCH_3)_2Cl_2(dppm)_2}$ has recently been reported, the related trans isomer was not obtained.[23] Of additional note is our finding that the bis-carboxylato species *cis*-$\mathrm{Re_2(O_2CR)_2X_4L_2}$ react with dppm in ethanol to produce paramagnetic $\mathrm{Re_2(O_2CR)X_4(dppm)_2}$, which in turn can be thermolyzed to give $\mathrm{Re_2X_4(dppm)_2}$ (X = Cl, Br, or I) in high yield. This affords an excellent synthetic route to this set of compounds.

Acknowledgment. We thank the National Science Foundation (Grant No. CHE85-06702) for support of this work and the

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[26] Representative electronic absorption spectral data (measured in $\mathrm{CH_2Cl_2}$) are as follows ($\lambda_{\max}$ in nm, $\epsilon_{\max}$ values in parentheses): *cis*-$\mathrm{Re_2(O_2CCH_3)_2Cl_2(dppm)_2}$, 815 (170), 550 sh, 465 (270), 365 sh, 300 (18 900); *cis*-$\mathrm{[Re_2(O_2CCH_3)_2Cl_2(dppm)_2]PF_6}$, 1110 (1200), 750 sh, 610 sh, 450 sh, 400 sh, 308 (15 300); *trans*-$\mathrm{[Re_2(O_2CCH_3)_2Cl_2(dppm)_2]PF_6}$, 930 (1100), 790 sh, 428 (1240), 285 sh. Further details are given in Table S13.

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National Institutes of Health (Grant No. RR-01077) and the National Science Foundation (Grant No. 8714258) for funds for the purchase of the NMR spectrometers. We are most grateful to Professor T. J. Smith (Kalamazoo College, MI) for the use of his Perkin-Elmer 330 UV/VIS/NIR spectrophotometer.

Supplementary Material Available: Listings of positional parameters and their errors for the phenyl carbon atoms of **1**, **2**, and **3**, the lattice solvent molecules of **1** and **3**, and the PF_6^- atoms of **3** (Tables S1, S2, and S3), thermal parameters (Tables S4, S5, and S6), complete listings of bond distances (Tables S7, S8, and S9) and bond angles (Tables S10, S11, and S12), electronic absorption spectral data for representative complexes of the type *cis*- and *trans*-$[Re_2(O_2CR)_2X_2(dppm)_2]^{0,+}$ (Table S13), and figures showing the full atomic numbering schemes for **2** and **3** (Figures S1 and S2) (29 pages); tables of observed and calculated structure factors (57 pages). Ordering information is given on any current masthead page.

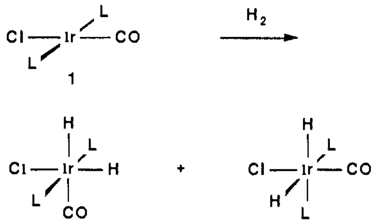
The Origin of the Directing Effect in H_2 Addition to Square-Planar d^8 Complexes

Mark J. Burk, Martin P. McGrath, Ralph Wheeler,† and Robert H. Crabtree*

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06520. *Received November 16, 1987*

Abstract: Hydrogen adds to square-planar d^8 complexes of the Vaska type [*trans*-$IrX(CO)(PR_3)_2$] to give oxidative addition products in which the H_2 has added parallel to the X–Ir–CO axis. In principle, however, addition perpendicular to this axis should also be possible. Three models have been discussed to account for the apparent preference for parallel adducts. We show that in contrast to the chloro complex (X = Cl, parallel adduct formed), the methyl, phenyl, or hydride analogues give perpendicular adducts. In one case (X = Ph), the perpendicular adduct is formed at −80 °C, but rearranges to the parallel adduct on warming via reductive elimination of H_2 and readdition. These findings seem to invalidate the previous theoretical models that have been proposed to explain the direction of H_2 addition. A new one is suggested that covers all the data gathered up to now.

Hydrogen may in principle add in one of two ways to a square-planar d^8 complex, as shown in eq 1 for the case of Vaskas complex (**1**). The two H ligands are cis to one another in both products, as expected from a concerted process, but in one case (**2**) H_2 is trans to Cl and CO, and in the other (**3**) H_2 is trans to the PPh_3 groups. For the parent complex (X = Cl), only the parallel adduct, **2**, is observed.



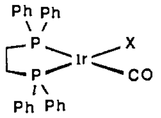
(1)

2
parallel
addition

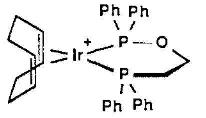
3
perpendicular
addition

In the formation of **2** and **3**, the H_2 has added parallel and perpendicular, respectively, to the Cl–Ir–CO symmetry axis. We shall therefore refer to **2** and **3** as the "parallel" and "perpendicular" adducts. In cases such as **4** in which neither of the two directions is coincident with an axis of symmetry of the molecule, we will choose an axis and indicate the choice in parentheses, e.g., parallel (CO) means parallel to the M–CO bond. Understanding the factors that determine which isomers are formed is a fundamental problem and may also be of help in rationalizing the course of asymmetric hydrogenation and other catalytic reactions.

Eisenberg et al.[1] have found that the parallel (CO) adducts are the kinetic products in the addition of H_2 to **4** (X = Cl, Br, I, CN), and they discussed two possible reasons. One proposal involves increased overlap of $\sigma^*(H_2)$ with the $d_\pi(M)$ orbital through the involvement of $\pi^*(CO)$ in the transition state. This picture predicts that addition should always take place parallel to the best π-acceptor ligand (i.e., CO in **4**, as observed). It also explains the formation of parallel adducts in H_2 addition to **1**, and was consistent with most of the available data known at the time it was proposed. This model requires a transition state[1e] closely resembling the square-planar starting material and unlike the trigonal-bipyramidal transition state of type **6** that we invoked.



4



5

In an alternative model, first suggested by Wolczanski and also considered by Eisenberg et al.,[1] addition should occur parallel to the highest trans effect ligand (see eq 9 and 10 and further discussion below).

We reported in 1983 that H_2 addition to **5** gave the perpendicular (P–O) adduct **7a**.[2a] In contrast, the parallel (P–O) adduct **7b** would be expected on the basis of the ideas subsequently developed by Eisenberg et al.,[1] since the Ph_2PO group is the better π-acceptor. We had proposed a different picture: that stereochemical preferences within a trigonal-bipyramidal transition state (or intermediate) of type **6** is the critical factor in deciding which isomer is formed. For example, in eq 2 we postulated that **7a** is formed rather than **7b** because **6a** is stabler than **6b**. Several useful theoretical studies of H_2 addition are available.[3a]

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† Address for this author: Department of Chemistry, Cornell University, Ithaca, NY 14853. Present address: Department of Chemistry, University of Houston, Houston, TX 77004.

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