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# Complex Halides of the Transition Metals. XX.[1] Reactions of the Octahalodirhenate(III) Anions with Bidentate Tertiary Phosphines and Arsines and Some Related Reactions of Dimers of the Type $Re_2X_4(PR_3)_4$[2]

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The reactions between the octahalodirhenate(III) anions $Re_2X_8^{2-}$, where X = Cl or Br, and the bidentate donors 1,2-bis(diphenylphosphino)ethane (dppe) and 1-diphenylphosphino-2-diphenylarsinoethane (arphos) afford routes to the metal–metal bonded rhenium(II) dimers $Re_2Cl_4(LL)_2$, where LL = dppe or arphos, and $Re_2Br_4(arphos)_2$. Under mild reaction conditions the unreduced magnetically dilute halogen-bridged dimers $Re_2Cl_6(dppe)_2$ and $Re_2Br_6(arphos)_2$ can also be isolated. The chloro complexes $Re_2Cl_4(LL)_2$ are most conveniently prepared from $Re_2Cl_4(PEt_3)_4$ by ligand exchange. In contrast to these results, the octahalodirhenate(III) anions react with bis(diphenylphosphino)methane (dppm) to give the new species $Re_2Cl_6(dppm)_2$, $Re_2Br_5(dppm)_2{\cdot}CH_3CN$, and $\alpha$-$[ReBr_2(dppm)]_n$. $Re_2Cl_6(dppm)_2$ resembles $Re_2Cl_6(dppe)_2$ in being a chlorine-bridged dimer but, in contrast to the latter complex, it contains a strong metal–metal bond and is diamagnetic. The partially reduced complex $Re_2Br_5(dppm)_2{\cdot}CH_3CN$ is probably related structurally to the analogous chloro complex which has recently been prepared and characterized by Cotton and Shive. The reaction of $Re_2Cl_4(PR_3)_4$, where R = Et or *n*-Pr, with dppm affords an excellent route to the rhenium(II) dimers, $Re_2Cl_4(PEt_3)_2(dppm)$ and $Re_2Cl_4(dppm)_2$. The reaction of $Re_2Br_4[P(n\text{-}Pr)_3]_4$ with dppm produces $\beta$-$[ReBr_2(dppm)]_n$ which exhibits spectral differences from the $\alpha$ form. The spectral and magnetic properties of these new complexes have been investigated, as have certain aspects of their chemical reactivities. In all instances, the rhenium(II) dimers $Re_2Cl_4(LL)_2$, where LL = dppm, dppe, and arphos, $Re_2Cl_4(PEt_3)_2(dppm)$, and $Re_2Br_4(arphos)_2$ are believed to contain bidentate ligands which bridge the rhenium atoms within the dimer.

## Introduction

The reduction of the octahalodirhenate(III) anions by monodentate tertiary phosphines affords complexes of the types $Re_2X_5(PR_3)_3$ or $Re_2X_4(PR_3)_4$,[3,4] with the extent of reduction being dependent upon the degree of phenyl substitution of the phosphine. Phosphines of the type $PRPh_2$ (R = Me or Et) produce exclusively $Re_2X_5(PRPh_2)_3$ whereas $PR_3$ (R = Me, Et, or *n*-Pr) and $PEt_2Ph$ yield the two-electron-reduced products $Re_2X_4(PR_3)_4$.[4] The related reactions of these anions with the bidentate donors $Ph_2P(CH_2)_nPPh_2$ (*n* = 1 or 2), $Ph_2PCH_2CH_2AsPh_2$, and $Ph_2AsCH_2CH_2AsPh_2$ are much more varied than those encountered with the monodentate phosphines but in several instances proceed with reduction to low oxidation state rhenium species. These reactions and the characterization of the resulting complexes, together with some related ligand substitution reactions of complexes of the types $Re_2X_4(PR_3)_4$ and $Re_2Cl_5(PR_3)_5$, are now reported in detail.[5] The structural relationships of these new complexes to other dimeric rhenium halide complexes[3,6,7] are discussed.

## Experimental Section

**Starting Materials.** The systematic names of the ligands used in this study are listed together with their common abbreviations: (a) 1-diphenylphosphino-2-diphenylarsinoethane, arphos; (b) bis(1,2-diphenylphosphino)ethane, dppe; (c) bis(1,2-diphenylarsino)ethane, dpae; (d) bis(diphenylphosphino)methane, dppm. All of these ligands were obtained from Strem Chemicals, Inc., and, with the exception of dppe, used without further purification. Most batches of dppe contained small amounts of a phosphine oxide impurity so recrystallization from acetonitrile was necessary.

The salts $[Bu_4N]_2[Re_2X_8]$, where X = Cl or Br, were prepared by the usual literature method.[8] Samples of the complexes $Re_2Cl_4(PEt_3)_4$, $Re_2Cl_4[P(n\text{-}Pr)_3]_4$, and $Re_2Cl_5(PEtPh_2)_3$ were prepared from $[Bu_4N]_2[Re_2Cl_8]$ as previously described.[4] The new complex $Re_2Br_4[P(n\text{-}Pr)_3]_4$ was prepared as black crystals by a similar procedure to that described for $Re_2Cl_4[P(n\text{-}Pr)_3]_4$.[4] Anal. Calcd for $Re_2Br_4[P(C_3H_7)_3]_4$: C, 32.4; H, 6.3. Found: C, 32.4; H, 6.5. Yield: 53%.

**Reaction Procedures.** *All reactions were carried out in a nitrogen atmosphere and solvents were deoxygenated by purging with $N_2$ gas for several hours.*

In several of the reactions in which a nitrogen-line reaction system was used, the reaction products contained rhenium–oxygen and/or phosphine oxide contaminants. To ensure the exclusion of oxygen and moisture in these reactions, an all-glass vacuum system, whose design and operation have been described elsewhere,[9] was used. This procedure is hereafter referred to as "the vacuum-line procedure".

**A. Reactions with 1,2-Bis(diphenylphosphino)methane (i) $(Bu_4N)_2Re_2Cl_8$.** $(Bu_4N)_2Re_2Cl_8$ (0.40 g) was carefully deoxygenated in a stream of $N_2$ and then dissolved in 5 ml of deoxygenated acetonitrile. This solution was mixed with one containing dppm (0.50 g) in 20 ml of acetonitrile and this reaction mixture was stirred at room-temperature for 1 h. The resulting brown precipitate was filtered off and washed with acetone until the solid had turned magenta and the washings were colorless. This insoluble product was then washed with diethyl ether and dried in vacuo. Anal. Calcd for $ReCl_3[(C_6H_5)_2PCH_2P(C_6H_5)_2]$: C, 44.3; H, 3.3; Cl, 15.7; N, 0.0. Found (for separate preparative samples): C, 44.15, 44.1; H, 3.4, 4.0; Cl, 15.4, 15.9; N, 0.0. Yield: ~5%.

If in the above procedure the reaction mixture was heated on a steam bath for 4 h, the resulting dark magneta product analyzed as the acetonitrile solvate $[ReCl_3(dppm){\cdot}CH_3CN]_n$. Anal. Calcd for $ReCl_3[(C_6H_5)_2PCH_2P(C_6H_5)_2]{\cdot}CH_3CN$: C, 45.1; H, 3.5; Cl, 14.8; N, 1.95. Found (for separate preparative samples): C, 45.4, 45.45; H, 3.5, 3.35; Cl, 13.9, 14.5; N, 1.9, 1.6. Yield: 60%.

This same reaction was also carried out using methanol, which contained 1 drop of concentrated hydrochloric acid, as the reaction solvent. After the reaction mixture had been refluxed for 24 h, it was filtered and the insoluble product was washed with acetone (to dissolve a green impurity), ethanol, and diethyl ether. The purple complex of stoichiometry $[ReCl_3(dppm)]_n$ was dried in vacuo prior to analysis. Anal. Found: C, 44.9; H, 3.5; Cl, 15.5. Yield: 52%. The infrared spectrum of this product, while otherwise identical with that of the complex of this same stoichiometry prepared from acetonitrile, had an additional fairly intense band at 1060 cm$^{-1}$.

None of these products showed any reactivity toward acetic acid–acetic anhydride and carbon tetrachloride–dichloromethane reaction mixtures.

**(ii) $Re_2Cl_4(PEt_3)_4$.** Using the vacuum-line procedure, $Re_2Cl_4(PEt_3)_4$ (0.30 g) and dppm (0.60 g) were refluxed and stirred in 15 ml of benzene for 15 h. The initial green solution turned deep purple, and eventually a purple powder precipitated. This product, which could be obtained as small purple crystals if the reaction mixture was not stirred, was filtered off under nitrogen, washed with several portions of benzene and diethyl ether, and dried in vacuo. Microanalytical data were consistent with the stoichiometry $[Re_2Cl_4(PEt_3)_2(dppm)]$. Anal. Calcd for $Re_2Cl_4[P(C_2H_5)_3]_2[(C_6H_5)_2PCH_2P(C_6H_5)_2]$: C, 39.1; H, 4.6; Cl, 12.5; P, 10.9. Found (for separate preparative samples): C, 38.8, 38.3; H, 4.7, 4.4; Cl, 12.4, 12.4; P, 10.9. Yield: ~75%.

A mixture of tetraphenylarsonium chloride (0.3 g) and $Re_2Cl_4(PEt_3)_2(dppm)$ (0.1 g) was dissolved in a mixture of carbon tetrachloride (5 ml) and dichloromethane (7 ml). The solution was then refluxed for 20 h whereupon the blue crystalline salt $(Ph_4As)_2Re_2Cl_8$ precipitated. The infrared spectrum of this complex (4000–200 $cm^{-1}$) confirmed its identity. Yield: ~90%.

**(iii) $Re_2Cl_4[P(n\text{-}Pr)_3]_4$.** A procedure exactly analogous to that described in section A(ii) afforded a complex of stoichiometry $[ReCl_2(dppm)]_n$. Anal. Calcd for $ReCl_2[(C_6H_5)_2PCH_2P(C_6H_5)_2]$: C, 46.8; H, 3.4; Cl, 11.1. Found (for separate preparative samples): C, 46.8, 47.5; H, 3.6, 3.7; Cl, 11.1, 11.2. Yield: ~50%. A molecular weight measurement in acetone showed that the complex was dimeric: calcd for $Re_2Cl_4[(C_6H_5)_2PCH_2P(C_6H_5)_2]_2$, 1282; found, 1164.

$Re_2Cl_4(dppm)_2$ reacted with tetraphenylarsonium chloride in an analogous fashion to reaction of $Re_2Cl_4(PEt_3)_2(dppm)$ (see A(ii)) to produce $(Ph_4As)_2Re_2Cl_8$ in very high yield.

**(iv) $(Bu_4N)_2Re_2Br_8$.** (a) Using the procedure described in A(i), the reaction between $(Bu_4N)_2Re_2Br_8$ and dppm in acetonitrile at room temperature afforded a red-brown complex of stoichiometry approximating to $[ReBr_{2.5}(dppm)\cdot 0.5CH_3CN]_n$. It was washed with ethanol and diethyl ether and dried in vacuo prior to analysis. Anal. Calcd for $ReBr_{2.5}[(C_6H_5)_2PCH_2P(C_6H_5)_2]\cdot 0.5CH_3CN$: C, 39.5; H, 3.0; Br, 25.3; N, 0.9. Found (for separate preparative samples): C, 39.2, 39.5; H, 3.1, 3.1; Br, 25.7, 26.6; N, 1.2, 1.35. Yield: 85%. Although this complex showed partial solubility in both acetic acid–acetic anhydride and carbon tetrabromide–dichloromethane mixtures, we found no evidence that it reacted to form either $Re_2(O_2CCH_3)_4Br_2$ or $ReBr_4(dppm)$.

(b) When the reaction between $(Bu_4N)_2Re_2Br_8$ and dppm was carried out under reflux conditions for 14 h, a gray complex of stoichiometry $[ReBr_2(dppm)]_n$ precipitated. This product was filtered off, washed with acetone, ethanol, and diethyl ether, and then dried in vacuo. Anal. Calcd for $ReBr_2[(C_6H_5)_2PCH_2P(C_6H_5)_2]$: C, 41.1; H, 3.0; Br, 22.0. Found: C, 41.2; H, 3.3; Br, 21.7. Yield: 75%. This complex showed partial solubility in dichloromethane but was not soluble enough for molecular weight measurements.

**(v) $Re_2Br_4[P(n\text{-}Pr)_3]_4$.** Using the vacuum-line procedure, $Re_2Br_4[P(n\text{-}Pr)_3]_4$ (0.09 g) and dppm (0.18 g) were refluxed in 10 ml of benzene for 5 days. The reaction mixture was then filtered and the filtrate evaporated to low volume whereupon a purple solid (0.075 g) precipitated. It was filtered off, washed with diethyl ether, and dried in vacuo. Microanalytical data were consistent with a complex of stoichiometry, $[ReBr_2(dppm)]_n$, containing a small amount of "lattice" benzene. Anal. Calcd for $ReBr_2[(C_6H_5)_2PCH_2P(C_6H_5)_2]\cdot 0.25C_6H_6$: C, 42.4; H, 3.1; Br, 21.3. Found: C, 42.5; H, 3.5; Br, 21.2. Yield: 63%.

**B. Reactions with 1,2-Bis(diphenylphosphine)ethane.** **(i) $(Bu_4N)_2Re_2Cl_8$.** A mixture of $(Bu_4N)_2Re_2Cl_8$ (0.15 g) and dppe (0.15 g) in 25 ml of acetonitrile was refluxed for 4 days and the resulting black crystals were filtered off, washed with ethanol and diethyl ether, and then dried in vacuo. Anal. Calcd for $ReCl_2[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$: Cl, 10.8. Found: Cl, 10.7. Yield: 12%.

**(ii) $Re_2Cl_6(dppe)_2$.** As previously documented in the literature,[8,10] the room-temperature reaction between $(Bu_4N)_2Re_2Cl_8$ and dppe in acetonitrile affords the rhenium(III) complex $Re_2Cl_6(dppe)_2$ which is a centrosymmetric chlorine-bridged dimer in which a metal–metal bond is no longer present.[7] The reactivity of this complex has been further explored in the present investigation.

(a) A yellow complex of stoichiometry $[ReCl_3(dppe)_{1.5}]_n$ precipitated when a mixture of $Re_2Cl_6(dppe)_2$ (0.15 g) and dppe (0.15 g) in 12 ml of acetonitrile was refluxed for 12 h. The insoluble complex was filtered off, washed with ethanol and diethyl ether, and dried in vacuo. Anal. Calcd for $ReCl_3[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_{1.5}$: C, 52.6; H, 4.0; Cl, 12.0; P, 10.4. Found: C, 52.25; H, 4.4; Cl, 11.6; P, 10.15. Yield: 21%.

This complex was slightly soluble in dichloromethane but insoluble in all other common organic solvents.

(b) When $Re_2Cl_6(dppe)_2$ (0.30 g) was refluxed with 7 ml of acetonitrile, an orange-brown insoluble product formed. Reaction was stopped after 6 h, and the insoluble material was washed with acetonitrile and diethyl ether and then dried in vacuo. It analyzed for a complex of stoichiometry $ReCl_3(dppe)\cdot CH_3CN$. Anal. Calcd for $ReCl_3[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]\cdot CH_3CN$: C, 45.9; H, 3.7; Cl, 14.55; P, 8.5; N, 1.9. Found: C, 45.8; H, 3.7; Cl, 14.6; P, 8.6; N, 2.4. Yield: 85%. In the infrared spectrum of this complex, a weak but sharp band at ~2275 $cm^{-1}$ is assigned to $\nu(C{\equiv}N)$ of $CH_3CN$.

**(iii) $Re_2Cl_4(PEt_3)_4$.** A mixture of $Re_2Cl_4(PEt_3)_4$ (0.25 g) and dppe (0.40 g) was refluxed in 15 ml of *n*-butyl alcohol for 6 days. The resulting brown reaction mixture was filtered while warm (dppe is soluble in warm 1-butanol) to obtain dark purple crystals of $[ReCl_2(dppe)]_n$ which were washed with benzene and diethyl ether and dried in vacuo. Anal. Calcd for $ReCl_2[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$: C, 47.6; H, 3.7; Cl, 10.8. Found: C, 46.5; H, 3.8; Cl, 10.8. Yield: ~78%. This product had properties identical with those of the complex prepared directly from $(Bu_4N)_2Re_2Cl_8$ (see B(i)).

This complex was insoluble in most common solvents with the exception of dichloromethane in which it was slightly soluble. It slowly reacted with a solution of tetraphenylarsonium chloride in carbon tetrachloride–dichloromethane to afford the salt $(Ph_4As)_2Re_2Cl_8$. A reflux time of 15 days was necessary for the reaction to occur.

**(iv) $Re_2Cl_5(PEtPh_2)_3$.** Using the vacuum-line procedure, $Re_2Cl_5(PEtPh_2)_3$ (0.20 g) was treated with dppe (0.40 g) in ~15 ml of benzene. After 2 days' reflux, a small amount of yellow-green solid containing phosphine oxide contaminants was sometimes present, so the reaction mixture was filtered, and any insoluble residues were discarded. After refrigeration (~10 °C) of the filtrate for 1 week, a gold crystalline solid formed and it was filtered off, washed with ethanol and diethyl ether, and dried in vacuo. The exact nature of this product was uncertain, but microanalytical data were consistent with a complex of stoichiometry $[ReCl_{2.5}(dppe)_{2.5}]_n$. Anal. Calcd for $ReCl_{2.5}[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_{2.5}$: C, 61.4; H, 4.7; Cl, 7.0; P, 12.2. Found (for separate preparative samples): C, 60.8, 61.2; H, 4.7, 4.5; Cl, 7.0, 6.8; P, 12.5. However, other formulations are equally consistent with the analytical data, e.g., $[ReCl_{2.5}(dppe)_{1.5}(PEtPh_2)_2]_n$ and $[ReCl_{2.5}(dppe)_2(PEtPh_2)]_n$, but we were unable to distinguish between them. This complex was found to be slightly soluble in benzene, dichloromethane, acetone, and nitromethane and insoluble in ethanol, methanol, acetonitrile, petroleum ether, and diethyl ether.

The subsequent characterization of this complex failed to provide a clue as to its structure. Consequently, it will not be discussed further.

**C. Reactions with 1-Diphenylphosphino-2-diphenylarsinoethane.** **(i) $(Bu_4N)_2Re_2Cl_8$.** The reaction between $(Bu_4N)_2Re_2Cl_8$ and arphos, carried out using procedure B(i) with a reaction time of 48 h, afforded glistening black crystals of stoichiometry $[ReCl_2(arphos)]_n$. Anal. Calcd for $ReCl_2[(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2]$: C, 44.6; H, 3.5; Cl, 10.1. Found: C, 44.7; H, 3.5; Cl, 10.1. Yield: 8%.

**(ii) $(Bu_4N)_2Re_2Br_8$.** (a) A dark green complex of stoichiometry $[ReBr_3(arphos)]_n$ precipitated when an acetonitrile solution (20 ml) of $(Bu_4N)_2Re_2Br_8$ (0.25 g) and arphos (0.15 g) was stirred for 30 min at room temperature. The precipitate was washed with acetone until the washings were colorless and then with diethyl ether. It was finally dried in vacuo prior to analysis. Anal. Calcd for $ReBr_3[(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2]$: C, 35.9; H, 2.8; Br, 27.6; N, 0.0. Found: C, 36.5; H, 2.8; Br, 25.95; N, 0.1. Yield: 17%.

The reactivity of this complex toward carbon tetrabromide and acetic acid–acetic anhydride was explored in some detail. A mixture of $[ReBr_3(arphos)]_n$ (0.10 g) and carbon tetrabromide (0.20 g) was added to 8 ml of dichloromethane and the reaction mixture refluxed for 1 h. Any unreacted $[ReBr_3(arphos)]_n$ was filtered off and the filtrate was evaporated to dryness and extracted with diethyl ether to remove excess carbon tetrabromide. Anal. Calcd for $ReBr_4[(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2]\cdot CBr_4$: C, 25.3; H, 1.9; Br, 49.9. Found: C, 25.6; H, 1.9; Br, 48.7. Yield: 42%.

$[ReBr_3(arphos)]_n$ (0.10 g) was heated with 8 ml of acetic acid and 2 ml of acetic anhydride on a steam bath for 1 hr. Any unreacted starting material was then filtered off, the filtrate evaporated to dryness, and the brown residue washed with diethyl ether and dried in vacuo. Yield: 0.03 g. The infrared and electronic absorption spectra of this material were identical with those exhibited by the rhenium(IV) complex $ReBr_4(arphos)\cdot CBr_4$, with the exception that the latter complex exhibited an intense band at 670 $cm^{-1}$ in its infrared spectrum assigned to the $\nu_3$ mode of lattice $CBr_4$.[11] The electronic absorption spectrum of an acetone solution of this complex exhibited the following absorption maxima which were typical of a rhenium(IV) species:[10] 1550, 1310 (sh) and 1270, ~970, 870, 780, ~700 (sh), 510 (sh), 430 (sh) nm.

(b) When the reaction between $(Bu_4N)_2Re_2Br_8$ and arphos was carried out under reflux conditions, reduction occurred. A mixture of $(Bu_4N)_2Re_2Br_8$ (0.60 g) and arphos (0.60 g) was refluxed in 40 ml of acetonitrile for 5 days. A large excess of acetonitrile is required in this reaction to prevent the precipitation of an unidentified insoluble impurity. The resulting black crystals of $[ReBr_2(arphos)]_n$ were worked up in the usual fashion (see B(i)). Anal. Calcd for $ReBr_2[(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2]$: C, 39.6; H, 3.0; Br, 20.3. Found: C, 39.3; H, 3.1; Br, 20.6. Yield: 7%.

**(iii) $Re_2Cl_4(PEt_3)_4$.** A mixture of $Re_2Cl_4(PEt_3)_4$ (0.20 g) and arphos (0.40 g) was refluxed in 8 ml of benzene for 2 days after which time a purple crystalline solid formed. The solid was removed by filtering the warm reaction mixture, washed with acetone, benzene, and diethyl ether, and dried in vacuo. The purple complex analyzed as $[ReCl_2(arphos)]_n$. Anal. Calcd for $ReCl_2[(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2]$: C, 44.6; H, 3.5; Cl, 10.1. Found: C, 44.7; H, 3.3; Cl, 10.4. Yield: ~30%. This product had properties identical with those of the complex of this same stoichiometry prepared from $(Bu_4N)_2Re_2Cl_8$ (see C(i)).

When a sample of this complex was refluxed for 8 days with a solution of tetraphenylarsonium chloride in carbon tetrachloride–dichloromethane (see A(ii)), blue crystalline $(Ph_4As)_2Re_2Cl_8$ was formed in quantitative yield.

The reaction between $[ReCl_2(arphos)]_n$ (0.05 g) and $PEt_3$ (0.8 ml) in 10 ml of refluxing benzene was carried out for 18 days. After this time, the reaction solution was evaporated to low volume and a quantity of dark gray-green solid filtered off. This product was washed with acetone and diethyl ether and dried in vacuo. Yield: 14%. Its infrared spectrum (4000–200 $cm^{-1}$) was identical with that of an authentic sample of $Re_2Cl_4(PEt_3)_4$.[4]

**(iv) $Re_2Cl_5(PEtPh_2)_3$.** A procedure analogous to that described in C(iii) afforded dark purple crystals of $[ReCl_2(arphos)]_n$. Anal. Calcd for $ReCl_2[(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2]$: C, 44.6; H, 3.5; Cl, 10.1. Found: C, 44.4; H, 3.4; Cl, 10.0. Yield: ~30%.

**D. Reactions with 1,2-Bis(diphenylarsino)ethane. (i) $(Bu_4N)_2Re_2Cl_8$.** A mixture of $(Bu_4N)_2Re_2Cl_8$ (0.20 g) and dpae (0.30 g) was dissolved in 12 ml of 1-butanol and the solution was refluxed for 10 days. The resulting green precipitate was filtered off, washed with methanol, acetone, and diethyl ether, and dried in vacuo. Anal. Calcd for $ReCl_3[(C_6H_5)_2AsCH_2CH_2As(C_6H_5)_2]$: C, 40.1; H, 3.1; Cl, 13.7. Found: C, 39.2; H, 3.9; Cl, 13.8.

**(ii) $(Bu_4N)_2Re_2Br_8$.** We were unable to isolate a pure product from the reaction between $(Bu_4N)_2Re_2Br_8$ and dpae in 1-butanol.

**Physical Measurements.** Infrared spectra in the region 4000–200 $cm^{-1}$ were recorded as Nujol mulls using a Beckman IR-12 spectrophotometer. Electronic absorption spectra were recorded on a Cary 14 spectrophotometer. Magnetic moments were measured by the Gouy method using $Hg[Co(SCN)_4]$ as the calibrant. X-ray photoelectron spectra were recorded using a Hewlett-Packard 5950A ESCA spectrometer. The aluminum $K\alpha_{1,2}$ line (1486.6 eV) was used as the x-ray excitation source. Full details of the experimental procedure are described elsewhere.[12,13]

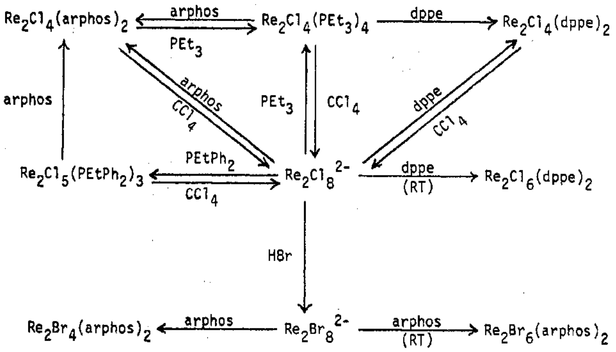
**Analytical Procedures.** Elemental microanalyses were performed by Dr. C. S. Yeh of the Purdue University microanalytical laboratory or by Galbraith Laboratories, Inc., Knoxville, Tenn. Molecular weight measurements were also performed by Dr. C. S. Yeh.

## Results and Discussion

The reactions of the octahalodirhenate(III) anions and certain of their derivatives with bis(1,2-diphenylphosphino)ethane, 1-diphenylphosphino-2-diphenylarsinoethane, bis(1,2-diphenylarsino)ethane, and bis(diphenylphosphino)methane are complicated and afford a wide range of reaction products. While dppe and arphos exhibit very similar reactivity patterns, these are quite different from the related behavior of dpae and dppm. Accordingly, the results we have obtained are discussed according to the reactivity of the ligands.

**(a) $Ph_2PCH_2CH_2PPh_2$ and $Ph_2PCH_2CH_2AsPh_2$.** The reactions of these ligands are summarized in Scheme I. It has previously been shown[7,8,10] that the $Re_2Cl_8{}^{2-}$ anion reacts with dppe in acetonitrile at *room temperature* to produce the centrosymmetric chlorine-bridged dimer $Re_2Cl_6(dppe)_2$. A black crystalline complex of stoichiometry $[ReCl_2(dppe)]_n$ was isolated from the filtrate of the above reaction mixture upon prolonged reflux, but because of the very low yield (~6%) in which it was obtained, it was not adequately characterized.[10] In the present study, we were able to isolate this same complex from the reaction between the $Re_2Cl_8{}^{2-}$ anion and dppe in refluxing acetonitrile in a slightly improved yield (12%) provided the initial insoluble complex $Re_2Cl_6(dppe)_2$ was not isolated from the reaction mixture. The latter product redissolved and black crystals of $[ReCl_2(dppe)]_n$ slowly separated as reduction proceeded. However, we subsequently found that a superior route to this complex is via the reaction of dppe with the rhenium(II) dimer $Re_2Cl_4(PEt_3)_4$ which produces it in ~80% yield.

**Scheme I.** Reactions of Rhenium Complexes with dppe and arphos[a]



[a] RT signifies that the reaction was carried out at room temperature.

The related arphos complex $[ReCl_2(arphos)]_n$ was prepared from either $Re_2Cl_8{}^{2-}$ or $Re_2Cl_4(PEt_3)_4$ using procedures similar to those used to prepare $[ReCl_2(dppe)]_n$. Once again, the use of $Re_2Cl_4(PEt_3)_4$ gave a higher yield of the desired product. Although $[ReCl_2(arphos)]_n$ was also formed when $Re_2Cl_5(PEtPh_2)_3$ was used as the starting material, the analogous reaction between $Re_2Cl_5(PEtPh_2)_3$ and dppe was not successful (see Experimental Section).

Although we did not isolate the complex $Re_2Cl_6(arphos)_2$ from the reaction between $Re_2Cl_8{}^{2-}$ and arphos, the reaction of $Re_2Br_8{}^{2-}$ with this ligand produced either $Re_2Br_6(arphos)_2$ or $[ReBr_2(arphos)]_n$, depending upon reaction conditions. The former complex has a close structural relationship to $Re_2Cl_6(dppe)_2$ and its bromide analogue.[7,10] Its electronic absorption spectrum (Table I) is very similar to the related spectra of $Re_2X_6(dppe)_2$,[10] and it reacts with both carbon tetrabromide and acetic acid–acetic anhydride (see Experimental Section) to produce the rhenium(IV) complex $ReBr_4(arphos)$. These reactions are characteristic of magnetically dilute rhenium(III) species such as $Re_2X_6(dppe)_2$.[10]

In the reduction of the $Re_2Cl_8{}^{2-}$ anion by dppe, it is unlikely that $Re_2Cl_6(dppe)_2$ is formed as a reaction intermediate for the following reasons. (1) Even when $Re_2Cl_6(dppe)_2$ is not isolated from the reaction mixture, there is little increase in the yield of $[ReCl_2(dppe)]_n$. Indeed, the yields of $[ReCl_2(dppe)]_n$ and $[ReX_2(arphos)]_n$ were rarely in excess of about 10% when prepared directly from the $Re_2X_8{}^{2-}$ anions. (2) The reaction of $Re_2Cl_6(dppe)_2$ with an excess of dppe in refluxing acetonitrile leads to the formation of an insoluble yellow complex of stoichiometry $[ReCl_3(dppe)_{1.5}]_n$, which like $Re_2Cl_6(dppe)_2$ is a magnetically dilute derivative of rhenium(III) ($\mu_{eff}$ = 2.0 BM at 300 K). There is no evidence for the formation of $[ReCl_2(dppe)]_n$ in this latter reaction. We note that in the absence of dppe, $Re_2Cl_6(dppe)_2$ reacts with acetonitrile to afford the paramagnetic complex $ReCl_3(dppe)\cdot CH_3CN$ ($\mu_{eff}$ = 1.89 BM). These observations are in accord with previous experience[14] which suggests that once the Re–Re bond is disrupted, it does not readily re-form. However, while $[ReCl_2(dppe)]_n$ and $[ReCl_2(arphos)]_n$ are clearly minor products from the reduction reactions of

**Table I.** Spectral Properties of Rhenium Complexes Containing Bidentate Ligands

| Complex | Medium | Electronic absorption maxima, nm[a] | Infrared spectra, $\nu$(Re–X), cm$^{-1}$ |
|---|---|---|---|
| $Re_2Br_6(arphos)_2$ | Nujol mull | 1780 s, 1500–1100 vbr, 620 s | |
| | $CH_2Cl_2$[b] | 1760 s, 1150 m, br, 900 sh, 610 vs, 535 s | |
| $ReCl_3(dppe)_{1.5}$ | Nujol mull | 435 | 317 vs, 275 s |
| | $CH_2Cl_2$ | 442, 355 sh | |
| $ReCl_3(dppe)\cdot CH_3CN$ | Nujol mull | 590 sh, 460 | 322 vs, 259 s |
| $Re_2Cl_4(dppe)_2$ | Nujol mull | 625 sh, 540 s, 500 s | 333 vs, 303 ms |
| | $CH_2Cl_2$ | 625 sh, 525 (335), 500 sh | |
| $Re_2Cl_4(arphos)_2$ | Nujol mull | ~630 sh, 550 sh, 510 | 330 s, 300 ms |
| | $C_6H_6$ | 620 sh, 510 | |
| $Re_2Br_4(arphos)_2$ | $CH_2Cl_2$ | 550, 425 sh | 240 m |
| $Re_2Cl_6(dpae)_2$ | $CH_2Cl_2$ | 685 vs, 575 vw, sh, 450 vw, sh, 350 m, sh | ~335 vs, br |
| $Re_2Cl_6(dppm)_2$ | Nujol mull[c] | 540, 400 sh | 313 s, 281 m, 272 sh |
| | $CH_2Cl_2$[c] | 540, 400 sh | |
| $Re_2Cl_6(dppm)_2\cdot 2CH_3CN$ | Nujol mull | 1450 m[d], 520 s | 313 s, 281 m, 272 sh |
| | $CH_2Cl_2$[c] | 1450 (230–280),[d] 520 (1600–2000) | |
| $Re_2Br_5(dppm)_2\cdot CH_3CN$ | Nujol mull | 1525 m, 520 sh, 480 s | 225 ms |
| | $CH_2Cl_2$ | 1525 (408), 525 sh, 480 (2320) | |
| $Re_2Cl_4(dppm)_2$ | Nujol mull | 610 sh, 500 | 335 s, 309 s |
| | Acetone | 680 sh, 510 (470), 420 sh | |
| $Re_2Cl_4(PEt_3)_2(dppm)$ | Nujol mull | 600 sh, 500 | 329 w, 315 s, 285 s |
| | $CH_2Cl_2$ | 575 (297), 476 (360) | |
| $\alpha$-$[ReBr_2(dppm)]_n$ | Nujol mull | 585 ms, 525 s, 375 sh | *e* |
| | $CH_2Cl_2$ | ~900 w, br?, 600 m; 525 s | |
| $\beta$-$[ReBr_2(dppm)]_n$ | Nujol mull | ~1000 vw, br?, ~650 sh, 555, 450 sh[d] | *e* |
| | $C_6H_6$ | 540,[f] 445[d] | |

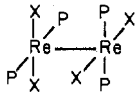
[a] Molar extinction coefficients are given in parentheses. When appropriate, relative peak intensities are given for certain solid-state and solution spectra. [b] Spectrum recorded on a freshly prepared solution. Upon exposure to air this solution decomposes and changes color from green to orange. [c] Electronic absorption spectral data are for the complex of this stoichiometry prepared from methanol. [d] This absorption band is due to a contaminant. [e] See Figure 2. [f] Asymmetric on its low-energy side.

$Re_2Cl_8^{2-}$, they are the major products of the ligand substitution reactions of $Re_2Cl_4(PEt_3)_4$ with dppe and arphos.

Before considering the structures of these rhenium(II) complexes, it is worth commenting further upon the species $[ReCl_3(dppe)_{1.5}]_n$ and $ReCl_3(dppe)\cdot CH_3CN$. Both of these complexes have electronic absorption spectra (Table I) which are different from that of centrosymmetric dinuclear $Re_2Cl_6(dppe)_2$.[10] Both exhibit low-frequency infrared spectral patterns which are very similar and the relative simplicity of these spectra in the $\nu$(Re–Cl) region, as compared to those of ionic dimers such as $[InCl_2(bpy)_2]^+[InCl_4(bpy)]^-$ [15] (see Table I), argues against $[ReCl_3(dppe)_{1.5}]_n$ possessing the ionic structure $[ReCl_2(dppe)_2]^+[ReCl_4(dppe)]^-$. These complexes most likely arise from cleavage of the $ReCl_2Re$ bridging unit of $Re_2Cl_6(dppe)_2$ by dppe or acetonitrile, so that $[ReCl_3(dppe)_{1.5}]_n$ is in reality $Re_2Cl_6(dppe)_3$ and probably contains two $[ReCl_3(dppe)]$ units bridged by a further dppe molecule in the trans conformation.

Although the rhenium(II) complexes with dppe and arphos were not soluble enough for molecular weight measurements to be carried out, there is little doubt that they are correctly formulated as the dimers, $Re_2X_4(LL)_2$, where LL = dppe or arphos. Preliminary crystallographic results on the chloride complexes indicate that they are dimeric and isomorphous.[16] The chemical reactivity patterns of $Re_2Cl_4(LL)_2$ are also in accord with this conclusion (Scheme I). The complexes $Re_2Cl_4(PEt_3)_4$ and $Re_2Cl_4(arphos)_2$ are readily interconverted, and both $Re_2Cl_4(dppe)_2$ and $Re_2Cl_4(arphos)_2$ are reoxidized to $Re_2Cl_8^{2-}$ upon prolonged reflux (15 and 8 days, respectively) in mixtures of dichloromethane and carbon tetrachloride. The latter reactions are analogous to those previously reported[4] in which both $Re_2Cl_4(PEt_3)_4$ and $Re_2Cl_5(PEtPh_2)_3$ are oxidized to $Re_2Cl_8^{2-}$ by a similar chlorocarbon mixture. The structural similarity of $Re_2Cl_4(dppe)_2$ and $Re_2Cl_4(arphos)_2$ is further substantiated by the similarity of their electronic and infrared spectra (Table I). Furthermore, the infrared spectra of $Re_2Cl_4(arphos)_2$ and $[ReBr_2(arphos)]_n$ are so similar in the 1700–400-cm$^{-1}$ region, with respect to both band frequencies and relative intensities, that they probably possess closely related structures.[17]

The most intriguing aspect of these rhenium(II) dimers concerns the details of their molecular structure. It is immediately apparent that these complexes cannot be isostructural with the related derivatives with monodentate tertiary phosphines, $Re_2X_4(PR_3)_4$ (structure I), unless the



I

bidentate ligands bridge adjacent $Re_2$ units and in doing so assume the trans conformation, in which case these complexes would be polymeric. That these complexes are not isostructural with $Re_2Cl_4(PR_3)_4$ is supported by the marked differences between their electronic absorption spectra (Table I) and those of $Re_2X_4(PR_3)_4$[1,4] and their paramagnetism (vide infra). Thus, we have previously noted[1,4,18] that the electronic spectra of solutions of $Re_2X_4(PR_3)_4$ are extremely sensitive to trace amounts of oxygen due to oxidation to paramagnetic $Re_2X_5(PR_3)_3$. This oxidation results in the growth of an intense band in the near-infrared region at ~1400 nm. In contrast to this, dichloromethane solutions of $Re_2Cl_4(dppe)_2$ and $Re_2X_4(arphos)_2$ do not exhibit this behavior even when exposed to the atmosphere for several weeks. The stability of these complexes to oxidation parallels the results of the carbon tetrachloride oxidation experiment; oxidation of $Re_2Cl_4(PEt_3)_4$ to $Re_2Cl_8^{2-}$ is accomplished within 1 day[4] whereas the related oxidation of $Re_2Cl_4(LL)_2$ requires from 1 to 2 weeks.

Additional information which relates to the possible structure of $Re_2Cl_4(LL)_2$ includes the observation that the $\nu$(Re–Cl) stretching vibrations at ~330 and 300 cm$^{-1}$ (Table I) are typical[4] of terminal Re–Cl bonds. There is no evidence for bands below 300 cm$^{-1}$ which could be attributable to vibrations of bridging Re–Cl–Re units. Furthermore, the x-ray photoelectron spectra of these two chloro complexes (Table I) show only one type of chlorine environment,[12] in accord with the results of the low-frequency infrared spectra. The rhenium $4f_{5/2,7/2}$ binding energies of $Re_2Cl_4(dppe)_2$ and $Re_2X_4$(arp-

**Table II.** X-Ray Photoelectron Spectra (eV) of Dinuclear Rhenium Complexes Containing Bidentate Ligands[a]

| Complex | Re $4f_{5/2}$ | Re $4f_{7/2}$ | Halide[b] $np_{1/2}$ | Halide[b] $np_{3/2}$ | P 2p | C 1s |
|---|---|---|---|---|---|---|
| $Re_2Cl_4(dppe)_2$ | 43.3 (1.3) | 40.9 (1.3) | 199.6 | 198.1 (1.1) | 131.1 (1.5) | 284.3 (1.3) |
| $Re_2Cl_4(arphos)_2$ | 43.3 (1.2) | 40.9 (1.1) | 199.6 | 198.0 (1.1) | 130.7 (1.6) | 284.1 (1.0) |
| $Re_2Cl_4(dppm)_2$ | 43.2 (1.5) | 40.8 (1.3) | 199.2 | 197.8 (1.2) | 130.9 (1.6) | 284.1 (1.3) |
| $Re_2Cl_4(PEt_3)_2(dppm)$ | 43.7 (1.3) | 41.4 (1.2) | 199.4 | 198.2 (1.1) | 131.4 (1.6) | 284.6 (1.2) |
| $Re_2Br_4(arphos)_2$ | 43.0 (1.3) | 40.7 (1.1) | 188.5 | 181.6 (2.0) |  | 284.0 (1.2) |
| $\alpha$-$[ReBr_2(dppm)]_n$ | 44.1 (1.3) | 41.7 (1.3) | 188.9 | 182.0 (2.5) | 131.6 (1.6) | 284.9 (1.2) |
| $Re_2Br_5(dppm)_2 \cdot CH_3CN$ | 43.5 (1.7) | 41.1 (1.5) | 188.5 | 181.5 (2.1) | 131.0 (1.6) | 284.1 (1.2) |
| $Re_2Cl_6(dppm)_2$[c] | 43.9 (1.4) | 41.5 (1.3) | 200.5 199.0 | 197.6 (1.2) |  | 284.2 (1.1) |
| $Re_2Cl_6(dppm)_2 \cdot 2CH_3CN$ | 44.3 (1.7) | 41.9 (1.5) | 201.2 199.6 | 198.1 (1.3) | 131.4 (1.6) | 284.5 (1.3) |
| $[ReCl_3(dppe)_{1.5}]_n$ | 44.0 (1.5) | 41.6 (1.5) | 199.7 | 198.2 (1.7) | 131.2 (1.8) | 284.4 (1.4) |
| $ReCl_3(dppe) \cdot CH_3CN$[d] | 44.4 (1.9) | 42.0 (1.8) | 199.2 | 197.8 (1.6) | 130.8 | 284.6 (1.6) |

[a] All spectra are referenced to the carbon 1s binding energy of graphite taken as 284.0 eV; fwhm values are given in parentheses. [b] The halide is either chloride (with $2p_{3/2}$ ~198 eV) or bromide (with $3p_{3/2}$ ~182 eV). [c] Sample prepared from methanol. [d] Nitrogen 1s binding energy at 399.5 eV.

**Table III.** Binding Energies (eV) of Selected Dinuclear Rhenium Complexes Internally Referenced to a Phosphine Carbon (1s) Energy of 285.0 eV

| Complex | Rhenium $4f_{5/2}$ | Rhenium $4f_{7/2}$ | Complex | Rhenium[a] $4f_{5/2}$ | Rhenium[a] $4f_{7/2}$ |
|---|---|---|---|---|---|
| $Re_2Cl_4(dppe)_2$ | 44.0 | 41.6 | $Re_2Cl_4(PEt_3)_4$ | 43.4 | 41.0 |
| $Re_2Cl_4(arphos)_2$ | 44.2 | 41.8 | $Re_2Cl_4[P(n\text{-}Pr)_3]_4$ | 43.6 | 41.3 |
| $Re_2Cl_4(dppm)_2$ | 44.1 | 41.7 | $Re_2Cl_4(PEt_2Ph)_4$ | 43.8 | 41.4 |
| $Re_2Cl_4(PEt_3)_2$-(dppm) | 44.1 | 41.8 | $Re_2Br_4(PEt_3)_4$ | 43.7 | 41.3 |
|  |  |  | $Re_2Cl_5(PEtPh_2)_3$ | 44.5 | 42.1 |
| $Re_2Br_4(arphos)_2$ | 44.0 | 41.7 | $Re_2Br_5(PEtPh_2)_3$ | 44.6 | 42.3 |
| $\alpha$-$[ReBr_2$-$(dppm)]_n$ | 44.2 | 41.8 | $Re_2Cl_6(PEt_3)_2$ | 45.2 | 42.8 |
|  |  |  | $Re_2Cl_6[P(n\text{-}Pr)_3]_2$ | 45.3 | 42.8 |
| $Re_2Br_5(dppm)_2 \cdot CH_3CN$ | 44.4 | 42.0 | $Re_2Cl_6(PEt_2Ph)_2$ | 45.5 | 43.0 |
|  |  |  | $Re_2Br_6(PEt_3)_2$ | 45.5 | 43.1 |
| $Re_2Cl_6(dppm)_2$ | 44.7 | 42.3 |  |  |  |
| $Re_2Cl_6(dppm)_2 \cdot 2CH_3CN$ | 44.8 | 42.4 |  |  |  |

[a] Data taken from ref 19.

hos)2 (Tables II and III) are similar to those observed for the rhenium(II) dimers $Re_2X_4(PR_3)_4$[19] and are consistent with our formulation of the former complexes as derivatives of rhenium(II).

On the basis of the preceding structural information, we constructed scaled molecular models of $Re_2Cl_4(dppe)_2$, and the two structures shown in Figure 1 are considered by us to be the most likely possibilities[20] based upon the requirement that there be no bridging Re–Cl–Re units and that unfavorable steric interactions between the ligand molecules be minimized. To our knowledge, the structure shown in Figure 1(A) involving bridging dppe molecules is quite novel but sterically favored. At the present time, we feel it is the most probable of the two for the following reasons. (1) The similarity in position and relative intensity of the ν(Re–Cl) modes of $Re_2Cl_4(LL)_2$ with those of rhenium(II) dimers of the type $Re_2Cl_4(PR_3)_4$ suggests that within the individual $[ReCl_2L_2]$ units a trans disposition of Re–Cl bonds is maintained. (2) The proposed structure would contain two six-membered rings in the chair formation and accordingly may be expected to exhibit some differences in reactivity from other dimeric rhenium(II)–phosphine complexes. The greater relative kinetic stability of $Re_2X_4(LL)_2$ toward oxidation may be a reflection of this structural feature. (3) The change from an eclipsed configuration of $[ReX_2L_2]$ groups in $Re_2X_4(PR_3)_4$ to a staggered configuration in $Re_2X_4(LL)_2$ implies that the δ component of the multiple Re–Re bond[21] has been disrupted. The paramagnetism of $Re_2Cl_4(LL)_2$ may be consistent with this conclusion. The room-temperature magnetic moments of $Re_2Cl_4(dppe)_2$ and $Re_2Cl_4(arphos)_2$ were 1.7 and 1.3 (±0.1) BM, respectively.[22] In the absence of temperature range studies, we cannot comment further on the significance of the magnetic moments, other than to note that the room-temperature $\mu_{eff}$ values, which are far less than expected for two unpaired electrons, may indicate that both spin singlet and triplet states become thermally populated as the δ interaction diminishes.

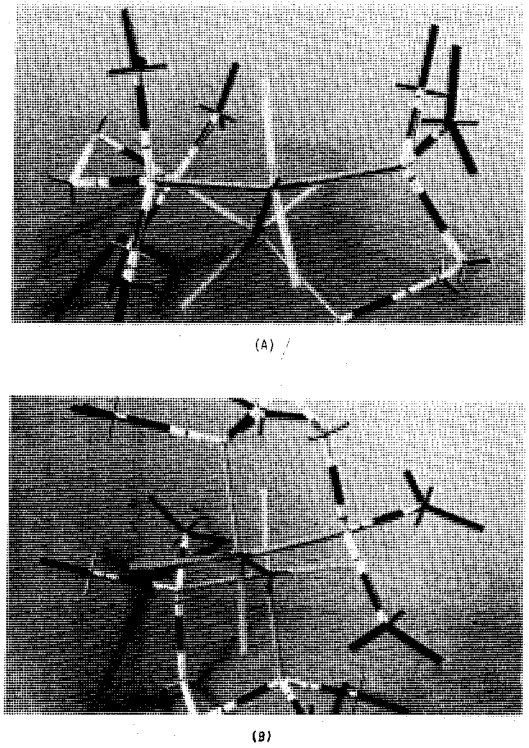
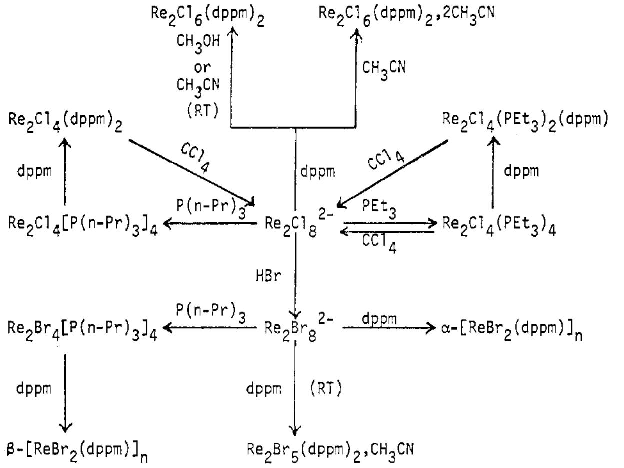


**Figure 1.** Possible structures for $Re_2Cl_4(dppe)_2$ with (A) bridging dppe ligands and (B) chelating dppe ligands.

**(b) $Ph_2AsCH_2CH_2AsPh_2$.** The weaker reducing characteristics of tertiary arsines are illustrated by the failure of dpae to reduce either of the $Re_2X_8^{2-}$ anions. In the case of the reaction between $Re_2Cl_8^{2-}$ and dpae, we are able to isolate a green complex of stoichiometry $[ReCl_3(dpae)]_n$. Its electronic absorption spectrum (Table I) is consistent with its formulation as a metal–metal bonded dimer $[Re_2Cl_6(dpae)_2]$.[23] Like the related 2,5-dithiahexane derivative of this type,[10] it probably contains monodentate ligand molecules. In view of the absence of reduction, we did not pursue these particular systems further.

**(c) $Ph_2PCH_2PPh_2$.** The reactions of this di(tertiary phosphine) which are presented in Scheme II are quite different from those exhibited by dppe. The reaction of dppm with $Re_2Cl_8^{2-}$ produces a complex of stoichiometry $[ReCl_3(dppm)]_n$, provided the reaction is carried out at room temperature in acetonitrile or in refluxing methanol. If the acetonitrile reaction mixture is refluxed prior to work-up, Scheme II. Reactions of Rhenium Complexes with dppm[a]



[a] RT signifies that the reaction was carried out at room temperature.

$Re_2Cl_6(dppm)_2$ is converted to its acetonitrile "solvate" $Re_2Cl_6(dppm)_2{\cdot}2CH_3CN$. Although these products have microanalytical data which are consistent with their formulation as derivatives of rhenium(III), we have spectroscopic evidence which suggests that the products isolated from acetonitrile are impure. The low-frequency vibrational spectra of $Re_2Cl_6(dppm)_2$ (prepared from both acetonitrile and methanol) and $Re_2Cl_6(dppm)_2{\cdot}2CH_3CN$ are identical (Table I), with the exception that the acetonitrile solvate exhibits additional low-frequency absorptions at 380 (w), 330 (w), and 220 (mw) $cm^{-1}$ due to a contaminant of unknown origin. However, the most striking spectral differences concern the electronic absorption of these derivatives (Table I). Samples of $Re_2Cl_6(dppm)_2$ prepared from methanol have a relatively simple spectrum (Table I) and exhibit no bands in the near-infrared region. On the other hand, both $Re_2Cl_6(dppm)_2$ and $Re_2Cl_6(dppm)_2{\cdot}2CH_3CN$ prepared from acetonitrile show a band at 1450 nm in their solution and solid-state spectra. Its position is reminiscent of the characteristic low-energy absorption at ~1400 nm observed in the spectra of paramagnetic complexes of the type $Re_2X_5(PR_3)_3$,[1,4] and, in view of its variable intensity for different preparative samples of these dppm complexes, we attribute its appearance to the presence of some contaminant whose electronic structure is related to that of $Re_2X_5(PR_3)_3$. The complex $Re_2Cl_5(dppm)_2$, which has recently been prepared and structurally characterized by Cotton and Shive,[24] would seem to be a likely candidate in view of its close relationship to $Re_2Cl_5(PR_3)_3$. In summary, then, it is apparent that under our experimental conditions the use of acetonitrile as reaction solvent leads to impure products and only in methanol is spectroscopically pure $Re_2Cl_6(dppm)_2$ isolated.

While we did not uncover a route to the synthesis of the partially reduced complex $Re_2Cl_5(dppm)_2$,[24] we found that the reaction of $Re_2Br_8^{2-}$ with dppm in acetonitrile affords what appears to be its bromide analogue, $Re_2Br_5(dppm)_2{\cdot}CH_3CN$. In contrast to the diamagnetic nature of $Re_2Cl_6(dppm)_2$ ($\chi_g = -0.30 \times 10^{-6}$ cgsu at 292 K), this bromide complex is paramagnetic ($\mu_{eff} = 2.0$ BM) and its electronic absorption spectrum displays a low-energy absorption at 1525 nm (Table I). By analogy with the related complexes of the type $Re_2X_5(PR_3)_3$[1,4] the magnetic and spectral properties of this dppm complex are in accord with its dimeric formulation.

While the dppe complex $Re_2Cl_4(dppe)_2$ can be generated directly from both $Re_2Cl_8^{2-}$ and $Re_2Cl_4(PR_3)_4$, the related dinuclear dppm complex $Re_2Cl_4(dppm)_2$ can only be prepared by the latter route. However, in this case, the nature of the monodentate tertiary phosphine $PR_3$ that is displaced is very important (see Scheme II). With $Re_2Cl_4(PEt_3)_4$ as the starting material, substitution of only two $PEt_3$ groups occurs and the diamagnetic ($\chi_g = -0.185 \times 10^{-6}$ cgsu at 292 K) mixed-phosphine complex $Re_2Cl_4(PEt_3)_2(dppm)$ is formed. Infrared and $^1H$ NMR spectral measurements confirmed the presence of both $PEt_3$ and dppm. Use of $Re_2Cl_4[P(n\text{-}Pr)_3]_4$ is necessary in order to facilitate complete substitution of the four $PR_3$ ligands. The dimeric nature of $Re_2Cl_4(dppm)_2$ was confirmed by a molecular weight measurement in acetone. Both $Re_2Cl_4(PEt_3)_2(dppm)$ and $Re_2Cl_4(dppm)_2$ react with dichloromethane–carbon tetrachloride solutions containing tetraphenylarsonium chloride to afford $(Ph_4As)_2Re_2Cl_8$ in high yield. Once again this supports the belief that a multiple rhenium–rhenium bond is present.

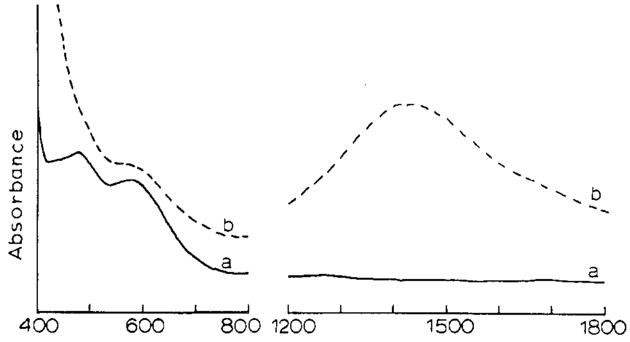


Figure 2. Electronic absorption spectrum of $Re_2Cl_4(PEt_3)_2$-(dppm) in $CH_2Cl_2$ (a) under anaerobic conditions (———) and (b) after exposure to the atmosphere for 1 day (- - - -).

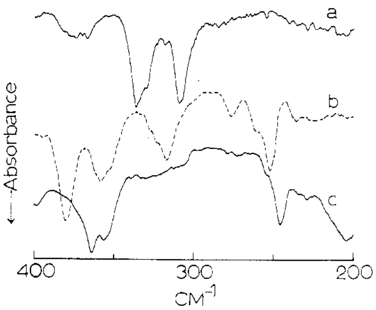


Figure 3. Low-frequency infrared spectra (Nujol mulls) of (a) $Re_2Cl_4(dppm)_2$, (b) α-$[ReBr_2(dppm)]_n$, and (c) β-$[ReBr_2$-$(dppm)]_n$.

While the electronic absorption spectra of the dppm complexes of rhenium(II) (Table I) are different from those of $Re_2Cl_4(PR_3)_4$,[4] they do resemble the latter complexes in one important respect, namely, the growth of a band between 1400 and 1500 nm when solutions of these complexes are exposed to oxygen for up to 2 days (Figure 2). These spectral changes, which are similar to those observed for $Re_2X_4(PR_3)_4$,[1,4] indicate that like the latter complexes, $Re_2Cl_4(dppm)_2$ and $Re_2Cl_4(PEt_3)_2(dppm)$ can readily undergo one-electron oxidations. Accordingly, our observations suggest a close structural and chemical relationship between $Re_2Cl_4(PR_3)_4$ and these dppm complexes.

Products of stoichiometry $[ReBr_2(dppm)]_n$ can be isolated when either $Re_2Br_8^{2-}$ or $Re_2Br_4[P(n\text{-}Pr)_3]_4$ is treated with dppm. However, these products are not identical as indicated by differences between their spectral properties (Table I), and, accordingly, they will be referred to as the α and β forms, respectively. In particular, α-$[ReBr_2(dppm)]_n$ has a much more complex low-frequency infrared spectrum (Figure 3). The solution and solid-state electronic absorption spectra of α-$[ReBr_2(dppm)]_n$ are identical and showed no time dependence. In contrast to this, benzene solutions of β-

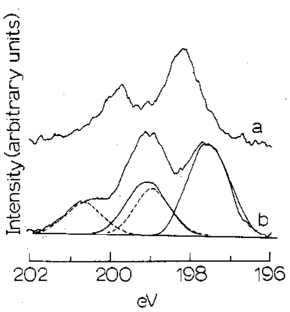
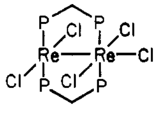


**Figure 4.** Chlorine 2p binding energy spectra of (a) $Re_2Cl_4(dppe)_2$ and (b) $Re_2Cl_6(dppm)_2$. Spectrum b is deconvoluted into two sets of Cl $2p_{1/2},_{3/2}$ doublets using the procedure described in ref 12.

$[ReBr_2(dppm)]_n$ rapidly decomposed, as shown by the growth of an intense absorption band at 445 nm. The solution spectra of neither species exhibited an absorption band in the near-infrared region even when these solutions were exposed to the air for prolonged periods. Clearly, neither undergoes an oxidation in solution related to that experienced by $Re_2Cl_4(dppm)_2$ and $Re_2Cl_4(PR_3)_4$.[1,4]

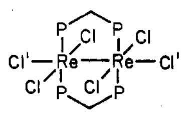
While it is possible that the $\alpha$ and $\beta$ forms of $[ReBr_2(dppm)]_n$ are metal–metal bonded dimers containing either chelating or bridging dppm, we have no direct evidence for this. $\alpha$-$[ReBr_2(dppm)]_n$ is essentially diamagnetic ($\chi_g \approx -0.25 \times 10^{-6}$ cgsu at 301 K) but it is not oxidized to $Re_2Br_8{}^{2-}$ when treated with tetraphenylarsonium chloride in a mixture of carbon tetrabromide and dichloromethane. If either the $\alpha$ or $\beta$ form is structurally related to $Re_2Cl_4(dppm)_2$, it is difficult to understand this stability toward oxidation.

In contrast to dppe, the dppm ligand can bridge the rhenium atoms of a metal–metal bonded $[Re_2X_8]$ unit with retention of an eclipsed configuration of $ReX_4$ groups. This type of bridging occurs in the complex $Re_2Cl_5(dppm)_2$ (see structure II)[24] and is also found in $Fe_2(CO)_7(dppm)$[25] and $Mn_2(CO)_5(dppm)_2$.[26] Consequently, it is reasonable to conclude that $Re_2Cl_6(dppm)_2$, $Re_2Cl_4(PEt_3)_2(dppm)$, and $Re_2Cl_4(dppm)_2$ adopt structures which are closely related to II.

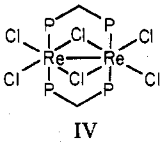


II

In the case of $Re_2Cl_6(dppm)_2$, structure III would seem to be the most obvious possibility. However, the x-ray photoelectron spectrum of this complex favors an alternative structure. The results of our studies on the x-ray photoelectron spectra of several of the complexes prepared in the present work are summarized in Table II. If we internally reference the rhenium 4f binding energies to a carbon 1s binding energy of 285.0 eV for the tertiary phosphine ligands to correct for small residual charging effects which are not eliminated by other methods,[27,28] we see that the rhenium 4f binding energies decrease with decrease in formal oxidation state (Table III). This same trend is likewise followed within the related series of mono(tertiary phosphine) complexes of the type $Re_2X_{6-n}(PR_3)_{2+n}$, where X = Cl or Br and $n$ = 0, 1, or 2.[19] All of the chloro complexes in Table II, except $Re_2Cl_6(dppm)_2$ and its acetonitrile solvate, have well-resolved chlorine $2p_{1/2,3/2}$ doublets (Figure 4) characteristic of the presence of only terminal Re–Cl bonds. In contrast to this, the complex $Re_2Cl_6(dppm)_2$ exhibits a three-peak chlorine 2p binding energy spectrum (Figure 4) arising from the near coincidence of a chlorine $2p_{1/2}$ component of one type of chlorine with the chlorine $2p_{3/2}$ component of another type. The values of these binding energies (Table II) and the observed relative intensities of the deconvoluted peaks (Figure 4) of 1:2.1:2.1:4.3 are in good agreement with those expected for a 1:2 stoichiometric ratio of bridging to terminal Re–Cl bonds.[12,29] Thus, the chlorine 2p binding energy spectrum, together with the observed diamagnetism of this complex, is consistent with structure IV. For structure III to be correct, what are presumably the more weakly bound axial chlorines (labeled Cl' in structure III) would need to possess higher core binding energies than the four equatorial chlorines. At the present time, this possibility seems the less likely of the two.

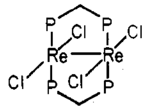


III

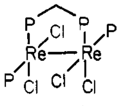


IV

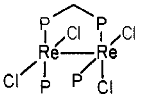
On the basis of an examination of scaled molecular models,[20] it is likely that with the rhenium(II) dimers $Re_2Cl_4(dppm)_2$ and $Re_2Cl_4(PEt_3)_2(dppm)$ (1) dppm is once again bridging the two rhenium centers and (2) the triethylphosphine ligands are not eclipsed with respect to one another if bound to different rhenium centers. Structures V–VII are consistent with these restrictions and with the spectral properties and chemical reactivities of these complexes.



V



VI



VII

**(d) Some Concluding Remarks and Observations on the Relationship between Rhenium and Molybdenum Dimers Containing Bidentate Ligands.** The present study is the first that has been devoted exclusively to the synthesis and characterization of rhenium halide dimers stabilized by bidentate phosphine and arsine donors. Of particular significance is the observation that varying the number of methylene groups in $Ph_2P(CH_2)_nPPh_2$ may affect the structures of the rhenium halide dimers, particularly with regard to whether an eclipsed or staggered conformation is maintained between the $ReX_4$ units of the $[Re_2X_8]$ moiety. The bridging nature of the phosphine ligands within these complexes is to be contrasted with the chelating behavior of 2,5-dithiahexane in the complex $Re_2Cl_5(DTH)_2$.[30] In addition, it is of interest that San Filippo and co-workers[31] have succeeded in isolating several dimeric molybdenum(II) complexes of the type $Mo_2X_4(LL)_2$, where X = Cl or Br and LL = 2,2'-bipyridyl, 1,2-bis(dimethylphosphino)ethane, 2,5-dithiahexane, and other bidentate sulfur donors. It was suggested[31] that in all of these complexes the bidentate ligands are chelating. In keeping with this conclusion, the $\nu$(Mo–Cl) spectral pattern for these complexes was found to be different from that displayed by complexes of the type $Mo_2Cl_4L_4$, in which the *trans*-$MoCl_2L_2$ geometry is present. Our observation that the low-frequency infrared spectra of $Re_2Cl_4(LL)_2$, where LL = dppm, dppe, and arphos, closely resemble those of $Re_2Cl_4(PR_3)_4$[4] and $Mo_2Cl_4L_4$, where L = $PR_3$, py, and RCN,[31] is support for our contention that a trans disposition of Re–Cl bonds is preserved within the individual $[ReCl_2L_2]$ units of $Re_2Cl_4(LL)_2$.

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**Registry No.** $Re_2Cl_6(dppm)_2$, 58312-74-6; $Re_2Cl_4(PEt_3)_2(dppm)$, 58298-38-7; $Re_2Cl_4(dppm)_2$, 58298-10-5; $Re_2Br_5(dppm)_2$, 58396-14-8; $[ReBr_2(dppm)]_n$, 58312-72-4; $Re_2Cl_4(dppe)_2$, 58298-35-4; $[ReCl_3(dppe)_{1.5}]_n$, 58298-36-5; $ReCl_3(dppe)\cdot CH_3CN$, 58298-37-6; $Re_2Cl_4(arphos)_2$, 58396-16-0; $Re_2Br_6(arphos)_2$, 58298-34-3; $ReBr_4(arphos)$, 58342-99-7; $Re_2Br_4(arphos)_2$, 58396-15-9; $Re_2Cl_6(dpae)_2$, 58312-73-5; $(Bu_4N)_2Re_2Cl_8$, 14023-10-0; $Re_2Cl_4(PEt_3)_4$, 55400-06-1; $Re_2Cl_4[(P(n\text{-}Pr)_3]_4$, 55400-08-3; $(Bu_4N)_2Re_2Br_8$, 14049-60-6; $Re_2Br_4[P(n\text{-}Pr)_3]_4$, 58298-33-2; $Re_2Cl_6(dppe)_2$, 53139-98-3; $Re_2Cl_5(PEtPh_2)_3$, 55450-45-8; $CBr_4$, 558-13-4.

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# Inorganic Coordination Polymers. XIX. Steric Effects of Hydrocarbon Side Groups on the Structure and Properties of Zinc(II), Cobalt(II), Manganese(II), Nickel(II), and Copper(II) Bis(phosphinates)[1]

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The metal(II) dialkylphosphinates $M[OPR_2O]_2$ (M = Mn, Co, Ni, Cu, Zn; R = $C(CH_3)_3$, $CH_2CH_2CH_2CH_3$, $CH(CH_3)CH_2CH_2CH_3$) have been investigated. The structures of the complexes with straight-chain R substituents vary for the different metals and include polymers with both octahedrally and tetrahedrally coordinated metal centers. On the other hand, the metal(II) phosphinates which contain bulky alkyl R substituents all appear to have the same structure which contains tetrahedrally coordinated metal centers and symmetrically bridging O,O' phosphinate groups.

Metal(II) bis(phosphinates) have received attention in a number of laboratories because of their polymeric structures.[2] Ripamonti, et al., have made a number of single-crystal x-ray studies of beryllium(II), zinc(II), and cobalt(II) bis(phosphinates) and reported that the structures contain chains of tetrahedrally coordinated metal atoms linked by symmetrical O,O' phosphinate bridges.[3] Other workers have assigned similar polymeric structures to other metal(II) bis(phosphinates) including those of nickel(II)[4] and manganese(II).[5] Recently our investigations have shown that a variety of structures occur for these materials, including octahedrally coordinated metal atoms linked by unsymmetrical phosphinate bridges.[6] In order to extend our understanding of these systems further, we have investigated the properties and structural changes that occur with some of these metal centers upon changing the bulkiness and chain lengths of hydrocarbon substituents on the phosphorus.

## Experimental Section

The dibutyl- and bis(1-methylbutyl)phosphinic acids were prepared by the procedure of Kosolapoff.[7] The dibutyl acid was purified by recrystallization from hexane. The bis(1-methylbutyl)phosphinic acid was found to be very impure after distillation at 178 °C and 2.2 mmHg. Further purification was accomplished through the preparation, purification, and hydrolysis of its acid chloride. To 11.5 ml of crude compound was added 22.5 ml of thionyl chloride in five increments, and after the initial exothermic reaction subsided, the